

Convenient Synthesis and Molecular Structure of PPN[RhCl₂(CO)₂] (PPN⁺ = Bis(triphenylphosphane)iminium)

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The reaction of hydrated rhodium(III) chloride with formic acid in refluxing ethoxyethanol afforded in a convenient way the known rhodium carbonyl chlorido complex anion *cis*-[RhCl₂(CO)₂][−]. This species was formed in good yield and was characterized as its PPN salt (PPN⁺ = bis(triphenylphosphane)iminium cation). The molecular structure of the title compound PPN[RhCl₂(CO)₂] was confirmed by X-ray diffraction and shown to be isomorphous to PPN[IrCl₂(CO)₂].

Key words: Rhodium, Carbonyl Complexes, Chlorido Complexes, Crystal Structure

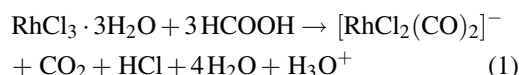
Introduction

Recently we reported an efficient synthesis of the complex anion *cis*-[IrCl₂(CO)₂][−] from hydrated iridium(III) chloride using formic acid as the carbonylating agent. The crystallographic characterization of this species was possible by the isolation of its PPN salt (PPN⁺ = bis(triphenylphosphane)iminium cation) [1]. In this light we were interested in searching for a similar convenient synthetic pathway affording the closely related complex anion *cis*-[RhCl₂(CO)₂][−]. It is known from the literature that in the case of rhodium the synthesis of the latter species is possible by the use of formic acid as the carbonylating agent [2]. Till now the crystal structure of the dichlorido-dicarbonylrhodate(1−) anion was only reported in its tetra-*n*-butylammonium salt as the only salt with a relatively simple cation [3]. Here we describe a convenient

synthesis and the crystallographic characterization of PPN[RhCl₂(CO)₂] (**1**).

Results and Discussion

As described for the synthesis of [IrCl₂(CO)₂][−] [1], we observed in the reaction of hydrated rhodium(III) chloride in a mixture of ethoxyethanol and formic acid under reflux for about one hour the formation of the corresponding complex *cis*-[RhCl₂(CO)₂][−]. The progress of the reaction according to Eq. 1 was obvious from the color change from red-brown to slightly yellow.



The addition of [PPN]Cl (PPN⁺ = bis(triphenylphosphane)iminium) allowed the isolation of the complex salt PPN[RhCl₂(CO)₂] (**1**) as pale-yellow crystals in good yield. It should be noted that crystals of compound **1** are stable in air for long times, however in solution the compound is decomposed within short periods. Compound **1** was characterized by elemental analysis, and IR and ¹H, ¹³C and ³¹P NMR spectroscopy (see Experimental Section), as well as by a single-crystal X-ray diffraction study. The ¹³C{¹H} NMR spectrum of **1** in CD₂Cl₂ exhibits a signal corresponding to the carbonyl ligand at 182.0 ppm as a doublet with a coupling *J*_{RhC} = 71.9 Hz. This finding is in accordance with the observations for other rhodium complexes bearing carbonyl groups, as also reported by us, *e. g.* in refs. [4, 5]. At this point we complement data concerning the ¹³C{¹H} NMR spectrum of the complex [{Rh(μ-Cl)(CO)(coe)}₂] (coe = *cis*-cyclooctene) [5] for which we reported a signal at 182.1 ppm as singlet (C₆D₆). We have revisited the NMR spectrum of this compound in detail and found indeed a doublet at 182.0 ppm with a corresponding coupling *J*_{RhC} = 82.5 Hz. Infrared absorption measurements on the compound [N^{*n*}Bu₄][RhCl₂(CO)₂] (**3**) had afforded two very strong ν(CO) bands at 2058 and 1974 cm^{−1} (KBr) [6]. For compound **1** we found a splitting of these two characteristic bands (2067sh, 2054s, 1981sh, 1976s cm^{−1}) using the ATR technique. A similar splitting of bands was also observed for PPN[IrCl₂(CO)₂] (2051sh, 2040s, 1958sh, 1955s cm^{−1}) [1].

