

Convenient Synthesis and Molecular Structure of the Cyclometallated Complex $[\text{IrCl}(\text{H})(\text{C}_6\text{H}_4\text{PPh}_2)(\text{PPh}_3)_2]$

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Z. Naturforsch. 2014, 69b, 1237–1240 / DOI: 10.5560/ZNB.2014-4160

Received July 21, 2014

Dedicated to Professor Hubert Schmidbaur on the occasion of his 80th birthday

The reaction of $[\{\text{Ir}(\mu\text{-Cl})(\text{coe})_2\}_2]$ (coe = *cis*-cyclooctene) with triphenylphosphane (molar ratio of Ir to P = 1 : 3) in dichloromethane at room temperature afforded after a short reaction time the cyclometallated complex $[\text{IrCl}(\text{H})(\text{C}_6\text{H}_4\text{PPh}_2)(\text{PPh}_3)_2]$ (**1**) in almost quantitative yield. The molecular structure of the title compound **1** was determined by an X-ray diffraction study.

Key words: Iridium, Oxidative Addition, Cyclometallated Phosphanes, Crystal Structure

Introduction

The chemistry of the well-known homogeneous catalyst complexes $[\text{MCl}(\text{PPh}_3)_3]$ (M = Rh, Ir) differs quite significantly. For example, whereas Wilkinson's catalyst $[\text{RhCl}(\text{PPh}_3)_3]$ can easily be prepared from hydrated rhodium(III) chloride and triphenylphosphane in refluxing ethanol [1], the same synthetic protocol is not applicable for the synthesis of the related iridium complex $[\text{IrCl}(\text{PPh}_3)_3]$. The reason is that under these rough conditions the latter undergoes a fast intramolecular oxidative addition of one of the *ortho* C-H bonds resulting in the cyclometallated title compound $[\text{IrCl}(\text{H})(\text{C}_6\text{H}_4\text{PPh}_2)(\text{PPh}_3)_2]$ (**1**) [2, 3]. The corresponding Rh compound $[\text{RhCl}(\text{H})(\text{C}_6\text{H}_4\text{PPh}_2)(\text{PPh}_3)_2]$ has been mentioned in only one paper and was obtained by UV irradiation of $[\text{RhCl}(\text{PPh}_3)_3]$ in the presence of a cyclic organotin compound [4]. However, a comparison of the ³¹P NMR data of this cyclometallated rhodium species with those of the corresponding iridium compound described herein puts the identity of the rhodium species strongly in question. For the cyclometallated rhodium compound no direct synthesis has been reported in the literature to date. Recently the iridium complex **1** has been described as an intermediate in a one-pot synthesis affording luminescent iridium(III)

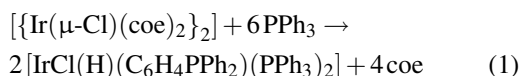
complexes bearing cyclometallated phenylpyridinato ligands beside phosphane ligands [5]. The synthesis of **1** has been performed starting from $[\text{IrCl}(\text{PPh}_3)_3]$ and using lithium or magnesium organometallic compounds [6]. Moreover, the crystal structure of the bromido derivative $[\text{IrBr}(\text{H})(\text{C}_6\text{H}_4\text{PPh}_2)(\text{PPh}_3)_2]$ has been reported [7]. From reaction mixtures containing $[\{\text{Ir}(\mu\text{-Cl})(\text{coe})_2\}_2]$ (coe = *cis*-cyclooctene) and PPh_3 (molar ratio of Ir to P = 1 : 3) in dichloromethane at room temperature we obtained the cyclometallated title complex **1** in high yield. However, during the characterization of **1** by ³¹P NMR spectroscopy we noticed some incompatible data reported in the literature [3, 5] which were in contradiction with the ones observed by us. For this reason we developed a convenient high-yield synthesis for **1** and examined the identity of this compound by X-ray crystallography.

Results and Discussion

Synthesis and characterization

Treatment of $[\{\text{Ir}(\mu\text{-Cl})(\text{coe})_2\}_2]$ with triphenylphosphane in a molar ratio of Ir:P = 1 : 3 in dichloromethane at room temperature is accompanied by a fast color change of the solution from yellow-orange to deep-red within a few minutes. From

this solution the title compound [IrCl(H)(C₆H₄PPh₂)(PPh₃)₂] (**1**) was obtained in almost quantitative yield as a pale-yellow powder after the addition of *n*-hexane (Eq. 1).



