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Structures of $[Ru_3(\mu\text{-}H)\{\mu\text{-}SC(CH_3)_3\}(dppm)(CO)_8]$ and $[Ru_3(\mu\text{-}H)\{\mu_3\text{-}SC(CH_3)_3\}(dppm)(CO)_7].0{\cdot}5CH_2Cl_2$ [dppm=bis(diphenylphosphino)-methane]

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Abstract. 1,2-μ-[Bis(diphenylphosphino)methane-*P,P′*]-1,3-μ-(*tert*-butylthiolato)-1,1,2,2,2,3,3,3-octacarbonyl-1,3-μ-hydrido-*triangulo*-triruthenium(0), $C_{37}H_{32}O_8P_2Ru_3S$, $M_r = 1001{\cdot}87$, triclinic, $P\bar{1}$, $a = 10{\cdot}896\,(2)$, $b = 11{\cdot}243\,(2)$, $c = 16{\cdot}760\,(3)$ Å, $\alpha = 72{\cdot}83\,(2)$, $\beta = 74{\cdot}73\,(2)$, $\gamma = 81{\cdot}37\,(2)°$, $V = 1886{\cdot}5$ Å^3, $Z = 2$, $D_m = 1{\cdot}74$, $D_x = 1{\cdot}764$ Mg m^{-3}, Mo $K\alpha$ radiation [$\lambda(\alpha_1) = 0{\cdot}70930$ Å], $\mu = 1{\cdot}35$ mm^{-1}, $F(000) = 992$, $T = 290$ K, $R = 0{\cdot}024$, 4390 observed reflections. The structure consists of a triangle of Ru atoms with the S and hydride bridging Ru(1) and Ru(3) and the dppm ligand bridging Ru(1) and Ru(2) with the P atoms close to the Ru_3 plane. Ru—Ru distances: 2·842 (1) Å (dppm bridging), 2·809 (1) Å (unbridged) and 2·868 (1) Å (S and H bridged); Ru—S: 2·399 (1) and 2·387 (1) Å. 1,2-μ-[Bis(diphenylphosphino)methane-*P,P′*]-1,2,3-μ_3-(*tert*-butylthiolato)-1,1,2,2,3,3,3-heptacarbonyl-1,2-μ-hydrido-*triangulo*-triruthenium(0)–dichloromethane (2/1), $C_{36}H_{32}O_7P_2Ru_3S.0{\cdot}5CH_2Cl_2$, $M_r = 1016{\cdot}43$, orthorhombic, *Pbca*, $a = 16{\cdot}955\,(3)$, $b = 20{\cdot}374\,(3)$, $c = 23{\cdot}205\,(3)$ Å, $V = 8016{\cdot}0$ Å^3, $Z = 8$, $D_m = 1{\cdot}65$, $D_x = 1{\cdot}684$ Mg m^{-3}, Mo $K\alpha$ radiation, $\mu = 1{\cdot}33$ mm^{-1}, $F(000) = 4024$, $T = 290$ K, $R = 0{\cdot}051$, 3539 observed reflections. The S atom is located above the Ru_3 triangle approximately equidistant from each. Two of the Ru atoms are bridged by the dppm ligand and most probably by a hydride as well. Ru—Ru distances: 2·879 (1) Å (dppm and H bridged), 2·775 (1) and 2·757 (1) Å; Ru—S: 2·334 (3), 2·322 (3) and 2·309 (3) Å.

Introduction. Metal clusters have attracted considerable interest in recent years (*e.g.* Raithby, 1980). This paper describes the structural investigation of two further examples of this type.

In the first compound the S atom of a *tert*-butylthiolate ligand acts as a three-electron donor and bridges two Ru atoms, whereas, in the second, it is a five-electron donor and is bonded to three Ru atoms.

