DALTON
COMMUNICATION

cis-Di(μ-trifluoroacetate)dirhodium tetracarbonyl: structure and chemistry†

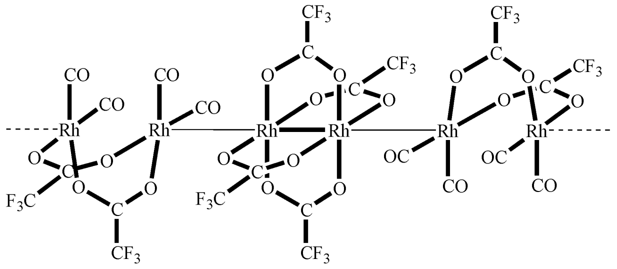
F. Albert Cotton,* Evgeny V. Dikarev and Marina A. Petrukhina

Laboratory for Molecular Structure and Bonding, Department of Chemistry, P. O. Box 30012, Texas A & M University, College Station, TX 77842-3012. E-mail: cotton@tamu.edu

Received 23rd August 2000, Accepted 23rd October 2000

The dirhodium(I) complex $Rh_2(\mu\text{-}O_2CCF_3)_2(CO)_4$ has been prepared by reduction of $Rh_2(\mu\text{-}O_2CCF_3)_4$ with CO in the vapor phase and its crystal structure reveals a polymeric nature with dinuclear molecules aligned along the metal–metal axis.

Recently we reported[1] the preparation and structure of a compound **1** consisting of the hexanuclear units shown in Scheme 1. The two identical outer dinuclear components, $Rh_2(\mu\text{-}O_2CCF_3)_2(CO)_4$, had never been structurally characterized before, although there are a number of earlier reports concerning possible (but unproven) $Rh_2(\mu\text{-}O_2CR)_2(CO)_4$ or $Rh_2(\mu\text{-}O_2CR)_2(CO)_nL_{4-n}$ compounds (R = H, Me, Et; L = PPh_3, PCy_3; $n = 3$).[2] Two such reports specifically discuss $Rh_2(\mu\text{-}O_2CCF_3)_2(CO)_4$.[3]



$\{Rh_2(O_2CCF_3)_4[Rh_2(\mu\text{-}O_2CCF_3)_2(CO)_4]_2\}$ (**1**)

Scheme 1

We noted then that we had preliminary evidence for the existence of pure $Rh_2(\mu\text{-}O_2CCF_3)_2(CO)_4$ (**2**). We now have conclusive results on the preparation and structure of that compound. We report here those results as well as information on two related compounds, $[Rh(\mu\text{-}O_2CCF_3)(\mu\text{-}CO)(THF)]_4$ (**3**) and $Rh_2(\mu\text{-}O_2CCF_3)_2(\eta^4\text{-cod})_2$ (**4**) (cod = 1,5-cyclooctadiene).

Our preparation of **1** was accomplished under the somewhat novel conditions that we refer[1] to as 'solventless' synthesis. The reaction took place between $Rh_2(O_2CCF_3)_4$ and $Mo(CO)_6$. The latter served both to reduce the rhodium(II) atoms and to supply the CO groups.[1] We reasoned that by using a substantial excess of molybdenum carbonyl, or carbonyls of some other metals, all of the $Rh_2(O_2CCF_3)_4$ could be made to react thereby producing, instead of **1**, the homogeneous compound **2**. This has proven to be the case. Solid state deposition from the vapor phase for the systems $Rh_2(O_2CCF_3)_4$–$W(CO)_6$ and $Rh_2(O_2CCF_3)_4$–$Cr(CO)_6$ at temperatures higher than those used to prepare **1**, 150–160 °C *vs.* 120–125 °C, resulted in the synthesis ‡ of pure crystalline $Rh_2(\mu\text{-}O_2CCF_3)_2(CO)_4$ (**2**) in moderate yields. The presence of trifluoroacetate and terminal carbonyl groups (two strong ν(CO) bands at about 2000 cm^{-1}) in **2** was confirmed by IR spectroscopy. Mass-spectroscopy afforded evidence for the existence of tetranuclear $[Rh_4(O_2CCF_3)_4(CO)_8]$ units and numerous products of its gradual fragmentation in the vapor phase. It is to be noted that compound **2** can be prepared in a more conventional way by the reaction of $Rh(acac)(CO)_2$ with CF_3CO_2H.[3] Golden, dichroic crystals of **2** are relatively air-stable, but easily disintegrate in the presence of any potentially coordinating solvents, a process that is most probably accompanied by a drastic change of the structure.

