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Solid state structure of P(*o*-(CF_3)Ph)$_3$ substituted $Rh_2(CO)_4(\mu\text{-}Cl)_2$. Formation of dimeric $[Rh_2(CO)_3(\mu\text{-}Cl)_2\{P(o\text{-}(CF_3)Ph)_3\}]_2$

Sirpa Jääskeläinen [a,*], Pekka Suomalainen [a], Matti Haukka [a], Helena Riihimäki [b],
Jouni T. Pursiainen [b], Tapani A. Pakkanen [a]

[a] *Department of Chemistry, University of Joensuu, P.O. Box 111, FIN-80101 Joensuu, Finland*
[b] *Department of Chemistry, University of Oulu, P.O. Box 3000, FIN-90401 Oulu, Finland*

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Abstract

Reaction of tris(*o*-trifluoromethylphenyl)phosphane with tetracarbonyldi-μ-chlorodirhodium chloride leads to replacement of one carbonyl group to give dimeric units $Rh_2(CO)_3(\mu\text{-}Cl)_2\{P(o\text{-}(CF_3)Ph)_3\}$. The crystal structure indicates direct Rh–Rh interactions within and between the primary units, confirming the tetranuclear chain compound $[Rh_2(CO)_3(\mu\text{-}Cl)_2\{P(o\text{-}(CF_3)Ph)_3\}_2$ as the actual solid state structure. The phosphane ligands, which are situated at the ends of the chain, prevent further interactions between neighboring tetrameric moieties and the formation of an infinite chain. © 2001 Elsevier Science B.V. All rights reseved.

Keywords: Rhodium; Carbonyl; Phosphane; Crystal structures

1. Introduction

Tetracarbonyldi-μ-chlorodirhodium $Rh_2(CO)_4(\mu\text{-}Cl)_2$ is an excellent source of other rhodium(I) species. Reactions with different types of donor lead to substitution of the carbonyl groups or the chloride bridges. Formation of mononuclear species by bridge splitting is also possible. The reactions with tertiary phosphanes are well documented. Depending on the phosphane and the reaction conditions dinuclear derivatives $Rh_2(CO)_{4-n}(\mu\text{-}Cl)_2L_n$ or mononuclear species $Rh(CO)_{3-n}ClL_n$ are formed. A wide range of structurally characterized dinuclear derivatives with two to four phosphane groups has been reported. Typically, the monosubstituted dinuclear species have been characterized solely by infrared and mass spectroscopy [1,2]. $Rh_2(CO)_3Cl(Cl/I)PPh_3$ [3] is one of the rare dinuclear compounds whose crystal structure has been determined. However, this compound was formed in an organometallic mediated reaction.

Here we report the synthesis and structural characterization of $[Rh_2(CO)_3(\mu\text{-}Cl)_2\{P(o\text{-}CF_3)Ph)_3]_2$.

2. Results and discussion

The reaction of trifluoromethyl substituted triphenylphosphane $P(o\text{-}(CF_3)Ph)_3$ with tetracarbonyldi-μ-chlorodirhodium $Rh_2(CO)_4Cl_2$ led to replacement of a single carbonyl group and the formation of dinuclear $Rh_2(CO)_3(\mu\text{-}Cl)_2\{P(o\text{-}(CF_3)Ph)_3\}$ units [4]. In the solid state, two units are linked together to form a tetranuclear chain structure $[Rh_2(CO)_3(\mu\text{-}Cl)_2\{P(o\text{-}(CF_3)\text{-}Ph)_3\}]_2$ (**1**). The crystal structure [5] and the numbering scheme are shown in Fig. 1.

At the terminal metals the two chloride bridges, the terminal carbonyl, and the terminal phosphorus are positioned on a plane. The chlorine bridges are symmetric: the Rh–Cl distances are in the range of 2.3823(7)–2.4354(7) Å and the Rh–Rh–Cl angles in the range of 51.06(2)–52.67(2)°. The dihedral angle between the planes defined by the metal bond and the chlorides is 116.93(3)°. In the parent compound $Rh_2(CO)_4(\mu\text{-}Cl)_2$ the corresponding angle is 126.8(3)° [6]. At the inner rhodium the chlorides and the carbonyls are approximately planar and the angle between the Rh(1)–Rh(2) bond and the plane is 53°. The carbonyls at both metals have typical Rh–C lengths, 1.807(3), 1.845(3), and 1.849(3) Å; the bond in the *cis* position to the phosphane is slightly shorter.

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* Corresponding author. Fax: + 358-2513390.
E-mail address: sirpa.jaaskelainen@joensuu.fi (S. Jääskeläinen).

