

# Studies of tetrakis(trifluoroacetate) dirhodium

## Part 4. Solventless synthesis of $\text{Rh}_2(\text{O}_2\text{CCF}_3)_2(\text{CO})_4$ combined with $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$ , a compound with infinite chains of rhodium atoms

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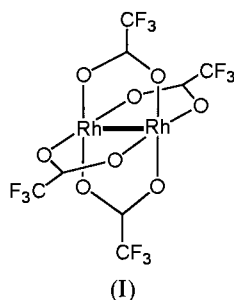
### Abstract

By reaction of  $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$  and  $\text{Mo}(\text{CO})_6$  in an evacuated sealed tube placed in a thermal environment where there is a thermal gradient (125–120°C), we have obtained a compound in which one  $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$  unit is sandwiched between two  $\text{Rh}_2(\text{O}_2\text{CCF}_3)_2(\text{CO})_4$  units, to give an essentially linear array of six rhodium atoms, with Rh–Rh distances of 2.960(1), 2.790(1) and 2.412(1) Å. These arrays of six rhodium atoms are then linked into infinite chains which lie parallel in the crystal, with Rh to Rh contacts of 3.062(1) Å. The crystals are markedly dichroic and relatively air stable. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Rhodium; Trifluoroacetate; Carbonyl; Crystal structure

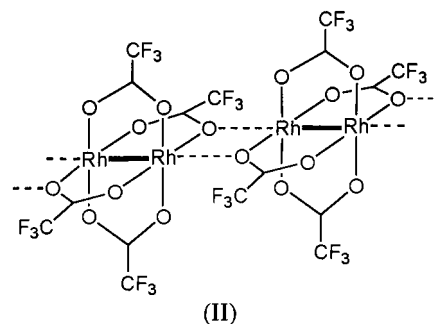
### 1. Introduction

Recently we began doing some chemistry that brings together two novel concepts: (1) the use of a powerful, two-ended Lewis acid as a structural element and (2) solventless synthesis.



The two-ended Lewis acid we have chosen is dirhodium(II) tetra(trifluoroacetate) (I). This is, of course, only one of hundreds of  $\text{Rh}_2(\text{O}_2\text{CR})_4$  and  $\text{Rh}_2(\text{O}_2\text{CR})_4\text{L}_2$

$\text{L}_2$  compounds [1–3]. It was discovered in 1963 [4], and a large number of  $\text{Rh}_2(\text{O}_2\text{CR})_4\text{L}_2$  adducts have been reported. In general, these are easily made by merely treating  $\text{Rh}_2(\text{O}_2\text{CR})_4$  with the donor and it is usually possible to obtain crystals of the di-adducts from solution. The  $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$  molecule is such a good Lewis acid that special precautions are necessary to avoid the formation of the diaqua adduct. As noted in the first report of its existence [4],  $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$  is volatile and can be sublimed without decomposition at temperatures up to 260°C [5]. Finally, we note that the ‘unliganded’ compound in the solid state [5] is ‘self-liganded’. That is, it forms infinite chains as shown in II.



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The range of organic functionalities that can form bonds to the axial position of  $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$  is almost unlimited. Only aliphatic hydrocarbons seem immune to its attraction. Olefins can be bound [6], as well as alkynes [7] and aromatics, such as benzene, xylene [7], and hexamethylbenzene [8]. A significant application of this nearly universal ability of  $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$  to bind organic molecules is the determination of the absolute chirality of an organic molecule by measuring the sign of the circular dichroism spectrum imposed on the  $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$  chromophore [6].

While bifunctional Lewis acids are, of course, well known in other contexts [9], the  $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$  molecule has a unique combination of properties: (a) it is a very strong Lewis acid; (b) it makes only a modest steric demand on its Lewis base partner; (c) its two Lewis acid sites are rather rigidly oriented in opposite directions; (d) it is soluble in a wide range of solvents; and (e) it is volatile.