Obviously, the reaction proceeds *via* the formation of [IrCl(PPh₃)₃], and it is known from the literature that the latter undergoes a fast intramolecular oxidative addition reaction under mild conditions resulting in the cyclometallation of one phosphane ligand. However, this literature procedure requires a two-step synthetic protocol [2, 3]. The procedure described herein is clearly favored over the protocol described in the literature in which in a first step [IrCl(PPh₃)₃] has to be prepared from [{Ir(μ-Cl)(coe)₂}]₂ and triphenylphosphane (89–95%); in a second step compound **1** is obtained by refluxing [IrCl(PPh₃)₃] in cyclohexane for 2 h (70%) [3].

Compound **1** was characterized by elemental analysis and ¹H NMR and ³¹P NMR spectroscopy (see Experimental Section). However, our ³¹P NMR data of **1** were found to be inconsistent with the ones from the literature [3, 5]: δ_A = 3.1, δ_M = -2.5 and δ_X = -69.6 ppm (AMX spin system: ²J_{AM} = 10.7 Hz, ²J_{MX} = 17.3 Hz, ²J_{AX} = 376.0 Hz, C₆D₆) [3]. The remarkable upfield shift of P_X is characteristic of a phosphorus atom in a cyclometallated four-membered ring system [8]. We were able to confirm the former data of **1** with the only exception of the signal in the upfield region: δ_A = 2.3, δ_M = -3.6 and δ_X = -92.6 ppm (AMX spin system: ²J_{AM} = 10.7 Hz, ²J_{MX} = 17.4 Hz, ²J_{AX} = 373.9 Hz, CD₂Cl₂). By contrast, the recently reported ³¹P NMR data of the title compound were completely incorrect (δ = -2.41, -7.54, -9.5 ppm, unresolved multiplets) [5]. To bring more insight into this matter we prepared single crystals of **1** to ensure the identity of this compound (*vide infra*).

In this context we were interested in the question whether the related cyclometallated rhodium species can be prepared by an analogous synthetic pathway. Thus we studied the reaction of [{Rh(μ-Cl)(coe)₂}]₂ with triphenylphosphane in a molar ratio of Rh to P = 1 : 3 in dichloromethane at room temperature. The reaction was accompanied by a fast color change of the solution from orange to deep red-brown within a few minutes. The investigation of the so-

lution by ³¹P NMR spectroscopy after 1 h at room temperature showed the presence of only two Rh-containing species, namely [RhCl(PPh₃)₃] and the dimeric complex [{Rh(μ-Cl)(PPh₃)₂}]₂. Both complexes were unambiguously identified by their characteristic ³¹P NMR data (see Experimental Section). It is well established that the chlorido-bridged dinuclear type of complex is easily formed in solution by dissociation of one phosphane ligand from [RhCl(PPh₃)₃], affording a reactive 14 valence electron species, see *e. g.* ref. [9]. Subsequently the latter intermediate is stabilized by dimerization resulting in a 16 valence electron configuration at both rhodium atoms. Interestingly, for the analogous iridium compounds [IrCl(PR₃)₃] such dissociation processes have not been described as yet. Obviously these complexes exhibit a higher kinetical inertness toward ligand exchange reactions, see *e. g.* ref. [10]. On the other hand, cyclometallation processes under similar conditions have not been observed for the related rhodium compounds. For [RhCl(H)(C₆H₄PPh₂)(PPh₃)₂] only two instead of the expected three ³¹P NMR chemical shifts have been reported: δ = 63.8 and 50.6 ppm [4]. Furthermore these data do not show the characteristic upfield shifts usually found for phosphorus atoms in cyclometallated four-membered ring systems [8]. Details of the isolation and further analytical data of [RhCl(H)(C₆H₄PPh₂)(PPh₃)₂] have not been reported [4].

We assume that the formation of the very stable Ir-C bond is the driving force of the title reaction (Eq. 1). Interestingly, for both complexes [MCl(PPh₃)₃] (M = Rh, Ir) agostic interactions between one H atom of a phenyl group and the metal atom were found in the crystal [10, 11]. This could facilitate the subsequent cyclometallation process. However, in the case of rhodium this reaction does not seem to be favored in solution. A possible reason could be the facile dissociation of one phosphane ligand, thereby preventing the cyclometallation which obviously needs an intact coordination sphere.

