Short Communication

Crystal Structures of $Rh_2(CO)_4(\mu\text{-SPh})_2$ and $Rh_2(CO)_4(\mu\text{-SEt})_2$

Jouni Pursiainen,[a] Tiina Teppana,[b] Sirpa Rossi[b,*] and Tapani A. Pakkanen[b]

[a]University of Oulu, Department of Chemistry, SF-90570 Oulu, Finland and [b]University of Joensuu, Department of Chemistry, PO Box 111, SF-80101 Joensuu, Finland

The chemistry of dimeric rhodium-group metal complexes with two bridging ligands such as halogenides, phosphines, thiolates and hydrocarbons is well known. Both alkyl and aryl thiolates have a strong affinity to transition metals. Many compounds of the type $M_2(CO)_4(\mu\text{-SR})_2$ and their phosphine and phosphite derivatives have been reported. IR spectroscopy has been the most frequently used method to characterize the structure and isomerism of the complexes. Only in some cases has the crystal structure been established: in particular, few of the basic carbonyl structures are known. The synthesis and spectroscopic characterization of $Rh_2(CO)_4(SR)_2$ $(R = Et, Bu^t, Ph)$ have been described in the literature.[1,2] Ligand replacement, e.g. with phosphines, has also been extensively studied, and in some experiments these rhodium dimer derivatives have shown catalytic activity for hydroformylation reactions.[3–6]

In this work we have determined the crystal structures of $Rh_2(CO)_4(\mu\text{-SPh})_2$ (1) and $Rh_2(CO)_4(\mu\text{-SEt})_2$ (2) and studied their molecular packings. The crystal structure of $Ir_2(CO)_4(\mu\text{-SPh})_2$[7] is related to the title compounds.

Experimental

Data were collected with Mo $K\alpha$ radiation $(\lambda = 0.71073\,\text{Å})$ on a Nicolet R3m diffractometer equipped with a graphite monochromator. Intensities were corrected for background, polarisation and Lorentz effects. Empirical absorption corrections were made from ψ-scan data for 2. Table 1 gives further crystallographic data. Rhodium and sulfur atom positions were identified by the direct methods of the SHELXTL Plus program.[8] Carbon and oxygen atoms were located by Fourier synthesis, and the hydrogen atoms were placed in calculated positions $[C-H = 0.96\,\text{Å}, \ U(H) = 0.08\,\text{Å}^2]$. All non-hydrogen atoms were refined anisotropically.

Results and discussion

Coordinates and equivalent isotropic U values for the Rh, S, O, and C atoms in compounds 1 and 2 are given in Tables 2 and 3, respectively. Hydrogen coordinates, anisotropic temperature parameters for the Rh, S, O, and C atoms, and structure factor lists for the two structures can be obtained from the authors on request.

Fig. 1 shows the molecular structure and atom numbering for molecules A and B of 1, and Fig. 2 shows the atomic numbering and structure of 2 with relevant bond distances and angles.

Table 1. Crystallographic data for $Rh_2(CO)_4(SPh)_2$ (1) and $Rh_2(CO)_4(SEt)_2$ (2).

	1	2
Formula weight	536.19	440.10
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	24.38(1)	8.549(5)
b/Å	9.002(5)	18.66(1)
c/Å	17.44(1)	9.148(7)
α/°	90	90
β/°	103.86(5)	104.25(6)
γ/°	90	90
V/Å^3	3716(3)	1414(2)
Centering reflexions	24	25
Centering 2θ/°	15–25	14–25
Z	8	4
D_{calc}/Mg m^{-3}	1.917(2)	2.067(2)
Crystal dimensions/mm	0.2 × 0.5 × 0.6	0.3 × 0.3 × 0.5
Crystal color	Red	Orange
2θ-limits/°	5–50	4–50
h, k, l range	±29, −10, 20	11, 23, ±11
No. of unique reflexions	6465	2485
Obsd. data $I \geqslant 3\sigma(I)$	3303	1945
μ/mm^{-1}	1.98	2.58
No. of parameters	433	145
R^a	0.0529	0.0381
$R_w{}^b$	0.0593	0.0373