In the work reported here as well as in other work which has been [8,10] or will soon be [7] reported, we have taken advantage of the volatility of  $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$  and its thermal stability, to synthesize compounds that could not be made at all (or at least only with great difficulty) in any other way than by reactions occurring via the gas phase at moderate temperatures. Practically all chemical reactions are carried out in a liquid medium. Solid-state reactions are rarely used because they are too slow. Gas-phase reactions are well known, but rarely used for preparation purposes, or to make new compounds. We describe here an interesting and surprising example of how synthesis may be carried out without a solvent, by way of the gas phase.

## 2. Experimental

### 2.1. General data

**Caution!** Metal carbonyls are potential sources of CO which can create a high pressure in a sealed ampoule upon heating. Avoid overheating or quick changes of temperature.

All the manipulations involving the synthesis of the starting material were carried out in a dry, oxygen-free nitrogen atmosphere by employing standard Schlenk techniques. The anhydrous form of  $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$  was prepared according to a literature procedure [5].  $\text{Mo}(\text{CO})_6$  was purchased from Strem Chemicals and recrystallized by sublimation before use. The IR spectrum was performed on a Perkin–Elmer 16PC FT-IR spectrophotometer using a KBr pellet. Elemental analysis was done by Canadian Microanalytical Services, Ltd. The EI/DP mass spectrum was acquired using a VG Analytical 70S high-resolution, double-focusing, sec-

tored (EB) mass spectrometer. The EDS X-ray spectrum was obtained on a Cameca SX50 electron microprobe using a PGT Imix EDS X-ray detector system.

### 2.2. Synthesis of $\{\text{Rh}_2(\text{O}_2\text{CCF}_3)_4\text{-}[\text{Rh}_2(\text{O}_2\text{CCF}_3)_2(\text{CO})_4]_2\}_\infty$ (**1**)

The title compound was prepared by heating an equimolar mixture of unligated dirhodium(II) tetrakis(trifluoroacetate) (0.070g, 0.11 mmol) and freshly sublimed molybdenum carbonyl (0.025 g, 0.10 mmol) at 120–125°C for 2 weeks in a sealed evacuated Pyrex ampoule. The yellow–greenish single crystals (with metallic reflectivity) of **1** were slowly grown in the same tube when it was placed in a temperature gradient of about 10°C. Yield: ~50%. The crystals of product **1** were recovered together with a powder, believed to be an oxidized form of molybdenum. Anal. Calc. for  $\text{C}_{24}\text{F}_{24}\text{O}_{24}\text{Rh}_6$ : C, 16.51; O, 22.00. Found: C, 16.54; O, 21.98%. IR (KBr pellet,  $\text{cm}^{-1}$ ): 2085 (m), 2020 (m), 1933 (w), 1863 (s), 1666 (s), 1192 (s), 861 (m), 839 (m), 805 (m), 785 (w), 740 (w), 724 (w), 684 (w), 540 (m). MS (EI/DP, 300°C,  $m/z$ ): 658 [ $(\text{Rh}_2(\text{O}_2\text{CCF}_3)_4)^+$ ] (**M1**), 544 [ $(\text{M1}-(\text{O}_2\text{CCF}_3))^+$ ] and [ $(\text{Rh}_2(\text{O}_2\text{CCF}_3)_2(\text{CO})_4)^+$ ] (**M2**), 516 [ $(\text{M2}-\text{CO})^+$ ], 488 [ $(\text{M2}-2\text{CO})^+$ ], 460 [ $(\text{M2}-3\text{CO})^+$ ], 432 [ $(\text{M1}-2(\text{O}_2\text{CCF}_3))^+$ ] and [ $(\text{M2}-(\text{O}_2\text{CCF}_3))^+$ ] and [ $(\text{M2}-4\text{CO})^+$ ], 403 [ $(\text{M2}-(\text{O}_2\text{CCF}_3-\text{CO})^+$ ], 375 [ $(\text{M2}-(\text{O}_2\text{CCF}_3)-2\text{CO})^+$ ], 347 [ $(\text{M2}-(\text{O}_2\text{CCF}_3)-3\text{CO})^+$ ], 319 [ $(\text{M1}-3(\text{O}_2\text{CCF}_3))^+$ ] and [ $(\text{M2}-(\text{O}_2\text{CCF}_3)-4\text{CO})^+$ ], 206 [ $(\text{Rh}_2)^+$ ].

