# *Notes*

# Studies of Tetrakis(trifluoroacetate) Dirhodium. 2.[†] A Pi Complex of Hexamethylbenzene with Tetrakis(trifluoroacetate) Dirhodium(II,II)

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*Summary: The solid-state reaction of $Rh_2(O_2CCF_3)_4$ with $C_6Me_6$ yields a one-dimensional copolymer $[Rh_2(O_2CCF_3)_4{\cdot}C_6Me_6]_\infty$ (**1**), which constitutes the first example of a dirhodium(II,II) carboxylate complex with arene. Compound **1** has been characterized by elemental analysis and IR and mass spectroscopy, and its structure has been determined by X-ray diffraction. In the crystal structure of **1** the alternating arrangement of $Rh_2(O_2CCF_3)_4$ and $C_6Me_6$ units forms infinite chains extended along the [100] direction. The coordination of hexamethylbenzene to the dirhodium unit is unsymmetrical, with two opposite edges of the arene ring approaching the axial sites of the dimers. This off-centered complexation causes no distortion of the aromatic system. The closest $Rh-C_{arene}$ contacts (2.770(6) and 2.787(6) Å) are the longest for any axial interactions to dirhodium carboxylates known to date. At the same time, the Rh−Rh distance (2.422(1) Å) is not as short as might have been expected in the case of total absence of axial donation.*

## Introduction

The exceptional ability of dirhodium(II) carboxylates to bind many types of axial ligands is now well-established and documented.[1] This property led Snatzke to exploit their use for the determination of absolute chiralities via the effect of chiral organic molecules in inducing CD/ORD effects into the readily observed visible spectrum of the $Rh_2^{4+}$ group.[2] As shown by spectral observations,[3] they are even capable of binding unfunctionalized olefins by direct attachment of C═C double bonds at axial positions. In confirmation of this, structural evidence has been obtained for the bisolefin complex 1:2 adduct of $Rh_2(O_2CCF_3)_4$ with ((−)*trans*-caryophyllene)[4] and the polymeric chain 1:1 complex of $Rh_2(O_2CBu^t)_4$ with 1,4-benzoquinone.[5] However, the complexation of dirhodium(II) carboxylates by arenes has not been systematically studied so far. We believe that many insights of interest to structural, theoretical, and organic chemistry should emerge from such an investigation.

At the time of our work on growing crystals of $Rh_2(O_2CCF_3)_4$ without any exogenous ligands,[6] it became apparent that the trifluoroacetate was forming an adduct with benzene, but we were unable to obtain suitable crystals from solution. After a recent report[7] on the preparation of the $Bi_2(O_2CCF_3)_4$ coordination copolymer with hexamethylbenzene, we have turned again to the solid-state approach in our research. We now present the synthesis and structural characterization of a one-dimensional coordination copolymer $[Rh_2(O_2CCF_3)_4{\cdot}C_6Me_6]_\infty$ (**1**)—the first example of a dirhodium(II) carboxylate complex with an arene.

## Results and Discussion

Complex **1** has been obtained by solid-state reaction of unligated dirhodium(II) tetrakis(trifluoroacetate) and hexamethylbenzene at 100 °C in a sealed evacuated ampule. The crystals of **1** were grown by sublimation in a small temperature gradient. These crystals are stable when exposed to air and are not soluble in common solvents unless there is dissociation to $Rh_2(O_2CCF_3)_4$ and $C_6Me_6$ as evidenced from NMR. The compound has been characterized in the solid state by elemental analysis and IR and mass spectroscopy, and its structure has been revealed in detail by X-ray diffraction.

Crystals of **1** adopt the triclinic $P\bar{1}$ space group with both the dirhodium molecule and the arene ring residing on inversion centers. The alternating arrangement of $Rh_2(O_2CCF_3)_4$ and $C_6Me_6$ units forms a chain structure (Figure 1) extended along the [100] direction of the unit

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[†] Part 1: Reference 6.