Experimental. $[Ru_3(\mu\text{-}H)\{\mu\text{-}SC(CH_3)_3\}(dppm)(CO)_8]$ (1): density by flotation in aqueous ZnI_2 solution; red-brown crystal $0{\cdot}22 \times 0{\cdot}21 \times 0{\cdot}28$ mm; Enraf–Nonius CAD-4F diffractometer, graphite-monochromatized Mo $K\alpha$ radiation; lattice parameters from setting angles of 25 reflections, $30 < 2\theta < 35°$; analytic absorption correction (T range 0·743–0·803) (de Meulenaer & Tompa, 1965); data collected $2\theta \le 45°$, $-11 \le h \le 11$, $0 \le k \le 12$, $-16 \le l \le 17$; θ–2θ scan; variations in intensities of standards <2%; 4910 unique reflections, 4390 with $I > 2{\cdot}3\sigma(I)$; Lp correction applied; direct methods, *MULTAN* (Germain, Main & Woolfson, 1971); anisotropic temperature factors for non-H atoms; H isotropic (dppm H's calculated, others from ΔF synthesis) and not refined except H(1) refined (*xyz*); refinement by full matrix on *F*; final $R = 0{\cdot}024$, $wR = 0{\cdot}034$, $S = 1{\cdot}45$; $w = \{[\sigma(F_o)]^2 + 0{\cdot}0004F_o^2\}^{-1}$; max. $\Delta/\sigma = 0{\cdot}05$; major features in final ΔF synthesis [all $< 0{\cdot}53\,(6)$ e Å^{-3}] near Ru atoms; VAX 11/750 computer (Larson & Gabe, 1978; Watkin & Carruthers, 1981; Trueblood, 1978); scattering factors from *International Tables for X-ray Crystallography* (1974).

$[Ru_3(\mu\text{-}H)\{\mu_3\text{-}SC(CH_3)_3\}(dppm)(CO)_7].0{\cdot}5CH_2Cl_2$ (2): density by flotation in aqueous ZnI_2 solution; yielded hexagonal prism $0{\cdot}37 \times 0{\cdot}23 \times 0{\cdot}26$ mm; Enraf–Nonius CAD-4F diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, lattice parameters from setting angles of 25 reflections, $20 < 2\theta < 32°$; analytic absorption correction (T range 0·730–0·777); data collected $2\theta \le 45°$, $0 \le h \le 18$, $0 \le k \le 21$, $0 \le l \le 24$; θ–2θ scan: variations in intensities of standards <3%; 5221 unique reflections, 3539 with $I > 2{\cdot}3\sigma(I)$; Lp correction applied; direct methods, *MULTAN*; anisotropic full-matrix refinement on *F* (except disordered CH_2Cl_2 isotropic); dppm H's calculated isotropic and not refined; final $R = 0{\cdot}051$, $wR = 0{\cdot}057$, $S = 1{\cdot}86$, $w = \{[\sigma(F_o)]^2 + 0{\cdot}0004F_o^2\}^{-1}$; max. $\Delta/\sigma = 0{\cdot}05$; largest feature in final ΔF synthesis [1·1 (1) e Å^{-3}] near Ru(1); VAX 11/750 computer; scattering factors from *International Tables for X-ray Crystallography* (1974). Presence of CH_2Cl_2 confirmed by mass spectroscopy.

Discussion. Thermal-ellipsoid diagrams (Davies, 1983) of the molecules displaying the atom labelling are

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shown in Figs. 1 and 2. The final atomic coordinates are given in Tables 1 and 2 and selected bond lengths and angles in Tables 3 and 4.*

A thermal-motion analysis was performed on each structure using the program *THMV*8 (Trueblood, 1978) with weights derived from the e.s.d.'s of the thermal parameters. The differences in mean-square vibration amplitudes (m.s.v.a.'s) of pairs of atoms along their joining lines were used to identify the rigid core of the molecule and groups that are in themselves rigid, but with motion relative to the central core (Rosenfield, Trueblood & Dunitz, 1978).