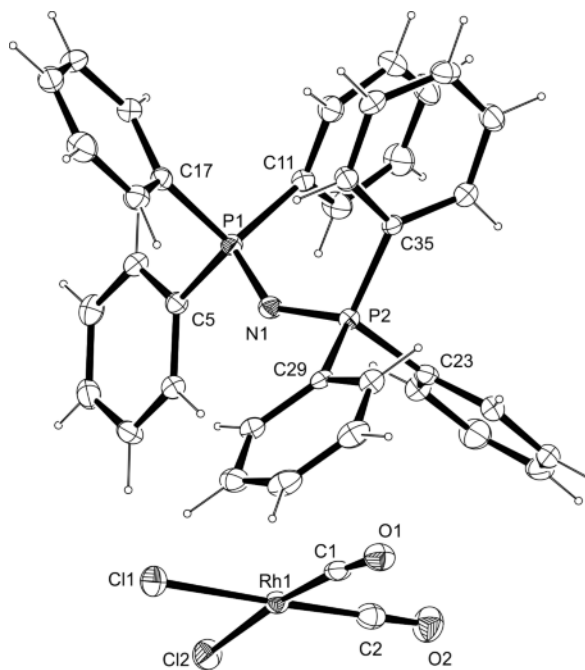


Fig. 1. Molecular structure of **1** in the crystal (only one of the two formula units in the asymmetric unit is shown). Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Rh1–C1 1.843(3), Rh1–C2 1.834(3), Rh1–Cl1 2.3650(7), Rh1–Cl2 2.3560(7), C1–O1 1.144(3), C2–O2 1.137(3), Rh1–C1–O1 174.1(2), Rh1–C2–O2 178.7(3), C1–Rh1–C2 89.72(12), C1–Rh1–Cl1 91.79(9), C1–Rh1–Cl2 174.31(9), C2–Rh1–Cl2 86.82(9), C2–Rh1–Cl1 177.54(10), Cl1–Rh1–Cl2 91.82(3).

Compound **1** crystallized as pale-yellow rods from dichloromethane-methanol by the slow diffusion method a room temperature overnight. Crystals of **1** belong to the triclinic space group $P\bar{1}$ with four formula units in the unit cell. A view of the molecular structure in the 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 closely related iridium compound $\text{PPN}[\text{IrCl}_2(\text{CO})_2]$ (**2**) [1]. Furthermore, the molecular structure of the anion of **1** in the crystal is similar to that in the known compound $[\text{N}^n\text{Bu}_4][\text{RhCl}_2(\text{CO})_2]$ (**3**) [3]. For **2** the following characteristic bonding parameters had been found: Ir1–C1 1.819(5), Ir1–C2 1.820(6), Ir1–Cl1 2.3601(9), Ir1–Cl2 2.3437(12) Å; Ir1–C1–O1 174.5(4), Ir1–C2–O2 178.8(5), C1–Ir1–C2 89.9(2), C1–Ir1–Cl1 92.32(15), C1–Ir1–Cl2 175.91(15), C2–Ir1–Cl2 88.32(15), C2–

Ir1–Cl1 177.26(16), Cl1–Ir1–Cl2 89.59(5)° [1]. In the literature the crystal structure of the complex $[\text{RhCl}_2(\text{CO})_2]^-$ in its tetra-*n*-butylammonium salt was reported [3]. Whereas the alkyl ammonium cation of the latter compound showed no unusual features, in the square-planar complex anion a disordering of one carbonyl and its chlorido ligand in *trans*-position was found. For comparative purposes relevant bonding parameters of the anion in compound **3** are given: Rh–C 1.72(3), Rh–Cl 2.345, and C–O, 1.19(3) Å; Rh–C–O, 173.4(23), and C–Rh–Cl, 178.4(9)° [3]. These findings are in a good accordance with the observed bonding characteristics of the title compound **1**.

In conclusion, we have reported a convenient synthesis and the crystallographic characterization of the compound $\text{PPN}[\text{RhCl}_2(\text{CO})_2]$. The crystal structure determination revealed that crystals of **1** are isotopic to those of the Ir analog $\text{PPN}[\text{IrCl}_2(\text{CO})_2]$. Both complex salts are available in good yields starting from the corresponding metal halides using formic acid as the reducing and carbonylating agent.

Experimental Section

All manipulations were carried out under a dry argon atmosphere using standard Schlenk techniques. Solvents were dried according to standard procedures and stored under argon. $[\text{PPN}]\text{Cl}$ and ethoxyethanol were purchased from ABCR and used as received. IR spectra were recorded from solids with a Jasco FT/IR-460 plus spectrometer equipped with an ATR unit. NMR spectra were recorded using Jeol Eclipse 270 and 400 instruments operating at 270 MHz (^1H), 109 MHz (^{31}P), and 100 MHz (^{13}C), respectively. Elemental analyses (C, H, Cl, N) were performed by the Microanalytical Laboratory of the Department of Chemistry, LMU Munich, using a Heraeus Elementar Vario El instrument.