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10.1021/om9901933 CCC: $18.00

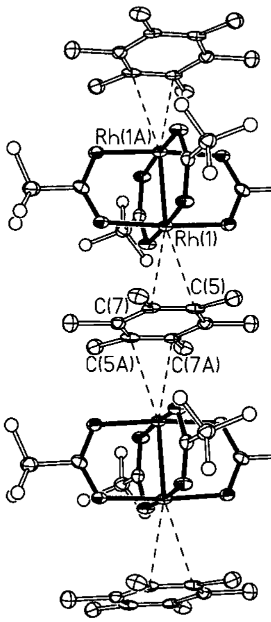


**Figure 1.** Fragment showing the alternating arrangement of $Rh_2(O_2CCF_3)_4$ and $C_6Me_6$ in the chain structure of **1**. The shortest $Rh-C_{arene}$ contacts are drawn by dashed lines. Hydrogen atoms of methyl groups are omitted.

cell. The distance between the metal and the center of the arene ligand (2.98 Å) is almost the same as that for the only analogue of **1**, the recently published[7] complex $[Bi_2(O_2CCF_3)_4{\cdot}C_6Me_6]_\infty$. However, the coordination of hexamethylbenzene is quite different in these two compounds. In the latter case the six-membered arene rings are simultaneously and equivalently attached to two Bi atoms lying opposite to each other above and below the center of the ring. Actually, this same way of building up chains with arene rings lying centrically on the line between two dimetal units was first discovered in this laboratory in 1988, in the compounds $[Cr_2(O_2CR)_4{\cdot}\text{arene}]_\infty$, where R = $CPh_3$ and arene = $C_6H_6$, $p$-$C_6H_4F_2$, and $p$-$C_6H_4Me_2$.[8] In these chromium compounds a theoretical analysis showed that the interactions were based on a donation of electrons of the $e_1$ orbitals of the arene ring to the empty $\pi^*$ orbitals of the quadruply bonded Cr−Cr units.

In the case of **1** off-center complexation takes place with opposite edges, on opposite sides of the ligand (C(5)−C(7) and C(5A)−C(7A)) approaching the axial sites of the neighboring dimers in $\eta^2(1,2){:}\eta^2(4,5)$ bridging fashion. Such unsymmetrical complexation is unusual for hexamethylbenzene and has been observed before[9] only in the ionic dimercury complex $[(C_6Me_6)Hg_2][AlCl_4]_2$ ($\eta^3$ and $\eta^2$ chelating). Of course there are prior examples of off-center donation of $\pi$ electrons of other arenes, including benzene, to an acceptor metal atom. The earliest such case is the $AgClO_4{\cdot}C_6H_6$ compound,[10] where it appears that there are also chains formed by alternating $Ag^+$ and $C_6H_6$ units with each benzene being approached by two silver ions in a manner similar to what we find here (Chart 1). This structure was originally described to display at room temperature a very peculiar disorder of both the $Ag^+$ and $ClO_4^-$ ions, which made the exact nature of the interaction ambiguous. In a recent publication[11] a correct and unambiguous determination of this structure at low temperatures has been reported. In the present case, the $Rh-C_{arene}$ distances are 2.770(6) and 2.787(6) Å for C(5) and C(7), respectively, while for the other four more distant atoms they lie in the range 3.275(6)−3.740(6) Å. It is worth noting here that for the dirhodium tetracarboxylate−olefin complexes with axial coordination of the C=C double bond, the Rh−C distances are *ca.* 0.3 Å shorter than in **1**, namely, 2.46(1) Å for caryophyllene[4] and 2.439(4) Å for benzoquinone.[5] The axial contacts in **1** are, in fact, longer than for any dirhodium carboxylate known to date.[1a] Actually, they are almost as long as the $Rh-C_{carboxyl}$ separations (Figure 2), 2.83 Å. The unsymmetrical complexation causes no corresponding distortion of the arene ring. The length of the C(5)−C(7) bond (1.40(1) Å) is between those of the other two crystallographically independent ones (1.396(9) and 1.421(9) Å). Still the axial interaction in **1**, which might be better called a “stacking interaction”, exists and is evidenced indirectly by the length of the Rh−Rh bond,

