The Crystal Structure of *trans*-[{Rh(μ-Cl)(CO)(coe)}$_2$] (coe = *cis*-cyclooctene)

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Single crystals of *trans*-[{Rh(μ-Cl)(CO)(coe)}$_2$] (**1**) obtained from the reaction of [{Rh(μ-Cl)(coe)$_2$}$_2$] (coe = *cis*-cyclooctene) with carbon monoxide have been analyzed by X-ray crystallography (monoclinic, $C2/c$, Z = 4, a = 15.6271(4), b = 13.6943(4), c = 10.4169(2) Å; β = 115.3549(17)°; V = 2014.50(9) Å^3; T = 200(2) K).

Key words: Rhodium, Carbonyl, Olefin Complex, Crystal Structure

Introduction

The synthesis of *trans*-[{Rh(μ-Cl)(CO)(coe)}$_2$] (**1**) was described by Varshavsky *et al.* some years ago [1, 2], but no crystal structure of this compound was reported. In an attempt to probe a possible convenient synthesis of [{Rh(μ-Cl)(CO)$_2$}$_2$] from the precursor [{Rh(μ-Cl)(coe)$_2$}$_2$] and carbon monoxide in diethyl ether, we found that the target complex was not available by this method. Instead, the title compound **1** was obtained in high yield. We report here its molecular structure and its characterization by NMR spectroscopy.

Results and Discussion

In 1974 the synthesis of **1** by the reaction of [{Rh(μ-Cl)(CO)$_2$}$_2$] with an excess of *cis*-cyclooctene in refluxing benzene was described and the product characterization was performed using elemental analysis and IR spectroscopy [1]. Now we observed that complex **1** is obtainable by treatment of [{Rh(μ-Cl)(coe)$_2$}$_2$] with carbon monoxide in diethyl ether at r. t. In this way compound **1** was obtained as yellow crystals suitable for an X-ray diffraction study. The compound was characterized by elemental analysis, IR and NMR spectroscopy, and mass spectrometry (see Experimental Section). Relevant NMR data of **1** agree well with those reported for [Rh(acac)(coe)$_2$] (acac = acetylacetonato) [3], except for the chemical shift value of the olefinic protons. For the reference compound the olefinic carbon atoms resonate at δ^{13}C = 78.3 ppm and the corresponding ^{1}H NMR signal is found at 2.51 ppm (C$_6$D$_6$), as confirmed by a ^{1}H-^{13}C HSQC experiment. On the other hand, for the compound [{Ir(μ-Cl)(CO)(coe)$_2$}$_2$] the corresponding signal of the olefinic protons appears at 4.90 ppm (CDCl$_3$) [4]. The ^{1}H NMR spectrum of **1** (C$_6$D$_6$) shows a multiplet centered at 4.59 ppm for the olefinic protons bound to rhodium, and the ^{13}C{^{1}H} NMR spectrum a corresponding signal at 81.3 ppm (C$_6$D$_6$). The assignment was confirmed by a ^{1}H-^{13}C HMQC NMR experiment (400 MHz, C$_6$D$_6$) indicating the expected cross peak. The ^{1}H resonances at 2.13 and 1.66 are both connected to the ^{13}C resonances at 31.3 and 30.5 ppm, respectively, and the ^{1}H resonance at 1.10 ppm is connected to the ^{13}C resonance at 26.0 ppm. Unfortunately, no Rh–C coupling was detectable, (*e. g.* [Rh(acac)(coe)$_2$]: $J_{\mathrm{Rh-C}}$ = 13 Hz [3]). However, in the ^{1}H NMR spectrum of **1** (multiplet at δ = 4.59 ppm) the coupling to rhodium is observed. In the ^{13}C{^{1}H} NMR spectrum of **1** the signal corresponding to the carbonyl group appears at 182.1 ppm only as singlet.