### 2.3. X-ray crystallographic procedures

The yellow–greenish crystal selected was mounted on the tip of a quartz fiber with silicon grease, and the setup was quickly placed in the cold  $\text{N}_2$  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  $\text{Mo-K}_\alpha$  radiation. Fifty reflections were used in cell indexing and 243 reflections in cell refinement ( $18^\circ < 2\theta < 42^\circ$ ). Axial images were performed to confirm the Laue group and all dimensions. A total of 10 085 reflections in the range  $4^\circ < 2\theta < 45^\circ$  were collected. Data were corrected for Lorentz and polarization effects by the MADNES program [11]. Reflection profiles were fitted and values of  $F^2$  and  $\sigma(F^2)$  for each reflection were obtained by the program PROCOR [12].

Systematic absences in the data uniquely determined the space group to be  $P2_1/c$ . The coordinates of rhodium atoms were found in direct-method  $E$  maps using the structure solution program SHELXTL [13]. The positions of the remaining atoms were located by use of a combination of least-squares refinement and difference Fourier maps in the SHELXL-93 program [14]. The

fluorine atoms of all  $\text{CF}_3$  groups were found to be disordered over two or three different rotational orientations. Anisotropic displacement parameters were assigned to all atoms, except the disordered fluorines. Final refinement of 364 parameters and 48 restraints resulted in  $R = 0.042$  (for 2546 reflections with  $I > 2\sigma(I)$ ) and  $R = 0.051$  (for all 2951 data). The largest peak in the final difference Fourier map was  $1.02 \text{ e } \text{Å}^{-3}$ , lying  $0.99 \text{ Å}$  from the Rh(1) atom.

Table 1  
Crystal data and structure refinement for **1**

Empirical formula	$\text{C}_{24}\text{F}_{24}\text{O}_{24}\text{Rh}_6$
Formula weight	1745.70
Temperature (K)	213(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
$a$ (Å)	11.519(4)
$b$ (Å)	13.158(2)
$c$ (Å)	15.728(2)
$\beta$ (°)	108.22(1)
Volume (Å <sup>3</sup> )	2264.3(9)
$Z$	2
$D_{\text{calc}}$ (g cm <sup>-3</sup> )	2.560
$\mu$ (mm <sup>-1</sup> )	2.317
Crystal size (mm)	$0.13 \times 0.08 \times 0.05$
Maximum $2\theta$ (°)	45.0
No. unique reflections	2951
No. observed data [ $I > 2\sigma(I)$ ]	2546
Final $R$ indices [ $I > 2\sigma(I)$ ]	
$R_1^a$	0.0418
$wR_2^b$	0.0943
$R$ indices (all data)	
$R_1$	0.0510
$wR_2$	0.1018
Goodness-of-fit <sup>c</sup> on $F^2$	1.078
Largest difference peak ( $\text{e } \text{Å}^{-3}$ )	1.02 (0.988 Å from Rh(1))

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$^b wR_2 = \frac{[\sum [w(F_o^2 - F_c^2)^2]]^{1/2}}{[\sum w(F_o^2)]^{1/2}}$$

<sup>c</sup> Goodness-of-fit =  $[\sum [w(F_o^2 - F_c^2)^2] / (N_{\text{obs}} - N_{\text{params}})]^{1/2}$ , based on all data.

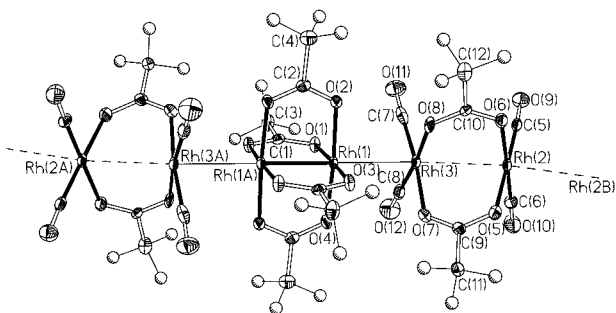


Fig. 1. A fragment showing the arrangement of  $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$  and  $\text{Rh}_2(\text{O}_2\text{CCF}_3)_2(\text{CO})_4$  units in the chain structure of **1**. Atoms are represented by thermal ellipsoids at the 40% probability level. Fluorine atoms are shown as spheres of arbitrary radius, with only one orientation of  $\text{CF}_3$  group depicted.