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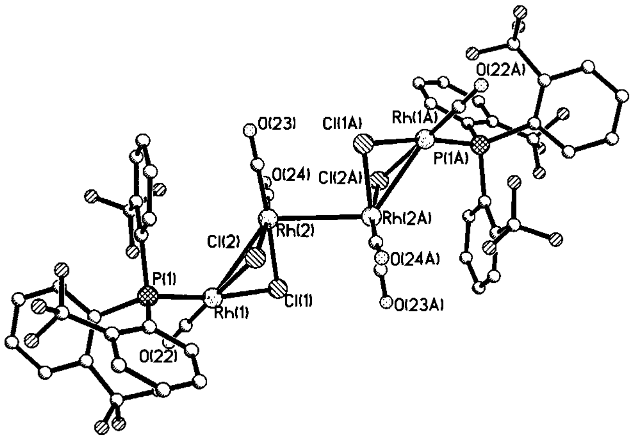

Fig. 1. Structure of $[Rh_2(CO)_3(\mu\text{-}Cl)_2\{P(o\text{-}(CF_3)Ph)_3\}]_2$. Selected bond distances (Å) and angles (°): Rh(1)–Rh(2), 2.9753(3); Rh(2)–Rh(2A), 3.2203(4); Rh(1)–P(1), 2.2485(7); P(1)–Rh(1)–Rh(2), 120.99(2); Rh(1)–Rh(2)–Rh(2A), 123.66(11).

The two $Rh_2(CO)_3(\mu\text{-}Cl)_2\{P(o\text{-}(CF_3)Ph)_3\}$units are linked by weak Rh–Rh interaction, where the dinuclear units are joined with the Rh–Rh–Rh angle of 123.66(11)°. The torsion angles Cl(1)–Rh(2)–Rh(2A)–Cl(1A) and Rh(1)–Rh(2)–Rh(2A)–Rh(1A) are both 180.0° due to symmetry. The Rh–Rh distance within the units is 2.9753(3) Å, while the Rh–Rh distance between the primary units (3.2203(4) Å) is significantly longer, indicating weaker metal–metal interaction. In the solid state of the parent compound $Rh_2(CO)_4(\mu\text{-}Cl)_2$ the molecules are 'nearly bonded'; the intermolecular metal–metal distance is longer than in **1** (3.324 Å) forming zig-zag chains [6]. Similarly, the chlorine bridged Rh–Rh bond is slightly longer (3.138 Å) than in **1**. Thus, the inter- and intramolecular metal–metal interactions in the parent compound are somewhat weaker than the corresponding interactions in **1**.

In the earlier reported structure of $Rh_2(CO)_3(\mu\text{-}Cl)(\mu\text{-}Cl/I)PPh_3$ [3] the intramolecular metal bond is 3.014(2)Å, and thus only slightly longer than in **1**, but there is no interaction between the adjacent molecules. Several phosphane substituted species with two to four phosphane groups have been reported, and in $Rh_2(CO)_2Cl_2(PMe_2Ph)_2$, for example, the Rh···Rh distance is 3.167 Å. This is comparable to the distances found in most other structures of bent di-μ-chloro complexes of Rh(I) and is considered as a weak metal–metal interaction [7].

In **1**, one carbonyl in each of the parent $Rh_2(CO)_4(\mu\text{-}Cl)_2$ units is replaced by a phosphane group. While the phosphanes enhance metal–metal interaction and the association of the primary units, their bulkiness prevents interactions between the tetranuclear $[Rh_2(CO)_3(\mu\text{-}Cl)_2\{P(o\text{-}(CF_3)Ph)_3\}]_2$ units and the growth of an infinite chain.

The properties of the trifluoromethyl derivative of triphenylphosphane make it suitable for controlling the level of ligand substitution in $Rh_2(CO)_4Cl_2$. The formation of a stable monosubstituted species is not typical; the substitution with phosphanes usually proceeds further. Even though the compound in solution appears to be dimeric, in the solid state the dinuclear species are coupled.

3. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 159196 for compound **1**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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[4] The compound was formed by reaction between $Rh_2(CO)_4Cl_2$ and $P(o\text{-}(CF_3)Ph)_3$ in MeOH in Rh/L ratio 1:1 and successive crystallization in CH_2Cl_2 at room temperature. IR (CH_2Cl_2, cm^{-1}): 2093s, 2024s, 2008m. IR (KBr, cm^{-1}): 2082s, 2028s, 2010vs. ^{31}P-NMR (ppm): $\delta = 63.5$ (d, $^1J_{P-Rh} = 195$ Hz). Owing to the presence of small amounts of free ligand, as evidenced by NMR spectroscopy, there were slight deviations from theoretical values in the results of the elemental analysis.

[5] Crystal data for $[Rh_2(CO)_3(\mu\text{-}Cl)_2\{P(o\text{-}(CF_3)Ph)_3\}]_2$: $C_{48}H_{24}Cl_4F_{18}O_6P_2Rh_4$, M = 1654.05, monoclinic, $a = 8.25540(10)$, $b = 20.5824(3)$, $c = 15.8659(4)$ Å, $\beta = 91.6300(10)°$, $V = 2694.78(8)$ Å^3, $T = 120$ K, space group $P2_1/c$, $Z = 2$, $D_{calc} = 2.038$ g cm^{-3}, μ (Mo–K$_\alpha$) = 1.572 mm^{-1}, 20 758 reflections collected, 5568 unique ($R_{int} = 0.0343$), no. parameters 418. The final R_1 [$I > 2\sigma(I)$] was 0.0260 and wR_2 was 0.0536. The largest difference peak and hole (e Å^{-3}): 0.854 and −0.852. An orange plate-like crystal with dimensions 0.30 × 0.20 × 0.05 mm was used. Data was collected on a Nonius–Kappa CCD diffractometer. All non-hydrogen atoms were refined anisotropically and phenyl hydrogens were refined isotropically.

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