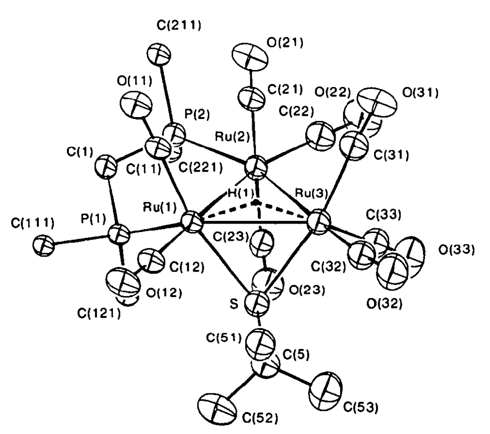

Fig. 1. Thermal-ellipsoid diagram of [$Ru_3(\mu$-H){μ-SC$(CH_3)_3$}-(dppm)$(CO)_8$], (1). Only the *ipso* carbon atoms of the phenyl groups and the hydridic hydrogen atoms are shown here and in Fig. 2. Ellipsoids enclose 50% probabilities except for the hydride bridge which is drawn as a sphere of arbitrary small radius.

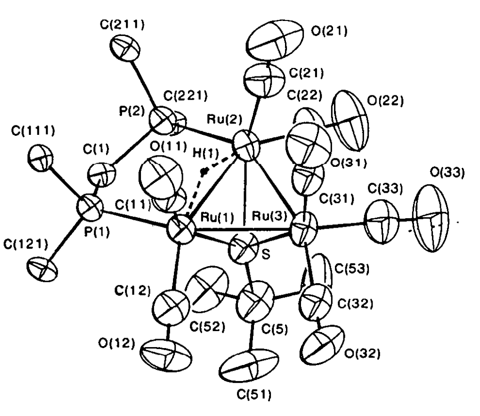

Fig. 2. Thermal-ellipsoid diagram of [$Ru_3(\mu$-H){μ_3-SC$(CH_3)_3$}-(dppm)(CO)], (2).

Examination of the m.s.v.a. differences in (1) showed that the carbonyl atoms and *meta* and *para* atoms of the phenyl rings should be excluded from the segmented rigid-body analysis; and that analysis of the *tert*-butyl group would be only approximate. Several models were examined and are outlined in the supplementary material. Corrections to bond lengths due to thermal motion were deduced from relevant models and are given in Table 4. Corrections for the carbonyl groups were derived from a riding-motion model (Busing & Levy, 1964).

The precision of the structure determination of (2) is lower and the differences in the m.s.v.a.'s are considerably larger [as are the $\sigma(U_{ij})$'s], suggesting that the thermal-motion parameters are suffering from significant random or systematic errors (Hirshfeld, 1976). A

Table 1. *Final fractional atomic coordinates and isotropic thermal parameters for the non-hydrogen atoms of* [$Ru_3(\mu$-H){μ-SC$(CH_3)_3$}*(dppm)*$(CO)_8$], (1)