All calculations were performed on a DEC Alpha running VMS. Relevant crystallographic data for complex **1** are summarized in Table 1.

### 3. Results

#### 3.1. Synthetic aspects

Compound **1** has been obtained by crystallization from the vapor phase. It contains one part of dirhodium(II) tetra(trifluoroacetate),  $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$ , and two parts of dirhodium(I) complex,  $\text{Rh}_2(\text{O}_2\text{CCF}_3)_2(\text{CO})_4$ . Crystals of **1** are relatively air stable, but quickly decompose when contacted by water or other solvents. In designing this experiment we expected the realization of one of two different scenarios: the binding in axial positions of  $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$  either molybdenum carbonyl through O atoms, or carbonyl ligands themselves (since some CO molecules are always present in a vapor phase over  $\text{Mo}(\text{CO})_6$ ). Instead, we observed the partial substitution of carboxyl groups by carbonyl ligands in  $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$  and reduction of  $\text{Rh}^{\text{II}}$  to  $\text{Rh}^{\text{I}}$  (four of every six rhodium atoms). EDS X-ray and mass-spectroscopic data clearly show that there is no molybdenum present in **1**. The  $\text{Mo}^0$  in  $\text{Mo}(\text{CO})_6$  is presumably oxidized, but we cannot be sure about the degree of oxidation and the composition of the molybdenum product. However, we can state that there was no molybdenum carbonyl left in the reaction mixture, nor was there any remaining pressure of free carbon monoxide in the ampoule. It may well be that by using different ratios of starting materials other compounds could be formed. Thus the use of less  $\text{Mo}(\text{CO})_6$  could lead to the 1:1 product of the composition  $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4\text{Rh}_2(\text{O}_2\text{CCF}_3)_2(\text{CO})_4]$ , in which reduction of only half of the Rh atoms has occurred. On the other hand, an excess of molybdenum carbonyl or the use of other carbonyls might result in full reduction of  $\text{Rh}^{\text{II}}$  to  $\text{Rh}^{\text{I}}$ , thus affording only  $\text{Rh}_2(\text{O}_2\text{CCF}_3)_2(\text{CO})_4$  molecules. We have preliminary evidence for this which will be reported in the future.

#### 3.2. Structural aspects

Compound **1** crystallizes in the monoclinic space group  $P2_1/c$  with two  $\{\text{Rh}_2(\text{O}_2\text{CCF}_3)_4[\text{Rh}_2(\text{O}_2\text{CCF}_3)_2(\text{CO})_4]_2\}$  fragments per unit cell. The structure consists of one  $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$  unit sandwiched between two  $\text{Rh}_2(\text{O}_2\text{CCF}_3)_2(\text{CO})_4$  units to give an essentially linear array of six rhodium atoms (Fig. 1). The dirhodium(II) tetra(trifluoroacetate) molecule has in its axial positions the Rh(3) atoms of  $\text{Rh}_2(\text{O}_2\text{CCF}_3)_2(\text{CO})_4$  molecules (the angle Rh(1A)–Rh(1)–Rh(3) is  $177.15(4)^\circ$ ). The distance Rh(1)–Rh(3) is  $2.790(1) \text{ Å}$  (Table 2) and is among the longest for any axial interactions to

Table 2  
Selected bond distances (Å), angles (°) and torsion angles (°) in **1**