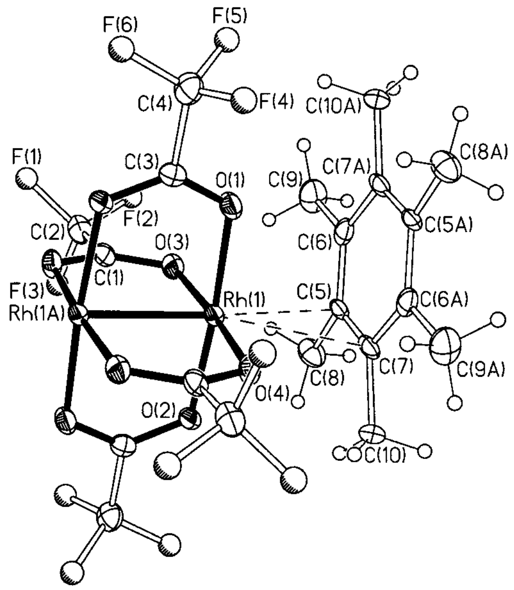
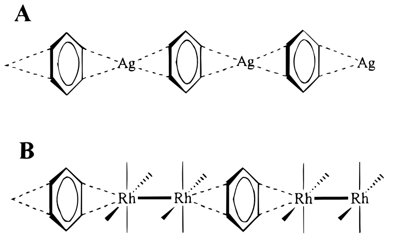


**Figure 2.** Perspective drawing showing one labeled unit of the one-dimensional copolymer **1**. Atoms are represented by thermal ellipsoids at the 40% probability level. Fluorine and hydrogen atoms are shown as spheres of arbitrary radii. Mean values of some principal dimensions (distances, Å; angles, deg) not given in the text: Rh(1)−O, 2.032(4); C−F, 1.33(1); Rh(1A)−Rh(1)−O, 87.7(1); O−Rh(1)−O, 90.0(2) and 175.4(2); O−C−O, 129.0(6); C−C−C, 119.9(6).

**Chart 1**



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2.422(1) Å. Were there no axial donation at all to the rhodium atoms, a Rh−Rh distance shorter than those found[1a,6] in all tetracarboxylate structures (2.38−2.47 Å) where axial ligation occurs might have been expected. However, the present value is right in the middle of this range. All other geometrical characteristics of the dirhodium fragment in **1** (Figure 2) are in no essential way different from those in previously described $Rh_2(O_2CCF_3)_4$ [6] molecules. The $CF_3$ groups all show high mobility and were refined as disordered over three different rotational orientations.

The first dirhodium tetracarboxylate adduct with arene as reported here reveals a rare $\eta^2$:$\eta^2$ orientation of the ligand on the metal axial sites. It is believed that the coordination of arene can be affected by the nature of the $O_2CR$ group, e.g. its steric and electronic features. It will be of interest to study the coordination of aromatic systems with other $Rh_2(O_2CR)_4$ molecules.

## Experimental Section

**General Information.** All the experimental manipulations involving the synthesis of the starting materials were carried out under dry, oxygen-free argon by employing Schlenk techniques. The anhydrous form of $Rh_2(O_2CCF_3)_4$ was prepared using literature procedures.[6] $C_6Me_6$ was purchased from Aldrich and recrystallized by sublimation prior use. The IR spectra were performed on a Perkin-Elmer 16PC FT-IR spectrophotometer using KBr pellets. $^1$H NMR spectra were obtained on a UNITY-plus 300 multinuclear spectrometer. Resonances were referenced internally to the residual proton impurity in the deuterated solvent. The EI/DP mass spectra were acquired using a VG Analytical 70S high-resolution, double-focusing, sectored (EB) mass spectrometer. Elemental analysis was done by Canadian Microanalytical Services, Ltd.

**Synthesis of $Rh_2(O_2CCF_3)_4 \cdot C_6Me_6$.** Compound **1** was prepared in almost quantitative yield by heating an equimolar mixture of unligated dirhodium(II) tetrakis(trifluoroacetate) (0.080 g, 0.12 mmol) and freshly sublimed hexamethylbenzene (0.019 g, 0.12 mmol) at 100 °C for 2 weeks in a sealed evacuated Pyrex ampule. The greenish brown single crystals of **1** were slowly grown in the same tube when it was placed in a temperature gradient of about 10°.