	x	y	z	B_{eq}*
Ru(1)	0·65099 (3)	0·33079 (3)	0·14308 (2)	2·26
Ru(2)	0·58270 (3)	0·39677 (3)	0·30115 (2)	2·60
Ru(3)	0·39746 (3)	0·43031 (3)	0·20568 (2)	2·83
S	0·46359 (8)	0·21774 (9)	0·20654 (6)	2·88
P(1)	0·80130 (8)	0·19080 (8)	0·20436 (6)	2·35
P(2)	0·78204 (8)	0·34476 (9)	0·33296 (6)	2·55
C(11)	0·7702 (4)	0·4512 (3)	0·0979 (2)	2·82
O(11)	0·8436 (3)	0·5228 (3)	0·0663 (2)	4·04
C(12)	0·6896 (3)	0·2816 (3)	0·0401 (2)	2·98
O(12)	0·7225 (3)	0·2513 (3)	−0·0217 (2)	4·67
C(21)	0·6334 (4)	0·5575 (4)	0·2283 (3)	3·43
O(21)	0·6629 (3)	0·6536 (3)	0·1896 (2)	4·95
C(22)	0·4865 (4)	0·4656 (4)	0·3902 (3)	4·09
O(22)	0·4214 (4)	0·5116 (4)	0·4400 (2)	7·60
C(23)	0·5225 (3)	0·2324 (4)	0·3612 (2)	3·22
O(23)	0·4847 (3)	0·1404 (3)	0·4020 (2)	4·51
C(31)	0·3824 (4)	0·6028 (4)	0·2028 (3)	4·18
O(31)	0·3673 (4)	0·7047 (3)	0·2019 (3)	6·65
C(32)	0·2740 (4)	0·4603 (4)	0·1380 (3)	3·63
O(32)	0·1923 (3)	0·4852 (3)	0·1049 (2)	5·20
C(33)	0·2807 (4)	0·3862 (4)	0·3136 (3)	4·12
O(33)	0·2105 (3)	0·3565 (4)	0·3780 (2)	6·25
C(1)	0·8873 (3)	0·2616 (3)	0·2576 (2)	2·64
C(111)	0·9376 (3)	0·1349 (3)	0·1291 (2)	2·51
C(112)	0·9894 (4)	0·0131 (3)	0·1479 (3)	3·42
C(113)	1·0934 (4)	−0·0266 (4)	0·0912 (3)	4·09
C(114)	1·1439 (4)	0·0551 (4)	0·0144 (3)	3·88
C(115)	1·0943 (4)	0·1755 (4)	−0·0048 (2)	3·69
C(116)	0·9910 (3)	0·2156 (3)	0·0514 (2)	3·26
C(121)	0·7498 (3)	0·0448 (3)	0·2805 (2)	2·66
C(122)	0·7737 (4)	0·0025 (4)	0·3618 (3)	3·43
C(123)	0·7309 (4)	−0·1105 (4)	0·4160 (3)	4·46
C(124)	0·6689 (4)	−0·1817 (4)	0·3892 (3)	4·87
C(125)	0·6477 (4)	−0·1414 (4)	0·3078 (3)	4·63
C(126)	0·6863 (4)	−0·028/ (4)	0·2542 (3)	3·73
C(211)	0·8739 (3)	0·4739 (3)	0·3242 (2)	2·87
C(212)	0·9398 (4)	0·5414 (4)	0·2466 (3)	3·75
C(213)	1·0078 (4)	0·6394 (4)	0·2414 (3)	4·88
C(214)	1·0088 (5)	0·6698 (4)	0·3142 (3)	5·09
C(215)	0·9415 (5)	0·6059 (4)	0·3915 (3)	4·80
C(216)	0·8735 (4)	0·5086 (4)	0·3972 (3)	3·86
C(221)	0·7984 (3)	0·2458 (3)	0·4386 (2)	2·91
C(222)	0·6947 (4)	0·2097 (5)	0·5042 (3)	4·52
C(223)	0·7117 (5)	0·1360 (6)	0·5836 (3)	7·37
C(224)	0·8316 (6)	0·1018 (6)	0·5968 (3)	6·99
C(225)	0·9348 (5)	0·1375 (4)	0·5323 (3)	5·03
C(226)	0·9190 (4)	0·2084 (4)	0·4537 (3)	3·49
C(5)	0·3896 (4)	0·1664 (4)	0·1343 (3)	3·70
C(51)	0·4016 (4)	0·2511 (4)	0·0444 (3)	4·30
C(52)	0·4549 (5)	0·0378 (5)	0·1294 (3)	5·79
C(53)	0·2520 (4)	0·1546 (5)	0·1824 (3)	5·53

* $B_{eq} = 8\pi^2(U_1 + U_2 + U_3)/3$ where the U_n are the principal axes of the thermal ellipsoid in Å^2.

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* Tables of hydrogen-atom coordinates, anisotropic temperature factors, distances and angles in the phenyl rings, least-squares planes, details of the thermal-motion analyses and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42784 (87 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

rigid-body analysis restricted to the core atoms alone (Ru_3SP_2) failed as did models with segmented rigid groups.

The structure of (1) closely resembles that of $[Os_3(\mu\text{-}H)(\mu\text{-}SEt)(CO)_{10}]$ (Allen, Mason & Hitchcock, 1977) and related $[M_3(\mu\text{-}H)(\mu\text{-}X)(CO)_{10}]$ complexes (Raithby, 1980). It consists of a triangle of Ru atoms with the S atom of the *tert*-butylthiolate group and the hydride, H(1), bridging Ru(1) and Ru(3). The S and H atoms lie out of the Ru_3 plane on opposite sites of it [−1·851 (1) Å for S, 0·88 (3) Å for H(1)]. The dppm ligand bridges Ru(1) and Ru(2); the P atom on Ru(1) is *trans* to the hydride and that on Ru(2) lies approximately in the Ru_3 plane. Terminal carbonyl groups complete irregular octahedra at each Ru atom.