$^a R = \sum ||F_o| - |F_c||/\sum |F_o|$. $^b R_w = \sum w^{1/2}[|F_o| - |F_c|]/\sum w^{1/2} |F_o|$, weight $= 1/[\sigma^2(F) + 0.0005F^2]$.
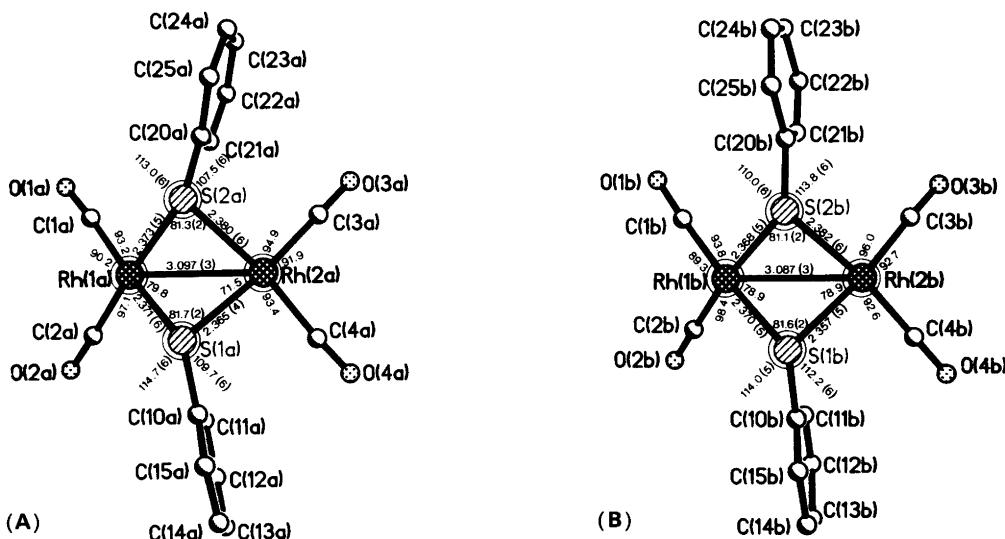
Fig. 1. Structure and numbering scheme of Rh₂(CO)₄(μ-SPh)₂ (1).