Synthesis of $\text{PPN}[\text{RhCl}_2(\text{CO})_2]$ (**1**)

Hydrated rhodium(III) chloride (374 mg, 1.42 mmol) was dissolved in a mixture of ethoxyethanol (8 mL) and formic acid (8 mL) at room temperature. The mixture was refluxed for 70 min, during which period a color change from red-brown to slightly yellow occurred. The hot solution was treated with $[\text{PPN}]\text{Cl}$ (900 mg, 1.57 mmol) by stirring for some minutes and then cooled to room temperature. In contrast to the preparation of the analogous iridium compound [1], no precipitate was obtained at this point. The product was precipitated as a pale-yellow powder by addition of diethyl ether (60 mL). Compound **1** was filtered off, washed twice with 10 mL of diethyl ether, and dried

in vacuo. Yield 740 mg (68%); m.p. 170–172 °C (decomp.). – $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta = 22.2$ (s, PPN^+). – ^1H NMR (CD_2Cl_2): $\delta = 7.67$ – 7.45 (m, 30 H, C_6H_5). – $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta = 182.0$ (d, $J_{\text{RhC}} = 71.9$ Hz, Rh-CO), 133.8 (s, C_6H_5), 132.2 (m, C_6H_5), 129.5 (m, C_6H_5), 127.1 (d, $J_{\text{PC}} = 108.3$ Hz, *ipso*- C_6H_5). – IR (ATR, cm^{-1}): $\nu(\text{CO}) = 2067$ (sh), 2054 (s), 1981 (sh), 1976 (s). – $\text{C}_{38}\text{H}_{30}\text{Cl}_2\text{NO}_2\text{P}_3\text{Rh}$ (768.42): calcd. C 59.40, H 3.94, Cl 9.23, N 1.82; found C 59.37, H 4.04, Cl 9.45, N 1.78.

X-Ray crystal structure determination

Crystals of **1** for the X-ray structure analysis were obtained as described above. A suitable crystal was selected by means of a polarization microscope, mounted on the tip of a glass fiber, and investigated on an Oxford Diffraction XCalibur 3 diffractometer using $\text{MoK}\alpha$ radiation ($\lambda = 0.71073$ Å). The structure was solved by Direct Methods (SIR-97) [7] and refined by full-matrix least-squares calculations on F^2 (SHELXL-97) [8]. Anisotropic displacement parameters were refined for all non-hydrogen atoms. Details of crystal data, data collection, structure solution, and refinement parameters of **1** are summarized in Table 1.

CCDC 974441 (**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.

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

| | |
|--|--|
| Empirical formula | $\text{C}_{38}\text{H}_{30}\text{Cl}_2\text{NO}_2\text{P}_3\text{Rh}$ |
| M_r | 768.409 |
| Crystal size, mm^3 | $0.373 \times 0.202 \times 0.169$ |
| Temperature, K | 100(2) |
| Crystal system | triclinic |
| Space group | $P\bar{1}$ (no. 2) |
| a , Å | 9.7144(3) |
| b , Å | 17.2943(6) |
| c , Å | 21.6276(9) |
| α , deg | 74.914(3) |
| β , deg | 87.824(3) |
| γ , deg | 80.028(3) |
| V , Å ³ | 3455.2 (2) |
| Z | 4 |
| $D_{\text{calcd.}}$, g cm^{-3} | 1.48 |
| $\mu(\text{MoK}\alpha)$, mm^{-1} | 0.8 |
| $F(000)$, e | 1560 |
| θ range for data collection, deg | 4.15–26.37 |
| hkl range | $-12 \leq h \leq 11$, $-21 \leq k \leq 21$, $-19 \leq l \leq 27$ |
| Reflections collected/independent | 20864/13949 |
| R_{int} | 0.0252 |
| R_1/wR_2 [$I > 2\sigma(I)$] | 0.0356/0.0757 |
| R_1/wR_2 (all data) | 0.0503/0.0846 |
| S | 1.050 |
| $\Delta\rho_{\text{fin}}$ (max/min), e Å^{-3} | 0.54/–0.56 |

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