(2) comprises a triangle of Ru atoms with an S atom capping them to complete a pseudo-tetrahedron. The dppm ligand bridges two Ru atoms with the P atoms

Table 2. *Final fractional atomic coordinates and isotropic thermal parameters for the non-hydrogen atoms of* $[Ru_3(\mu\text{-}H)\{\mu_3\text{-}SC(CH_3)_3\}(dppm)(CO)_7].\text{-}0{\cdot}5CH_2Cl_2$, (2)

	x	y	z	B_{eq}*
Ru(1)	0·20035 (5)	0·28367 (4)	0·31663 (4)	3·34
Ru(2)	0·22794 (5)	0·40928 (4)	0·36978 (4)	3·58
Ru(3)	0·13670 (5)	0·31362 (5)	0·42274 (4)	3·90
S	0·26940 (16)	0·30676 (14)	0·40126 (12)	3·85
P(1)	0·29568 (15)	0·29900 (12)	0·24506 (11)	2·90
P(2)	0·33525 (15)	0·43452 (13)	0·30798 (12)	3·15
C(11)	0·1094 (8)	0·2878 (5)	0·2738 (5)	5·0
O(11)	0·0520 (5)	0·2919 (5)	0·2457 (4)	7·0
C(12)	0·1940 (6)	0·1919 (7)	0·3225 (5)	5·2
O(12)	0·1898 (6)	0·1359 (5)	0·3272 (5)	8·2
C(21)	0·1461 (8)	0·4651 (7)	0·3517 (6)	6·0
O(21)	0·0926 (6)	0·4979 (5)	0·3398 (5)	10·1
C(22)	0·2508 (8)	0·4570 (7)	0·4361 (6)	6·0
O(22)	0·2616 (7)	0·4863 (6)	0·4771 (5)	10·1
C(31)	0·0438 (7)	0·3464 (6)	0·3911 (5)	4·8
O(31)	−0·0143 (5)	0·3653 (5)	0·3698 (4)	7·8
C(32)	0·1017 (7)	0·2281 (7)	0·4425 (5)	5·1
O(32)	0·0800 (6)	0·1775 (5)	0·4535 (4)	7·9
C(33)	0·1272 (8)	0·3495 (7)	0·4970 (6)	6·4
O(33)	0·1173 (8)	0·3693 (7)	0·5428 (5)	11·8
C(1)	0·3689 (5)	0·3603 (4)	0·2684 (4)	3·0
C(111)	0·2608 (6)	0·3248 (5)	0·1749 (4)	3·1
C(112)	0·2888 (6)	0·3788 (6)	0·1457 (4)	3·8
C(113)	0·2614 (7)	0·3958 (6)	0·0923 (5)	4·9
C(114)	0·2028 (8)	0·3598 (7)	0·0674 (5)	5·9
C(115)	0·1747 (7)	0·3055 (7)	0·0956 (6)	5·5
C(116)	0·2034 (7)	0·2884 (6)	0·1491 (5)	4·5
C(121)	0·3618 (5)	0·2315 (4)	0·2283 (4)	2·9
C(122)	0·3850 (6)	0·1894 (6)	0·2713 (5)	4·4
C(123)	0·4387 (7)	0·1393 (5)	0·2605 (5)	4·5
C(124)	0·4712 (6)	0·1334 (6)	0·2073 (6)	4·5
C(125)	0·4496 (7)	0·1746 (6)	0·1649 (5)	4·5
C(126)	0·3942 (6)	0·2234 (5)	0·1741 (5)	4·1
C(211)	0·3230 (6)	0·4960 (4)	0·2508 (5)	3·3
C(212)	0·2486 (7)	0·5192 (6)	0·2361 (5)	5·1
C(213)	0·2391 (8)	0·5629 (7)	0·1912 (6)	5·8
C(214)	0·3017 (8)	0·5828 (6)	0·1613 (6)	5·7
C(215)	0·3759 (7)	0·5598 (7)	0·1727 (5)	6·0
C(216)	0·3861 (6)	0·5167 (6)	0·2175 (5)	4·8
C(221)	0·4273 (6)	0·4610 (5)	0·3421 (4)	3·1
C(222)	0·4247 (6)	0·5056 (5)	0·3866 (5)	4·4
C(223)	0·4911 (8)	0·5248 (6)	0·4169 (5)	5·5
C(224)	0·5629 (8)	0·4992 (7)	0·3998 (7)	6·1
C(225)	0·5683 (7)	0·4573 (6)	0·3550 (6)	5·6
C(226)	0·5014 (6)	0·4377 (5)	0·3259 (5)	4·5
C(5)	0·3548 (7)	0·2762 (7)	0·4474 (6)	6·2
C(51)	0·3430 (9)	0·1998 (8)	0·4527 (8)	9·6
C(52)	0·4309 (7)	0·2920 (8)	0·4153 (6)	7·2
C(53)	0·3500 (9)	0·3132 (11)	0·5044 (6)	10·9
Cl(1)†	0·4361 (11)	0·4667 (9)	0·0144 (8)	17·2‡
Cl(2)†	0·4440 (10)	0·4470 (8)	−0·0249 (8)	16·6‡
C(100)†	0·486 (3)	0·5043 (21)	−0·0375 (16)	10·8‡