<i>Bond lengths</i>					
Rh(1)–Rh(1A)	2.412(1)	Rh(2)–Rh(2B)	3.062(1)		
Rh(1)–Rh(3)	2.790(1)	Rh(2)–Rh(3)	2.960(1)		
Rh(1)–O(1)	2.027(5)	Rh(2)–O(5)	2.074(6)	Rh(3)–O(7)	2.068(6)
Rh(1)–O(2)	2.032(5)	Rh(2)–O(6)	2.080(6)	Rh(3)–O(8)	2.070(6)
Rh(1)–O(3)	2.043(6)	Rh(2)–C(5)	1.85(1)	Rh(3)–C(7)	1.86(1)
Rh(1)–O(4)	2.037(5)	Rh(2)–C(6)	1.837(9)	Rh(3)–C(8)	1.86(1)
<i>Bond angles</i>					
O(1)–Rh(1)–O(2)	88.9(2)	O(5)–Rh(2)–O(6)	89.3(2)	O(7)–Rh(3)–O(8)	90.6(2)
O(1)–Rh(1)–O(3)	176.1(2)	O(5)–Rh(2)–C(5)	179.3(3)	O(7)–Rh(3)–C(7)	173.3(3)
O(1)–Rh(1)–O(4)	89.9(2)	O(5)–Rh(2)–C(6)	91.4(3)	O(7)–Rh(3)–C(8)	90.4(3)
O(2)–Rh(1)–O(3)	90.8(2)	O(6)–Rh(2)–C(5)	90.1(3)	O(8)–Rh(3)–C(7)	89.0(3)
O(2)–Rh(1)–O(4)	175.7(2)	O(6)–Rh(2)–C(6)	178.6(3)	O(8)–Rh(3)–C(8)	174.2(3)
O(3)–Rh(1)–O(4)	90.1(2)	C(5)–Rh(2)–C(6)	89.1(4)	C(7)–Rh(3)–C(8)	89.3(4)
O(1)–Rh(1)–Rh(1A)	88.7(2)	O(5)–Rh(2)–Rh(3)	80.0(2)	O(7)–Rh(3)–Rh(1)	87.5(2)
O(2)–Rh(1)–Rh(1A)	87.9(2)	O(6)–Rh(2)–Rh(3)	82.4(2)	O(8)–Rh(3)–Rh(1)	87.6(2)
O(3)–Rh(1)–Rh(1A)	87.3(2)	C(5)–Rh(2)–Rh(3)	99.4(3)	C(7)–Rh(3)–Rh(1)	85.8(3)
O(4)–Rh(1)–Rh(1A)	88.0(2)	C(6)–Rh(2)–Rh(3)	96.6(3)	C(8)–Rh(3)–Rh(1)	86.8(3)
O(1)–Rh(1)–Rh(3)	93.9(2)	O(5)–Rh(2)–Rh(2B)	82.0(2)	O(7)–Rh(3)–Rh(2)	79.3(2)
O(2)–Rh(1)–Rh(3)	91.2(2)	O(6)–Rh(2)–Rh(2B)	86.2(2)	O(8)–Rh(3)–Rh(2)	77.6(2)
O(3)–Rh(1)–Rh(3)	90.0(2)	C(5)–Rh(2)–Rh(2B)	98.5(3)	C(7)–Rh(3)–Rh(2)	107.1(3)
O(4)–Rh(1)–Rh(3)	93.0(2)	C(6)–Rh(2)–Rh(2B)	95.1(3)	C(8)–Rh(3)–Rh(2)	108.1(3)
Rh(1A)–Rh(1)–Rh(3)	177.15(4)	Rh(3)–Rh(2)–Rh(2B)	158.78(4)	Rh(1)–Rh(3)–Rh(2)	159.92(3)
<i>Torsion angles</i>					
O(1)–Rh(1)–Rh(1A)–O(3A)	0.1(2)	O(5)–Rh(2)–Rh(2B)–C(5B)	0.6(3)		
O(2)–Rh(1)–Rh(1A)–O(4A)	–1.1(2)	O(6)–Rh(2)–Rh(2B)–C(6B)	0.6(3)		
O(1)–Rh(1)–Rh(3)–C(7)	38.6(3)	O(5)–Rh(2)–Rh(3)–O(7)	9.3(2)		
O(2)–Rh(1)–Rh(3)–O(8)	38.8(2)	O(6)–Rh(2)–Rh(3)–O(8)	7.0(2)		
O(3)–Rh(1)–Rh(3)–O(7)	38.6(2)	C(5)–Rh(2)–Rh(3)–C(7)	10.7(4)		
O(4)–Rh(1)–Rh(3)–C(8)	39.2(3)	C(6)–Rh(2)–Rh(3)–C(8)	5.9(4)		