The X-ray crystal structure analysis revealed that crystals of **1** belong to the monoclinic space group $C2/c$ with four independent molecules in the unit cell. A view of the molecule is shown in Fig. 1, selected bond lengths and angles are given in the caption. The molecular structure is comparable to those of [{Rh(μ-Cl)(C$_2$H$_4$)$_2$}$_2$] [5], [{Rh(μ-Cl)(CO)$_2$}$_2$] [6], *cis*-[{Rh(μ-Cl)(CO)(PMe$_2$Ph)}$_2$] [7], and *trans*-[{Rh(μ-Cl)(C$_2$H$_4$)(^{t}Bu$_2$PR)}$_2$] (R = 2.6-Me$_2$C$_6$H$_3$CH$_2$CH$_2$) [8]. Each rhodium atom is in an approximately square-planar configuration, being bonded to two bridging chlorido ligands, one carbonyl group, and two carbon atoms of the coe ligand occupying one coordination site. The olefinic bonds are symmetrically linked to the metal centers and lie nearly perpendicular to the coordination plane of each rhodium atom. The central Rh$_2$Cl$_2$ four-membered ring is folded, and

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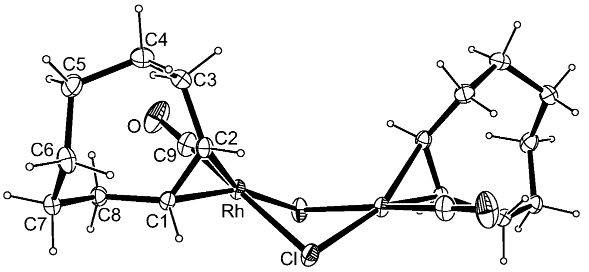

Fig. 1. Molecular structure of *trans*-[{Rh(μ-Cl)(CO)(coe)}$_2$] (**1**) in the crystal. Displacement ellipsoids at the 30 % probability level. Symmetry-equivalent atoms are not labeled. Selected distances (Å) and angles (deg): Rh–Cl^i 2.3955(6), Rh–C(9) 1.806(3), C(9)–O 1.146(3), Rh–C(1) 2.141(2), Rh–C(2) 2.153(2), C(1)–C(2) 1.391(3), C(1)–C(8) 1.503(3), C(2)–C(3) 1.506(3), Rh···Rh^i 3.1951(3); C(1)–Rh–C(2) 37.81(9), C(9)–Rh–Cl^i 92.31(8), C(9)–Rh–Cl 176.34(8), C(1)–Rh–Cl 90.89(6), C(1)–Rh–Cl^i 161.19(6), C(2)–Rh–Cl 90.84(6), C(2)–Rh–Cl^i 159.79(6), C(1)–Rh–C(9) 92.12(10), C(2)–Rh–C(9) 92.81(10), Cl–Rh–Cl^i 84.18(2), C(2)–C(1)–Rh 71.55(13), Rh–C(2)–C(1) 70.64(13), Rh–Cl–Rh^i 83.733(19), Rh–C(9)–O 179.0(3). Symmetry operation: ^{i} $-x, y, 3/2-z$.

the angle between the two planes defined by the atoms Cl, Rh, Cl^i and Cl, Rh^i, Cl^i is 128.15(3)°. A similar bending was found for the other compounds mentioned above [5–8], *e. g.* for [{Rh(μ-Cl)(CO)$_2$}$_2$] this angle was reported to be 126.8(3)° [6b]. The bonding characteristics of the Rh(coe) moiety in the molecule of **1** agree well with the corresponding ones for *e. g.* [Rh(acac)(C$_4$F$_6$)(coe)] (Rh–C(1), 2.196(11); Rh–C(2), 2.163(13); C(1)–C(2), 1.373(16) Å [9]), [Rh{(η^5-C$_5$H$_4$)CH(C$_2$H$_4$)$_2$NMe}(coe)$_2$] (Rh–C(1), 2.129(4); Rh–C(2), 2.139(5); C(1)–C(2), 1.415(7) Å [10]), and [Rh{ArNC(Me)CHC(Me)NAr}(coe)] (Ar = 2,6-Me$_2$C$_6$H$_3$; Rh–C(1), 2.072(5); Rh–C(2), 2.066(6); C(1)–C(2), 1.398(7) Å [11]).