* $B_{eq} = 8\pi^2(U_1 + U_2 + U_3)/3$ where the U_n are the principal axes of the thermal ellipsoid in Å^2.

† Occupancy 0·5.

‡ Isotropic.

Table 3. *Selected interatomic distances* (Å) *and angles* (°) *for* $[Ru_3(\mu\text{-}H)\{\mu\text{-}SC(CH_3)_3\}(dppm)(CO)_8]$, (1)

Distances corrected for thermal motion are given following the uncorrected value.

Ru(1)—Ru(2)	2·8423 (7)	2·846*	S—C(5)	1·876 (4)	1·878†
Ru(2)—Ru(3)	2·8094 (7)	2·811*	C(5)—C(51)	1·510 (6)	1·518†
Ru(3)—Ru(1)	2·8675 (8)	2·871*	C(5)—C(52)	1·527 (6)	1·537†
Ru(1)—S	2·3985 (11)	2·402*	C(5)—C(53)	1·508 (6)	1·518†
Ru(1)—P(1)	2·3178 (11)	2·320*	P(1)—C(1)	1·842 (3)	1·843†
Ru(1)—C(11)	1·870 (4)	1·873‡	P(1)—C(111)	1·842 (3)	1·845†
Ru(1)—C(12)	1·890 (4)	1·895‡	P(1)—C(121)	1·817 (4)	1·819†
Ru(1)—H(1)	1·82 (3)		P(2)—C(1)	1·844 (4)	1·846†
Ru(2)—P(2)	2·3213 (10)	2·323*	P(2)—C(211)	1·834 (4)	1·836†
Ru(2)—C(21)	1·925 (5)	1·929‡	P(2)—C(221)	1·830 (4)	1·832†
Ru(2)—C(22)	1·882 (4)	1·895‡	C(11)—O(11)	1·134 (5)	1·142§
Ru(2)—C(23)	1·943 (5)	1·946‡	C(12)—O(12)	1·137 (5)	1·146§
Ru(3)—S	2·3873 (11)	2·391*	C(21)—O(21)	1·128 (6)	1·138§
Ru(3)—C(31)	1·909 (5)	1·919‡	C(22)—O(22)	1·140 (5)	1·157§
Ru(3)—C(32)	1·912 (4)	1·917‡	C(23)—O(23)	1·127 (5)	1·136§
Ru(3)—C(33)	1·893 (5)	1·902‡	C(31)—O(31)	1·128 (6)	1·141§
Ru(3)—H(1)	1·79 (3)		C(32)—O(32)	1·127 (5)	1·135§
			C(33)—O(33)	1·135 (6)	1·148§