Anal. Calcd for **1**, $Rh_2O_8F_{12}C_{20}H_{18}$: C, 29.29; H, 2.21. Found: C, 29.00; H, 2.33. IR (KBr pellet, $\nu$ (cm$^{-1}$)): 2928 (m), 1663 (m), 1195 (s), 1167 (s), 860 (w), 739 (m). MS (EI/DP, 300 °C, $m/z$ (%)): 657 (100) [(**1** − $C_{12}H_{18})^+$], 544 (84) [$Rh_2(CF_3CO_2)_3^+$], 431 (100) [$Rh_2(CF_3CO_2)_2^+$], 318 (15) [$Rh_2(CF_3CO_2)^+$]. $^1$H NMR ($CD_2Cl_2$, 20 °C): $\delta$ 2.16 (s, 18H).

**X-ray Structure Determination.** The greenish-brown crystal selected was needle-shaped with dimensions 0.43 × 0.08 × 0.05 mm. It was mounted on the tip of a quartz fiber with silicon grease, and the setup was quickly placed in the cold $N_2$ stream (−60 °C) on the Model FR 558-S low-temperature controller. The X-ray diffraction study of **1** was carried out on a Nonius FAST diffractometer with an area detector using Mo Kα radiation. Fifty reflections were used in cell indexing and 248 reflections in cell refinement ($13° < 2\theta < 42°$). Axial images were performed to confirm the Laue group and all dimensions. A total of 3254 reflections in the range $4° < 2\theta < 46°$ were collected. Data were corrected for Lorentz and polarization effects by the MADNES program.[12] Reflection profiles were fitted and values of $F^2$ and $\sigma(F^2)$ for each reflection were obtained by the program PROCOR.[13] The intensities were also corrected for absorption anisotropy effects using a local adaptation of the program SORTAV[14] (transmission coefficients 0.752−0.934).

**Table 1. Crystallographic Data and Structure Refinement Details for $[Rh_2(O_2CCF_3)_4 \cdot C_6Me_6]_\infty$ (1)**

| | | | |
|---|---|---|---|
| formula | $Rh_2O_8F_{12}C_{20}H_{18}$ | $\gamma$, deg | 85.65(4) |
| fw | 820.16 | $V$, Å$^3$ | 646.7(4) |
| cryst syst | triclinic | Z | 1 |
| space group | $P\bar{1}$ (No. 2) | $\rho_{calc}$, g·cm$^{-3}$ | 2.106 |
| $a$, Å | 8.279(1) | $\mu$, mm$^{-1}$ | 1.407 |
| $b$, Å | 8.790(4) | radiation ($\lambda$, Å) | Mo Kα (0.710 73) |
| $c$, Å | 9.874(3) | temp, °C | −60 |
| α, deg | 70.26(3) | R1,[a] wR2[b] [$I > 2\sigma(I)$] | 0.038, 0.096 |
| $\beta$, deg | 73.05(3) | R1,[a] wR2[b](all data) | 0.041, 0.100 |

[a] $R1 = \sum[|F_o| - |F_c|]/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

Choice of the centrosymmetric space group $P\bar{1}$ revealed the positions of the Rh and O atoms, and successful refinement of the structure confirmed the choice. The fluorine atoms of $CF_3$ groups were found to be disordered over three different rotational orientations. Anisotropic displacement parameters were assigned to all non-hydrogen atoms, except disordered fluorines. Hydrogen atoms of methyl groups were then found in a difference Fourier map and also refined. Final refinement of 217 parameters and 38 restraints resulted in $R = 0.038$ (for 1542 reflections with $I > 2\sigma(I)$) and $R = 0.041$ (for all 1638 data). The largest peak in the final difference Fourier map was 0.76 e/Å$^3$, lying 0.97 Å from the Rh(1) atom.

All calculations were done on a DEC Alpha running VMS using programs SHELXTL[15] (structure solution) and SHELXL-93[16] (least-squares refinement). Relevant crystallographic data for complex **1** are summarized in Table 1.

**Acknowledgment.** We are grateful to the National Science Foundation for support.

**Supporting Information Available:** X-ray structural data for **1** including a summary of crystallographic parameters, atomic coordinates, bond distances and angles, and anisotropic displacement parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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