Both structures consist of bent molecules with a central Rh₂S₂ moiety; the (Rh1, Rh2, S1) ∧ (Rh1, Rh2, S2) dihedral angles are 115.2(2), 113.7(2) and 105.0(1)° for **1A**, **1B** and **2**, respectively. The two molecules of **1** are significantly different because of differences in packing in the unit cell. Two kinds of molecules were also found for Ir₂(CO)₄(μ-SPh)₂,[7] which is isomorphous with **1**. The phenyl groups of molecule **1B** are approximately coplanar (C10B, ..., C15B) ∧ (C20B, ..., C25B) = 6.6(7)°, but the phenyl rings of molecule **1A** are not, (C10A, ..., C15A) ∧ (C20a, ..., C25A) = 26.4(5)°. The molecules of **1B** are connected together in the crystal, forming zig-zag chains. The corresponding intermolecular distances are shown in Fig. 3. The Rh···Rh intermolecular distances are short enough to indicate a metal–metal interaction. In **1B** the shortest Rh···Rh distance is 3.381(3) Å, while Rh₆(CO)₁₆[9] has a Rh–Rh
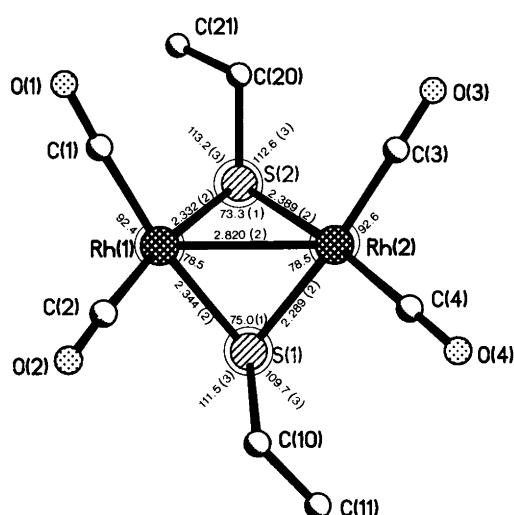
Fig. 2. Structure and numbering scheme of Rh₂(CO)₄-(μ-SEt)₂ (2).
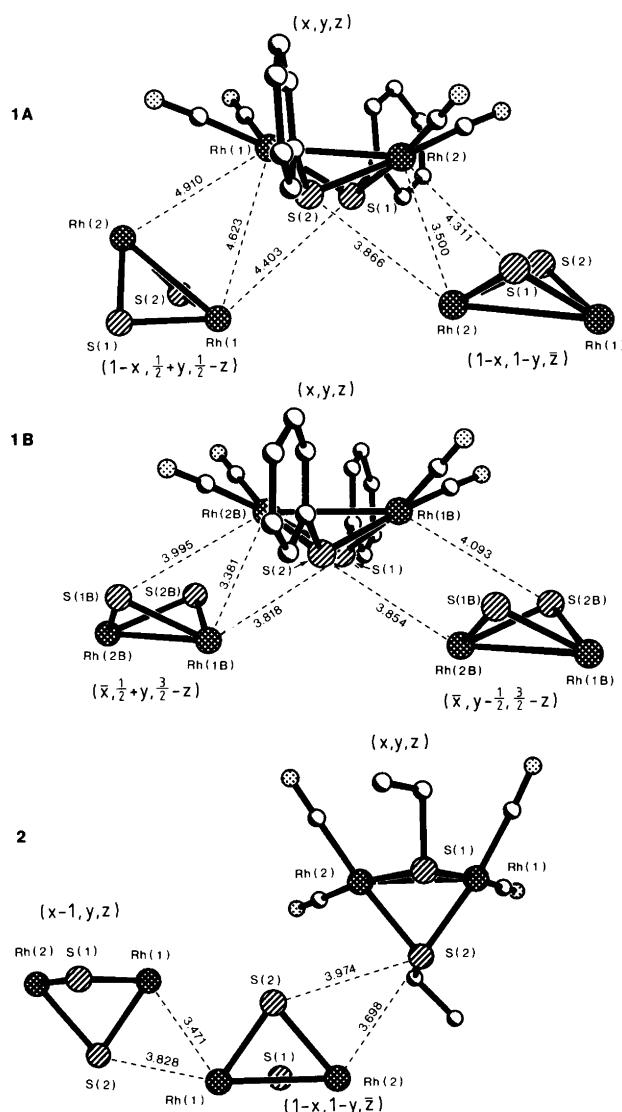
Fig. 3. Intermolecular distances for Rh₂(CO)₄(μ-SPh)₂ (1) and Rh₂(CO)₄(μ-SEt)₂ (2).

Table 2. Atomic coordinates ($\times 10^4$) and temperature factors ($\times 10^3$ Å) for $Rh_2(CO)_4(SPh)_2$ **(1)**.

Atom	x	y	z	U_{eq}[a]
Rh(1)	4797(1)	4659(2)	2306(1)	50(1)
Rh(2)	5077(1)	3658(2)	744(1)	51(1)
S(1)	5548(2)	5333(5)	1728(2)	55(1)
S(2)	4295(2)	5018(5)	975(3)	55(2)
O(1)	3739(5)	4172(16)	2884(8)	83(6)
O(2)	5506(6)	4212(18)	3989(7)	95(7)
O(3)	4362(6)	1516(18)	−413(8)	94(7)
O(4)	6141(6)	2010(18)	652(9)	94(7)
C(1)	4125(7)	4310(21)	2659(9)	62(7)
C(2)	5243(8)	4366(20)	3358(14)	73(9)
C(3)	4630(8)	2324(22)	13(11)	64(8)
C(4)	5760(9)	2599(23)	721(10)	68(8)
C(10)	6218(6)	4593(19)	2212(9)	48(6)
C(11)	6274(8)	3262(22)	2614(10)	67(8)
C(12)	6833(10)	2758(23)	2980(10)	82(9)
C(13)	7296(8)	3510(31)	2893(12)	90(11)
C(14)	7217(7)	4854(27)	2477(11)	78(9)
C(15)	6691(7)	5348(23)	2156(10)	69(7)
C(20)	3686(6)	3861(21)	692(9)	54(6)
C(21)	3631(8)	2494(21)	996(10)	66(8)
C(22)	315C(9)	1640(22)	684(12)	76(9)
C(23)	2732(8)	2109(30)	106(12)	85(10)
C(24)	2768(8)	3546(31)	−231(12)	90(10)
C(25)	3239(7)	4393(22)	69(11)	70(8)
Rh(1B)	−139(1)	351(2)	6592(1)	52(1)
Rh(2B)	120(1)	3712(2)	6657(1)	53(1)
S(1B)	607(2)	1728(5)	7404(2)	55(2)
S(2B)	−641(2)	2369(5)	6966(2)	53(2)
O(1B)	−1214(6)	−1108(18)	5713(9)	108(7)
O(2B)	573(6)	−1877(17)	5968(9)	95(7)
O(3B)	−583(6)	5899(17)	5543(8)	92(7)
O(4B)	1206(5)	5140(18)	6474(10)	106(7)
C(1B)	−787(8)	−593(25)	6029(12)	79(9)
C(2B)	295(7)	−1024(22)	6199(10)	62(7)
C(3B)	−334(8)	5073(22)	5970(11)	63(8)
C(4B)	784(8)	4579(20)	6532(11)	67(7)
C(10B)	1289(6)	1403(20)	7197(9)	54(6)
C(11B)	1348(6)	1309(26)	6411(11)	80(8)
C(12B)	1872(8)	1103(25)	6287(13)	85(9)
C(13B)	2342(9)	1014(23)	6925(15)	88(10)
C(14B)	2271(8)	1153(25)	7682(13)	86(9)
C(15B)	1721(7)	1357(22)	7802(11)	72(8)
C(20B)	−1301(6)	2609(19)	6260(10)	55(6)
C(21B)	−1365(8)	2655(29)	5482(11)	95(11)
C(22B)	−1871(9)	2891(28)	4973(13)	100(10)
C(23B)	−2363(9)	2931(26)	5252(14)	93(10)
C(24B)	−2309(7)	2861(24)	6049(14)	85(10)
C(25B)	−1775(7)	2684(22)	6559(12)	75(8)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U tensor.