dirhodium carboxylates known to date [7,8]. That fact does not affect the metal–metal bond in the  $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$  molecule (2.412(1) Å), which is within the range of distances 2.38–2.47 Å reported before [1,5]. Another component of the crystal structure, the dirhodium(I) bis-bridged molecule  $\text{Rh}_2(\text{O}_2\text{CCF}_3)_2(\text{CO})_4$  has two carbonyl groups in *cis* position on each metal atom. This unit is partially staggered (average torsion angle is 8.2(3)°), and the metal to metal distance of 2.960(1) Å suggests that there is no bonding interaction. It is rotated relative to the tetracarboxylate part with torsion angles about the Rh(1)–Rh(3) direction being 38.8(3)°. The Rh–O distances to carboxylate groups are noticeably longer (about 0.04 Å) for Rh<sup>I</sup> than for Rh<sup>II</sup> which is not surprising.

The arrays of six rhodium atoms are linked into infinite chains [15], which lie parallel in the crystal (Fig. 2) with Rh to Rh contacts of 3.062(1) Å. Where adjacent  $\text{Rh}_2(\text{O}_2\text{CCF}_3)_2(\text{CO})_4$  units meet the two sets of ligands on Rh(2) atoms are eclipsed so that a carbon atom of each CO group is opposite to the O atom of a carboxyl group. While the attachments to the axial positions of the  $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$  molecule are almost linear, the two other attachments in the infinite chain

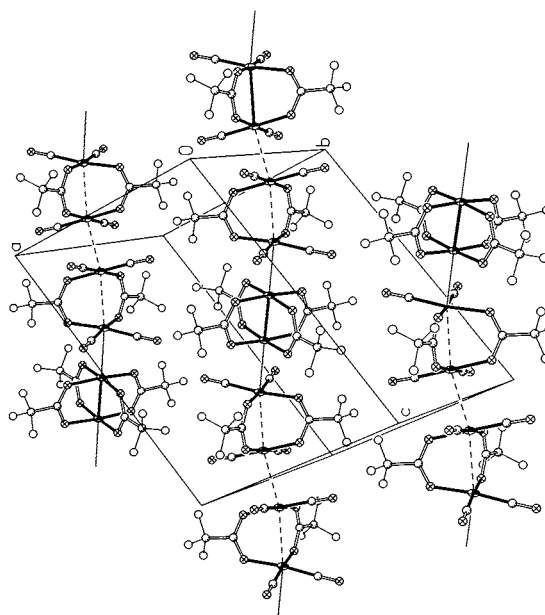


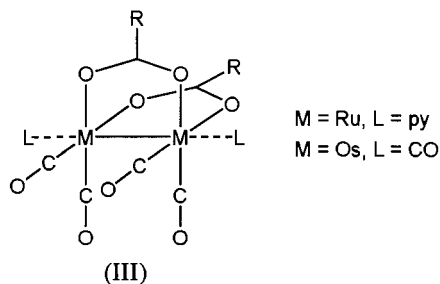
Fig. 2. Packing diagram of  $\{\text{Rh}_2(\text{O}_2\text{CCF}_3)_4[\text{Rh}_2(\text{O}_2\text{CCF}_3)_2(\text{CO})_4]_2\}_\infty^1$  (**1**) showing the arrangement of infinite chains in the unit cell. Atoms are not labeled for clarity.

show deviations from linearity, being  $159.92(3)^\circ$  for the Rh(2)–Rh(3)–Rh(1) and  $158.78(4)^\circ$  for the Rh(3)–Rh(2)–Rh(2B).

#### 4. Discussion

The compound we have obtained is remarkable in several ways. It consists of essentially linear units of the kind shown in Fig. 1. These, in turn, form essentially linear infinite chains as shown in Fig. 2. The two identical outer components of the repeating unit are potentially molecular in nature and presumably capable of independent existence. Surprisingly, however, there is no report of any discrete  $\text{Rh}_2(\text{O}_2\text{CR})_2(\text{CO})_4$  molecule [16]. What we have found here clearly suggests that designed synthesis of such molecules would be possible.