The molecular structure of **1**

Compound **1** crystallized as pale-yellow plates from dichloromethane-ethanol by the slow diffusion method at room temperature overnight. Crystals of **1** belong to the triclinic space group *P* $\bar{1}$ with two molecules in the unit cell. A view of the molecular structure in the

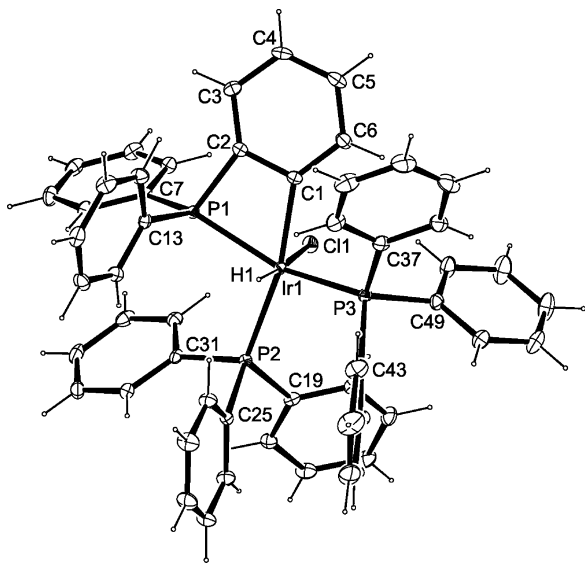


Fig. 1. Molecular structure of **1** in the crystal. Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Ir1–Cl1 2.498(1), Ir1–H1 1.44(3), Ir1–P1 2.345(1), Ir1–P2 2.365(1), Ir1–P3 2.312(1), Ir1–C1 2.103(2), P1–C2 1.793(2), C1–C2 1.398(3), C1–C6 1.400(3); P1–Ir1–Cl1 93.7(1), P1–Ir1–C1 67.3(1), P1–Ir1–P2 100.6(1), P1–Ir1–P3 150.2(1), P1–Ir1–H1 82.1(10), Cl1–Ir1–H1 175.8(10), P3–Ir1–Cl1 106.5(1), P3–Ir1–C1 92.7(1), P3–Ir1–P2 101.7(1), P1–C2–C1 100.8(2), C1–Ir1–Cl1 84.4(1).

crystal is shown in Fig. 1, selected bond lengths and angles are given in the caption.

The crystal structure determination revealed that compound **1** is isostructural to the corresponding bromido complex [IrBr(H)(C₆H₄PPh₂)(PPh₃)₂] [7], which also crystallized in the triclinic space group *P*1̄ with *Z* = 2 and similar cell metrics. The coordination sphere around the iridium atom in **1** can be best described as distorted octahedral with the phosphane ligands occupying the meridional sites, and the chlorido ligand is in *trans* position to the hydrido ligand. The main structural feature of **1** is the four-membered metallacyclic ring system (Ir–P1–C2–C1) resulting from an intramolecular oxidative addition of one of the originally two mutually *trans*-arranged triphenylphosphane ligands. All bond lengths and angles of the title complex are comparable to those of the bromido analog, including a high degree of bond angle distortion in the four-membered metallacycle [7].

In conclusion, we reported a convenient high-yield synthesis of the cyclometallated complex

[IrCl(H)(C₆H₄PPh₂)(PPh₃)₂] (**1**) prepared by the reaction of [{Ir(μ-Cl)(coe)₂]₂] (coe = *cis*-cyclooctene) with triphenylphosphane in dichloromethane at room temperature. In contrast to earlier reported erroneous ³¹P NMR data for **1** we were able to provide a full characterization of the title compound by NMR spectroscopy and an X-ray diffraction study. Moreover we showed that the analogous reaction of the corresponding rhodium species did not lead to a cyclometallation product under similar conditions.

Experimental Section

All manipulations were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. Solvents were dried according to standard procedures and stored under argon. All chemicals were purchased from ABCR and used as received. The complexes [{M(μ-Cl)(coe)₂]₂] (M = Rh, Ir) were prepared from the corresponding hydrated metal(III) chloride and *cis*-cyclooctene [12]. NMR spectra were recorded using a Jeol Eclipse 270 instrument operating at 270 MHz (¹H) and 109 MHz (³¹P), respectively. Elemental analyses (C, H, Cl) were performed by the Microanalytical Laboratory of the Department of Chemistry, LMU Munich, using a Heraeus Elementar Vario EL instrument.