Table 3. Atomic coordinates ($\times 10^4$) and temperature factors ($\times 10^3$ Å^2) for $Rh_2(CO)_4(SEt)_2$ **(2)**.

Atom	x	y	z	U_{eq}[a]
Rh(1)	1240.3(5)	5034.8(2)	1812.8(6)	45.1(2)
Rh(2)	4539.6(5)	4674.8(3)	2393.6(6)	48.5(2)
S(1)	2403(2)	3951.5(8)	1321(2)	51.6(6)
S(2)	3037(2)	5430.0(9)	437(2)	52.5(6)
O(1)	325(7)	6509(3)	623(8)	94(3)
O(2)	−650(6)	4316(4)	3799(7)	81(2)
O(3)	7071(6)	5739(3)	3419(8)	89(3)
O(4)	6118(8)	3616(3)	4866(8)	104(3)
C(1)	630(7)	5953(4)	2276(9)	64(3)
C(2)	36(8)	4598(4)	3013(9)	58(2)
C(3)	6125(8)	5334(4)	3006(9)	59(3)
C(4)	5529(8)	4018(4)	3933(10)	65(3)
C(10)	2171(9)	3227(3)	2708(10)	66(3)
C(11)	2990(11)	2562(5)	2409(12)	94(4)
C(20)	3573(9)	6378(4)	751(10)	71(3)
C(21)	2478(12)	6841(5)	−434(14)	105(4)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U tensor.

distance of 2.78 Å. $Rh_2(CO)_4Cl_2$ forms zig-zag chains with an intermolecular Rh $\cdots$ Rh distance of 3.324 Å.[10] Molecules of **1A** do not form chains. Instead, two molecules are linked together with intermolecular distances Rh $\cdots$ Rh = 3.500(3) and Rh $\cdots$ S = 3.866(6) or 4.311(5) Å. The shortest distances between adjacent pairs

of molecules are Rh $\cdots$ Rh = 4.623(4) and Rh $\cdots$ S = 4.403(5) Å, showing that no real chain is formed.

The packing of **2** differs from that of **1**. The intermolecular links between molecules form infinite chains of molecules. As shown in Fig. 3, the intermolecular bonds in **2** are formed between edges of Rh_2S triangles, so that these triangles are approximately in one plane. In both **1A** and **1B** only the faces of the Rh_2S triangles interact.

The intramolecular Rh–Rh distance in **2** is 2.820(2) Å, a typical bonding distance. In both molecules of **1** this distance is larger, being 3.096(3) and 3.087(3) Å in **1A** and **1B** respectively.

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