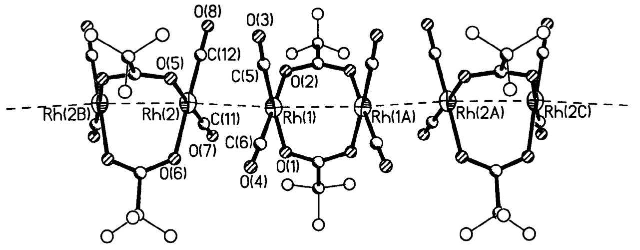


Fig. 1 A perspective view of $[Rh_2(\mu\text{-}O_2CCF_3)_2(CO)_4]_\infty$ (**2**). Selected distances (Å) and angles (°): Rh(1)–Rh(1A) 2.984(1), Rh(1)–Rh(2) 3.092(1), Rh(2)–Rh(2B) 2.994(1), Rh–O 2.087(5), Rh–C 1.839(9); Rh–Rh–Rh 162.23(1), O–Rh–O 85.2(2), C–Rh–C 89.0(4), Rh–Rh–O 79.6(2), Rh–Rh–C 101.4(3).

By dissolving yellow crystals of **2** in THF, a greenish solution was obtained, from which pale-green crystals of $[Rh(O_2CCF_3)(CO)(THF)]_4$ (**3**) were grown upon layering with hexanes.§ The IR spectra of **3** showed the continued presence of trifluoroacetate groups, but there appeared two new ν(CO) bands at 1873 and 1842 cm^{-1} which were indicative of the presence of bridging carbonyls. Crystals of **3** quickly lose THF. Previous studies[3b] of the reactions of the complexes $Rh_2(O_2CR)_2(CO)_4$ with other Lewis bases, such as pyridine and its derivatives, showed that they afford monomeric *cis*-$Rh(O_2CR)(CO)_2L$ compounds which then decompose to form unusual square-planar rhodium(I) clusters.

Another interesting example of the transformation of the $Rh_2(O_2CCF_3)_4$ core, accompanied by complete reduction of Rh(II) to Rh(I), is provided by studying the 'solventless' reaction of dirhodium(II) tetrafluoroacetate with 1,5-cyclooctadiene. Under very mild conditions (temperature in the range 70–80 °C) transparent yellow crystals of $Rh_2(O_2CCF_3)_2(cod)_2$ (**4**) have been isolated by deposition from the vapor phase.¶

The most important result of this work is the elucidation of the crystal structure of the dirhodium(I) trifluoroacetate carbonyl complex **2**. This long known but inadequately characterized compound turns out ‖ to display a polymeric array of axially connected *cis*-$Rh_2(\mu\text{-}O_2CCF_3)_2(CO)_4$ molecules (Fig. 1). The chains are essentially linear with all Rh–Rh–Rh angles being *ca.* 162°. The metal–metal distances inside (average 2.989(1) Å) and between the bridged dimers (3.092(1) Å) are very close to those we have seen[1] in the crystal structure of **1** with $Rh_2(O_2CCF_3)_4$ and suggest that there is little or no bonding interaction anywhere along the chain. However, it is not clear if the extended structural motif of **2** is characteristic for all analogous

---

† Studies of dirhodium(II) tetrakis(trifluoroacetate), part 9. Part 8: F. A. Cotton, E. V. Dikarev, M. A. Petrukhina and S.-E. Stiriba, *Polyhedron*, 2000, **19**, 1829.

DOI: 10.1039/b006894m

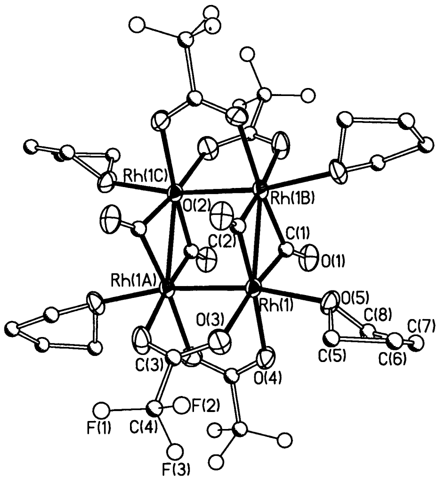


Fig. 2 A perspective view of $[Rh(\mu\text{-}O_2CCF_3)(\mu\text{-}CO)(THF)]_4$ (**3**). Selected bond distances (Å) and angles (°): Rh(1)–Rh(1A) 2.551(1), Rh(1)–Rh(1B) 2.624(1), Rh–C 1.959(8), Rh–O 2.153(6), $Rh\text{–}O_{THF}$ 2.220(5); Rh–Rh–Rh 90.0, O–Rh–O 82.4(3), C–Rh–C 95.1(3), Rh(1A)–Rh(1)–O 85.5(2), Rh(1A)–Rh(1)–C 94.8(3), Rh(1A)–Rh(1)–O_{THF} 169.8(2), Rh–C–Rh 84.1(4).