Synthesis of [IrCl(H)(C₆H₄PPh₂)(PPh₃)₂] (**1**)

To a slurry of [{Ir(μ-Cl)(coe)₂]₂] (224 mg, 0.25 mmol) in dichloromethane (20 mL) triphenylphosphane (394 mg, 1.50 mmol) was added and the mixture stirred at room temperature for 1 h. The solvent was reduced to 2 mL *in vacuo*, and **1** was precipitated by the addition of *n*-hexane (30 mL) as a pale-yellow powder. Compound **1** was filtered off, washed twice with 10 mL of *n*-hexane, and dried *in vacuo*. Yield 493 mg (97%); m. p. 185–187°C (decomp.). – ³¹P{¹H} NMR (CD₂Cl₂): δ_A = 2.3 (dd, ²J_{AM} = 10.7 Hz, ²J_{AX} = 373.9 Hz), δ_M = –3.6 (dd, ²J_{AM} = 10.7 Hz, ²J_{MX} = 17.4 Hz), δ_X = –92.6 ppm (dd, ²J_{MX} = 17.4 Hz, ²J_{AX} = 373.9 Hz). – ¹H NMR (CD₂Cl₂): δ = 7.70–6.53 (m, 44 H, C₆H₅ and C₆H₄), δ = –19.32 ppm (ddd, 1H, ²J_{PH} = 10.8 Hz, ²J_{PH} = 15.2 Hz, ²J_{PH} = 18.8 Hz). – C₅₄H₄₅ClIrP₃ (1014.53); calcd. C 63.93, H 4.47, Cl 3.49; found C 63.82, H 4.58, Cl 3.74.

Reaction of [{Rh(μ-Cl)(coe)₂]₂] with triphenylphosphane

To a slurry of [{Rh(μ-Cl)(coe)₂]₂] (180 mg, 0.25 mmol) in dichloromethane (20 mL) triphenylphosphane (394 mg, 1.50 mmol) was added and the mixture stirred at room temperature for 1 h. The solvent was reduced to 5 mL *in vacuo* and the solution immediately investigated by ³¹P{¹H} NMR spectroscopy. As the only phosphorus-containing components [RhCl(PPh₃)₃] (δ = 48.7, dt, *J*_{RhP} = 191.4 Hz,

$^2J_{PP} = 38.7$ Hz; $\delta = 32.0$ ppm, dd, $J_{RhP} = 143.2$ Hz, $^2J_{PP} = 38.7$ Hz) and $[\{\text{Rh}(\mu\text{-Cl})(\text{PPh}_3)_2\}_2]$ ($\delta = 52.1$ ppm, d, $J_{RhP} = 196.1$ Hz) were detected. These data correspond very well with the reported ones [13, 14]. Moreover some amounts of triphenylphosphane oxide ($\delta = 28.0$, s) were detected in the reaction solution.

Crystal structure determination

Single crystals of **1** suitable for X-ray diffraction analysis were obtained as described above. A crystal was selected by means of a polarization microscope, mounted on the tip of a glass fiber, and investigated on a Bruker D8 Venture TXS diffractometer using MoK α radiation ($\lambda = 0.71073$ Å). The structure was solved by Direct Methods (SIR97) [15] and refined by full-matrix least-squares calculations on F^2 (SHELXL-97) [16]. Anisotropic displacement parameters were refined for all non-hydrogen atoms. Crystals of **1** contained heavily disordered solvent molecules (ethanol) from the crystallization process. This was additionally confirmed by ^1H NMR measurements. Because it was not possible to model and refine the solvent molecule properly, electron density in voids was eliminated using the routine SQUEEZE as incorporated in PLATON [17, 18] (27 electrons fit quite well for ethanol) followed by the final least-squares refinement of the structural backbone. Details of crystal data, data collection, structure solution, and refinement parameters of **1** are summarized in Table 1.

CCDC 1014828 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystal data, data collection and structure refinement details for **1**.

Empirical formula	C ₅₄ H ₄₅ ClIrP ₃
M_r	1014.526
Crystal size, mm ³	0.12 × 0.10 × 0.07
Temperature, K	173(2)
Crystal system	triclinic
Space group	$P\bar{1}$
a , Å	10.9568(4)
b , Å	12.2532(5)
c , Å	19.4130(8)
α , deg	89.0097(12)
β , deg	76.8461(12)
γ , deg	66.3206(10)
V , Å ³	2316.21(16)
Z	2
$D_{\text{calcd.}}$, g cm ⁻³	1.46
μ (MoK α), mm ⁻¹	3.1
$F(000)$, e	1016
θ range for data collection, deg	3.24–27.54
hkl range	–13 → +14, ±15, +25
Reflections collected/independent	10 532/9447
R_{int}	0.04
R_1/wR_2 [$I > 2\sigma(I)$]	0.0242/0.0310
R_1/wR_2 (all data)	0.0531/0.0545
S	1.085
$\Delta\rho_{\text{fin}}$ (max/min), e Å ⁻³	0.92/–0.41

Acknowledgement

The authors are grateful to the Department of Chemistry, Ludwig-Maximilians-Universität München, for support of this work. Johnson Matthey plc, Reading, UK, is gratefully acknowledged for a generous loan of hydrated iridium(III) chloride.

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