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 nitrogen. The complex [{Rh(μ-Cl)(coe)$_2$}$_2$] was prepared according to the literature procedure [12]. ^{1}H and ^{13}C{^{1}H} spectra were recorded using Jeol Eclipse 270 and 400 instruments operating at 270 and 400 MHz (^{1}H) and 68 and 100 MHz (^{13}C). All chemical shifts (δ) are given in ppm relative to TMS. Mass spectra were measured using a Jeol Mstation JMS 700 in the direct EI (DEI) or DEI$^+$ mode. Infrared spectra were recorded from KBr pellets with Nicolet 520 FT-IR and Perkin Elmer Spectrum One FT-IR spectrometers. Elemental analyses (C, H, Cl) were performed by the Microanalytical Laboratory of the Department of Chemistry and Biochemistry, LMU Munich, using a Heraeus Elementar Vario El instrument.

Table 1. Details of the X-ray data collection and refinement for **1**.

Formula	$C_{18}H_{28}Cl_2O_2Rh_2$
M_r	553.13
Temperature, K	200(2)
Crystal system	monoclinic
Space group	$C2/c$
a, Å	15.6271(4)
b, Å	13.6943(4)
c, Å	10.4169(2)
β, deg.	115.3549(17)
V, Å^3	2014.50(9)
Z	4
D_{calc}, g cm^{-3}	1.8238(1)
μ(MoK_α), mm^{-1}	1.911
F(000), e	1104
θ Range for data collection, deg	3.41 – 27.51
hkl range	$-20 \le h \le 18$, $-17 \le k \le 17$, $-13 \le l \le 13$
Reflections collected/independent	16077/2301
R_{int}	0.034
Reflections with $I \ge 2\sigma(I)$	1993
Refined parameters	117
R_1 [$I \ge 2\sigma(I)$]	0.023
wR_2 (all data)	0.054
Goodness-of-fit on F^2	1.069
Peak and hole, e Å^{-3}	0.79, −0.58

*Synthesis of trans-[{Rh(μ-Cl)(CO)(coe)}$_2$] (**1**)*

A slurry of [{Rh(μ-Cl)(coe)$_2$}$_2$] (360 mg, 0.5 mmol) in 20 mL of diethyl ether was stirred at r. t., and a slow stream of carbon monoxide was bubbled through the solution for about 5 min. During this time a clear pale yellow solution resulted. The solution was evaporated to dryness. The residue was dried for 2 h *in vacuo* and dissolved in 10 mL of heptane. The solution was cooled overnight at 5 °C affording **1** as yellow needles suitable for the X-ray diffraction study. Yield: 266 mg (96 %). M. p. 132 – 134 °C (decomp.). – IR (KBr): ν (CO) = 1999 cm^{-1} (s). – ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 4.59 (m, 2H, C*H*, olefinic coe; $^2J_{Rh-H}$ = 5.5 Hz), 2.13 (m, br, 2H, C*H*$_2$, aliphatic coe), 1.66 (m, br, 2H, C*H*$_2$, aliphatic coe), 1.10 (m, br, 8H, C*H*$_2$, aliphatic coe). – ^{13}C{^{1}H} NMR (68 MHz, C$_6$D$_6$): δ = 182.1 (s, *C*O), 81.3 (s, *C*H, olefinic coe), 31.3 (s, *C*H$_2$, aliphatic coe), 30.5 (s, *C*H$_2$, aliphatic coe), 26.0 (s, *C*H$_2$, aliphatic coe). – MS (DEI$^+$): m/z (%) = 552 (4) [M]$^+$. – $C_{18}H_{28}Cl_2O_2Rh_2$ (553.14): calcd. C 39.09, H 5.10, Cl 12.82; found C 39.40, H 5.36, Cl 12.78.

X-Ray crystal structure determination

A single crystal of **1** was selected by means of a polarization microscope, mounted on the tip of a glass fiber, and investigated on a Nonius KappaCCD diffractometer using MoK_α radiation (λ = 0.71073 Å). The structure was solved by Direct Methods (SIR 97) [13] and refined by full-matrix least-squares calculations on F^2 (SHELXL-97) [14]. 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 658229 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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