Ru(3)—Ru(1)—Ru(2)	58·95 (2)	Ru(2)—Ru(3)—Ru(1)	60·08 (2)
Ru(1)—Ru(2)—Ru(3)	60·98 (2)		
Ru(2)—Ru(1)—S	82·29 (3)	S—Ru(1)—P(1)	100·94 (4)
Ru(2)—Ru(1)—P(1)	84·53 (3)	S—Ru(1)—C(11)	166·45 (1)
Ru(2)—Ru(1)—C(11)	90·29 (1)	S—Ru(1)—C(12)	94·83 (1)
Ru(2)—Ru(1)—C(12)	177·11 (1)	S—Ru(1)—H(1)	79·48 (6)
Ru(2)—Ru(1)—H(1)	84·07 (6)	P(1)—Ru(1)—C(11)	89·56 (1)
Ru(3)—Ru(1)—S	53·01 (3)	P(1)—Ru(1)—C(12)	95·84 (1)
Ru(3)—Ru(1)—P(1)	135·29 (3)	P(1)—Ru(1)—H(1)	168·43 (6)
Ru(3)—Ru(1)—C(11)	113·44 (1)	C(11)—Ru(1)—C(12)	92·58 (5)
Ru(3)—Ru(1)—C(12)	119·39 (1)	C(11)—Ru(1)—H(1)	88·52 (7)
Ru(3)—Ru(1)—H(1)	37·00 (6)	C(12)—Ru(1)—H(1)	95·64 (7)
Ru(1)—Ru(2)—P(2)	96·44 (3)	Ru(3)—Ru(2)—C(23)	87·21 (1)
Ru(1)—Ru(2)—C(21)	82·92 (1)	P(2)—Ru(2)—C(21)	91·18 (2)
Ru(1)—Ru(2)—C(22)	159·64 (2)	P(2)—Ru(2)—C(22)	103·48 (2)
Ru(1)—Ru(2)—C(23)	90·38 (1)	P(2)—Ru(2)—C(23)	94·24 (1)
Ru(3)—Ru(2)—P(2)	157·40 (3)	C(21)—Ru(2)—C(22)	92·41 (8)
Ru(3)—Ru(2)—C(21)	85·45 (1)	C(21)—Ru(2)—C(23)	171·82 (5)
Ru(3)—Ru(2)—C(22)	98·99 (2)	C(22)—Ru(2)—C(23)	92·28 (8)
Ru(1)—Ru(3)—S	53·37 (3)	S—Ru(3)—C(31)	167·73
Ru(1)—Ru(3)—C(31)	115·03 (3)	S—Ru(3)—C(32)	98·71 (2)
Ru(1)—Ru(3)—C(32)	119·76 (1)	S—Ru(3)—C(33)	93·07 (4)
Ru(1)—Ru(3)—C(33)	131·89 (3)	S—Ru(3)—H(1)	80·49 (8)
Ru(1)—Ru(3)—H(1)	37·91 (7)	C(31)—Ru(3)—C(32)	90·90 (7)
Ru(2)—Ru(3)—S	83·19 (3)	C(31)—Ru(3)—C(33)	93·46 (9)
Ru(2)—Ru(3)—C(31)	86·99 (2)	C(31)—Ru(3)—H(1)	91·48 (9)
Ru(2)—Ru(3)—C(32)	177·45 (3)	C(32)—Ru(3)—C(33)	96·16 (7)
Ru(2)—Ru(3)—C(33)	85·40 (2)	C(32)—Ru(3)—H(1)	92·91 (8)
Ru(2)—Ru(3)—H(1)	85·72 (7)	C(33)—Ru(3)—H(1)	169·59 (8)
Ru(1)—S—Ru(3)	73·62 (3)	Ru(1)—H(1)—Ru(3)	105·09 (3)
Ru(1)—S—C(5)	118·14 (3)	Ru(3)—S—C(5)	111·31 (3)
Ru(1)—P(1)—C(1)	112·58 (2)	Ru(2)—P(2)—C(1)	110·08 (1)
Ru(1)—P(1)—C(111)	116·04 (2)	Ru(2)—P(2)—C(211)	117·15 (2)
Ru(1)—P(1)—C(121)	118·54 (2)	Ru(2)—P(2)—C(221)	120·57 (2)
C(1)—P(1)—C(111)	99·64 (5)	C(1)—P(2)—C(211)	103·55 (6)
C(1)—P(1)—C(121)	106·32 (6)	C(1)—P(2)—C(221)	103·82 (6)
C(111)—P(1)—C(121)	101·46 (6)	C(211)—P(2)—C(221)	99·59 (6)
P(1)—C(1)—P(2)	113·90 (8)		
Ru(1)—C(11)—O(11)	176·18 (1)	Ru(1)—C(12)—O(12)	174·64 (3)
Ru(2)—C(21)—O(21)	176·21 (3)	Ru(3)—C(31)—O(31)	176·72 (8)
Ru(2)—C(22)—O(22)	174·37 (7)	Ru(23)—C(32)—O(32)	171·75 (4)
Ru(2)—C(23)—O(23)	174·27 (2)	Ru(3)—C(33)—O(33)	178·04 (1)