carboxylates or if it will occur only when there are fluorinated carboxylate ligands. Simple electrostatic interactions may play an essential role in the observed axial stacking. The adjacent *cis*-$Rh_2(\mu\text{-}O_2CCF_3)_2(CO)_4$ units approach each other so that the carbon atoms of CO groups on one molecule are opposite to the O atoms of the carboxyl groups on the next one. The crystal structure of the dirhodium(I) complex **2** is without precedent. We may note that in the diruthenium(I) compound,[4] $Ru_2(O_2CPh)_2(CO)_4$, there is also an extended arrangement, but the dinuclear molecules approach each other through axial coordination of carboxylate oxygen atoms to ruthenium atoms of neighboring units.

The structure of complex **3**** is built on the perfectly planar Rh_4 cluster of almost square shape (Fig. 2). The two shorter edges (2.551(1) Å) are bridged by two trifluoroacetate ligands each, while the two longer sides (2.624(1) Å) are each supported by two bridging carbonyl groups. In addition, the THF ligands are located almost axially with respect to the carboxylate-bridged rhodium pairs. That makes the coordination environment of each Rh (ignoring the carbonyl supported metal–metal contacts) a slightly distorted octahedron. An analogous 64-electron Rh_4 cluster was described a few years ago[3*1b*] for the complex $[Rh(O_2CCH_3)(CO)\ (NC_5H_4CH{=}NC_6H_4OC_{14}H_{29})]_4$, in which the pyridyl nitrogen atoms replace the THF oxygen atoms.

The two rhodium complexes can be compared with a structurally similar palladium complex,[5] $[Pd(O_2CCH_3)(CO)]_4$, in which there are no additional neutral donor atoms. There are two chief differences between the tetrametal cores of **3** and the palladium compound. In **3**, the Rh_4 unit is rigorously rectangular, while the Pd_4 unit is a rhombus with internal angles of 83 and 97°. More significant, perhaps, is the fact that while the CO-bridged M–M distances are very similar in the two cases (Pd–Pd = 2.663(1) and Rh–Rh = 2.624(1) Å) the carboxyl-bridged distances are very different with Pd–Pd = 2.909(1) and Rh–Rh = 2.551(1) Å. Since each rhodium atom has one less electron than a palladium atom, the structural difference indicates that in **3** there are two Rh–Rh single bonds, while there are no Pd–Pd bonds in the palladium compounds.

We have recently reported[6] on the rhenium(I) tetranuclear compound $[Re(O_2CCH_3)(CO)_3(THF)]_4$ in which acetate groups are bridging all four edges and carbonyl ligands are terminally bonded to metal atoms. The geometry of each acetate bridge is *anti-syn* providing a Re to Re separation of 5.40 Å.

The crystal structure of complex **4**†† consists of discrete $Rh_2(\mu\text{-}O_2CCF_3)_2(\eta^4\text{-cod})_2$ units (Fig. 3). The rhodium(I) atoms in this molecule are kept apart (3.4844(6) Å) by bulky 1,5-cyclooctadiene ligands. Steric hindrance is also a reason why this compound does not have an extended structure analogous to that of **2**. Coordination of half of the carbon atoms at the Rh···Rh–C angles of *ca.* 130° prevents any other dirhodium unit from coming into close proximity of the axial positions. The strong Rh–C contacts (2.096(6) Å) which are about 0.4 Å shorter than for axial coordination of alkenes to rhodium[7] do not seemingly disturb the double bond character of cod; the C=C bonds are still *ca.* 0.1 Å shorter than the rest of the C–C distances in 1,5-cyclooctadiene. A number of dirhodium(I) complexes analogous to **4** are known[8] for different carboxylate and diene ligands.