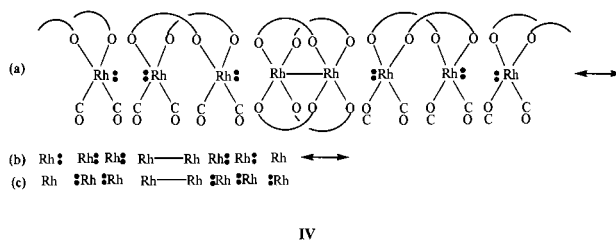
The  $\text{Rh}_2(\text{O}_2\text{CCF}_3)_2(\text{CO})_4$  ‘molecule’ can be compared with similar ones formed by ruthenium and osmium. In the Ru and Os cases, there are two additional ligands, for example pyridine or CO groups, in axial positions, as shown in **III**. In these molecules [17], the L ligands of course are donors and there are M–M bonds ( $\text{M}–\text{M} \approx 2.7 \text{ \AA}$ ), whereas here, each metal atom has one more electron and, to first order, no Rh–Rh bond would be expected. In accord with this, the Rh⋯Rh distance is much longer, that is, nearly  $3.0 \text{ \AA}$ .



In partial explanation of the formation of the unit shown in Fig. 1, we note first that each rhodium atom of the  $\text{Rh}_2(\text{O}_2\text{CCF}_3)_2(\text{CO})_4$  moiety is a square  $d^8$  complex. It may thus be expected to have a filled orbital, and this pair of electrons can serve to form a donor bond to an adjacent acceptor, which in this case is a rhodium atom of a  $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$  molecule. The entire repeat unit,  $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_2(\text{CO})_4][\text{Rh}_2(\text{O}_2\text{CCF}_3)_4][\text{Rh}_2(\text{O}_2\text{CCF}_3)_2(\text{CO})_4]$  can be thought of as being held together in this way. However, if the situation were really this simple, an obvious question is, why do we not see an infinite chain of alternating  $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$  and  $\text{Rh}_2(\text{O}_2\text{CCF}_3)_2(\text{CO})_4$  units? Perhaps, as we have already noted, such a chain could be formed under different conditions.

Another question concerns the contacts between the repeating hexanuclear units. They are relatively short ( $3.0 \text{ \AA}$ ), considering that to first order there is no basis

for even weak bonding. These adjacent pairs of rhodium atoms confront each other with filled orbitals. It could be that the electron distribution in the chains could be a resonance hybrid of the kind shown in **IV**, where **b** and **c** (which are equivalent) introduce some bonding between the Rh atoms in the  $\text{Rh}_2(\text{O}_2\text{CCF}_3)_2(\text{CO})_4$  units and lessen the repulsion between them. The entire situation is, of course, reminiscent of the many well-known planar stacking structures of platinum(II) compounds [18], but it has its own unique features, among which must be some type of electron delocalization along the chain.



What, in general, is going on in solventless synthesis? We can certainly say that one thing that is not going on is direct reaction of one solid with another. Important steps unquestionably occur in the vapor phase, but clearly the very process of product deposition may also constitute a part of the reaction pathway. In the present instance it would seem unlikely, though not impossible, that the hexanuclear molecules are fully formed in the vapor phase. Certainly in the synthesis of the  $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4(\text{THF})$  infinite polymer [10] the final step, that is, forming oxygen–rhodium bonds (or at least half of them) must occur concomitantly with the growth of the product crystals. On the other hand there could well be cases in which product molecules are fully formed in the vapor and it is only molecular packing that occurs as the product crystals grow.

What happens in a solventless synthesis is, therefore, not fundamentally different from what happens in conventional synthesis in a solvent, except that nothing is solvated, no solvent molecules need to be attached, detached or reattached, and the resulting crystals will necessarily be free of solvent of crystallization. In a conventional reaction in a solvent, we still have the possibilities analogous to those mentioned above for solventless synthesis, that in some cases product molecules may be fully formed in the liquid phase and simply fall out in the form of a crystal, or that additional chemical bonds are formed as the crystals are formed. The indispensable requirement for synthesis in a solvent is that the reactants dissolve, while the indispensable requirement for a solventless synthesis (unless it is one of those exceedingly rare solid–solid, solid–liquid or solid–gas cases) is that the reactants be volatile.

## 5. Supplementary material

Crystallographic data for compound **1** have been deposited with the Cambridge Crystallographic Data Centre (entries carrying the suffix *x* represent dummy atoms used for modeling disordered atoms). 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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