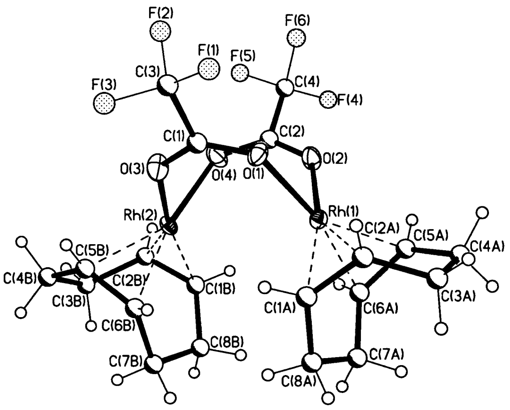


Fig. 3 A perspective view of $Rh_2(\mu\text{-}O_2CCF_3)_2(\eta^4\text{-cod})_2$ (**4**). Selected distances (Å) and angles (°) (averaged for two molecules): Rh···Rh 3.4844(6), Rh–O 2.102(4), Rh–C 2.096(6), C=C 1.389(9); O–Rh–O 88.6(2), Rh···Rh–O 72.6(1), Rh···Rh–C 97.0(2) and 131.1(2).

Acknowledgements

We are grateful to the Robert A. Welch Foundation (Grant No. A494) for financial support. We thank the Johnson Matthey Company for the loan of rhodium.

Notes and references

‡ Synthesis of $Rh_2(O_2CCF_3)_2(CO)_4$ (**2**). **Caution!** Metal carbonyls are potential sources of CO which can create a high pressure in a sealed ampule upon heating. Avoid overheating or quick changes of temperature. Compound **2** was prepared by heating a mixture of unligated $Rh_2(O_2CCF_3)_4$ (0.068 g, 0.10 mmol) and freshly sublimed tungsten carbonyl (0.041 g, 0.12 mmol) at 150–160 °C for 3 days in a sealed evacuated Pyrex ampule. Yellow crystals of **2** were collected from the 'cold' zone of the tube, where the temperature was set 5 °C lower. Yield: 0.033 g, 61%. Anal. Calc. for $Rh_2C_8F_6O_8$: C, 17.67; F, 20.96%. Found: C, 17.70; F, 20.93%. IR (KBr, cm^{-1}): 2085 (m), 2013 (m), 1932 (m), 1865 (s), 1682 (s, br), 1434 (m), 1209 (s), 1134 (s), 839 (s), 806 (m), 724 (m), 686 (s), 538 (m). MS (EI/DP, 300 °C, *m*/*z*): 1088 $[(Rh_2(O_2CCF_3)_2(CO)_4)_2{}^+]$ (M_2), 976 $[(M_2 - O_2CCF_3)^+]$, 920 $[(M_2 - O_2CCF_3 - 2\ CO)^+]$, 864 $[(M_2 - 2\ O_2CCF_3)^+]$, 544 $[(Rh_2(O_2CCF_3)_2(CO)_4)^+]$ (M), 517 $[(M - CO)^+]$, 489 $[(M - 2\ CO)^+]$, 460 $[(M - 3\ CO)^+]$, 432 $[(M - O_2CCF_3)^+]$, 403 $[(M - O_2CCF_3 - CO)^+]$, 375 $[(M - O_2CCF_3 - 2\ CO)^+]$, 347 $[(M - O_2CCF_3 - 3\ CO)^+]$, 319 $[(M - O_2CCF_3 - 4\ CO)^+]$, 206 $[(M - 2\ O_2CCF_3 - 4\ CO)^+]$.

§ Synthesis of $[Rh(O_2CCF_3)(CO)(THF)]_4$ (**3**). Crystals of **3** were grown from the THF (5 mL) solution containing **2** (0.045 g, 0.08 mmol) layered with 12 mL of hexanes. Yield: 0.032 g, 57%. IR (KBr, cm^{-1}): 1873 (s), 1842 (s), 1658 (s), 1262 (s), 1199 (s), 1156 (s), 1098 (s), 1031 (s), 860 (m), 803 (m), 764 (m), 733 (s), 478 (m, br).

¶ Synthesis of $Rh_2(O_2CCF_3)_2(cod)_2$ (**4**) (cod = 1,5-cyclooctadiene). Compound **4** was prepared by heating a mixture of unligated $Rh_2(O_2CCF_3)_4$ (0.066 g, 0.10 mmol) and a few drops of cod at 70–80 °C for 2 days in a sealed evacuated Pyrex ampule. Pale yellow crystals of **4** were grown when the tube was slowly cooled to room temperature over 24 hours. Yield: 0.028 g, 43%. Anal. Calc. for $Rh_2C_{20}F_6O_4H_{24}$: C, 37.06; H, 3.74%. Found: C, 37.02; H, 3.72%.

|| Crystal data for **2**: $C_8F_6O_8Rh_2$, $M = 543.90$, monoclinic, space group $C2/m$ (No. 12), $a = 31.137(2)$, $b = 11.866(2)$, $c = 8.4282(9)$ Å, $\beta = 96.90(1)°$, $V = 3091.4(6)$ Å^3, $Z = 8$, $T = 273(2)$ K, $\mu(\text{Mo-K}\alpha) = 2.236$ mm^{-1}. Full-matrix refinement on F^2 (Nonius FAST area detector, SHELXL-93[9]), $R1 = 0.0514$, $wR2 = 0.1227$, GOF = 1.102 for 2122

unique reflections and 265 parameters. $R1 = 0.0436$ and $wR2 = 0.1139$ for 1786 reflections with $I > 2\sigma(I)$. CCDC reference number 186/2251. See http://www.rsc.org/suppdata/dt/b0/b006894m/ for crystallographic files in .cif format.

** Crystal data for **3**: $C_{28}H_{32}F_{12}O_{16}Rh_4$, $M = 1264.18$, monoclinic, space group $C2/m$ (No. 12), $a = 10.140(1)$, $b = 22.979(3)$, $c = 8.786(1)$ Å, $\beta = 102.636(2)°$, $V = 1997.6(4)$ Å^3, $Z = 2$, $T = 213(2)$ K, μ(Mo-Kα) = 1.746 mm^{-1}. Full-matrix refinement on F^2 (Bruker SMART CCD, SHELXL-93), $R1 = 0.0784$, $wR2 = 0.1462$, GOF = 1.084 for 2331 unique reflections and 175 parameters. $R1 = 0.0514$ and $wR2 = 0.1259$ for 1675 reflections with $I > 2\sigma(I)$.

†† Crystal data for **4**: $C_{20}H_{24}F_6O_4Rh_2$, $M = 648.21$, orthorhombic, space group $Pbca$ (No. 61), $a = 18.3351(9)$, $b = 16.5713(5)$, $c = 29.009(2)$ Å, $V = 8814.0(8)$ Å^3, $Z = 16$, $T = 213(2)$ K, μ(Mo-Kα) = 1.573 mm^{-1}. Full-matrix refinement on F^2 (Nonius FAST area detector, SHELXL-93), $R1 = 0.0407$, $wR2 = 0.0906$, GOF = 1.088 for 5731 unique reflections and 625 parameters. $R1 = 0.0361$ and $wR2 = 0.0847$ for 5225 reflections with $I > 2\sigma(I)$.

1 F. A. Cotton, E. V. Dikarev and M. A. Petrukhina, *J. Organomet. Chem.*, 2000, **596**, 130.

2 (*a*) D. N. Lawson and G. Wilkinson, *J. Chem. Soc.*, *Dalton Trans.*, 1965, 1900; (*b*) G. Csontos, B. Heil and L. Marko, *J. Organomet. Chem.*, 1972, **37**, 183; (*c*) M. A. Esteruelas, O. Lahuerta, J. Modrego, O. Nürnberg, L. A. Oro, L. Rodriguez, E. Sola and H. Werner, *Organometallics*, 1993, **12**, 266.

3 (*a*) L. Yu Ukhin and Yu. A. Shvetsov, *Bull. Russ. Acad. Sci.*, *Ser. Chem.*, 1972, **7**, 1597; (*b*) F. J. Lahoz, A. Martin, M. A. Esteruelas, E. Sola, J. L. Serrano and L. A. Oro, *Organometallics*, 1991, **10**, 1794.

4 M. Spohn, T. Vogt and J. Strahle, *Z. Naturforsch.*, *Teil B*, 1986, **41**, 1373.

5 (*a*) I. I. Moiseev, T. A. Stromnova, M. N. Vargaftig, G. J. Mazo, L. G. Kuz'mina and Yu. T. Struchkov, *J. Chem. Soc.*, *Chem. Commun.*, 1978, 27; (*b*) L. G. Kuz'mina and Yu. T. Struchkov, *Koord. Khim.*, 1979, **5**, 1558.

6 F. A. Cotton, E. V. Dikarev and M. A. Petrukhina, *Inorg. Chim. Acta*, 1999, **284**, 304.

7 F. A. Cotton, L. R. Falvello, M. Gerards and G. Snatzke, *J. Am. Chem. Soc.*, 1990, **112**, 8979.

8 (*a*) R. Fornika, E. Dinjus, H. Gorls and W. Leitner, *J. Organomet. Chem.*, 1996, **511**, 145; (*b*) E. Mieczynska, A. M. Trzeciak, J. J. Ziolkowski and T. Lis, *Polyhedron*, 1994, **13**, 665; (*c*) S. M. Tetrick, F. S. Tham and A. R. Cutler, *J. Am. Chem. Soc.*,1997, **119**, 6193.

9 G. M. Sheldrick, SHELXL-93, Program for structure refinement, University of Göttingen, 1993.