* Corrected for thermal motion: rigid body consisting of Ru and P atoms, with S librating about Ru(1)—Ru(3) axis.

† Corrected for thermal motion: rigid body consisting of Ru, P and S atoms and adjacent non-carbonyl C atoms, with *ortho*-C atoms librating about P—C bonds and methyl C atoms librating about S—C bond.

‡ Corrected for motion of C riding on Ru.

§ Derived from distance Ru—C (corrected for C riding on Ru), distance Ru···O (corrected for O riding on Ru) and angle Ru—C—O.

essentially equatorial, but slightly out of the Ru_3 plane, on the same side as the S. Deviations from the Ru_3 plane are 0·461 (3) Å for P(1), 0·654 (3) Å for P(2) and 1·664 (3) Å for S. Two terminal carbonyl groups are bonded to each of the P-substituted Ru atoms and three to the other.

The ^1H NMR spectrum of (2) indicates the presence of bridging hydride species. Inspection of the arrangement of the ligands about the core indicates that, in the solid state, the hydride probably bridges Ru(1) and Ru(2), lying on the opposite side of the Ru_3 plane from the S, in a manner similar to that in $[Fe_3(\mu\text{-}H)(\mu_3\text{-}SC_3H_7)(CO)_9]$ (Bau, Don, Greatrex, Haines, Love & Wilson, 1975) and $[Fe_3(\mu\text{-}H)(\mu_3\text{-}SC_6H_{11})(CO)_9]$ (Winter, Zsolnai & Huttner, 1982). In fact, the second largest peak in an inner-data difference electron density map [0·61 (9) e Å^{-3} at 0·199, 0·355, 0·326] is located here. However, the Ru—peak distances of 1·47 and 1·57 Å are very short for a bridging hydride (Teller & Bau, 1981) so assignment of this peak to the missing hydride is tentative and it has not been included in the structure determination. It is, however, shown in Fig. 2.

Table 4. *Selected interatomic distances* (Å) *and angles* (°) *for* $[Ru_3(\mu\text{-}H)\{\mu_3\text{-}SC(CH_3)_3\}(dppm)(CO)_7].0{\cdot}5\text{-}CH_2Cl_2$, (2)

Ru(1)—Ru(2)	2·8792 (13)	S—C(5)	1·905 (11)
Ru(2)—Ru(3)	2·7752 (13)	C(5)—C(51)	1·57 (2)
Ru(3)—Ru(1)	2·7568 (12)	C(5)—C(52)	1·53 (2)
Ru(1)—S	2·334 (3)	C(5)—C(53)	1·52 (2)
Ru(1)—P(1)	2·338 (3)	P(1)—C(1)	1·843 (9)
Ru(1)—C(11)	1·838 (15)	P(1)—C(111)	1·811 (10)
Ru(1)—C(12)	1·877 (14)	P(1)—C(121)	1·816 (9)
Ru(2)—S	2·322 (3)	P(2)—C(1)	1·859 (10)
Ru(2)—P(2)	2·373 (3)	P(2)—C(211)	1·837 (10)
Ru(2)—C(21)	1·842 (14)	P(2)—C(221)	1·831 (10)
Ru(2)—C(22)	1·862 (13)	C(11)—O(11)	1·17 (2)
Ru(3)—S	2·309 (3)	C(12)—O(12)	1·15 (2)
Ru(3)—C(31)	1·861 (13)	C(21)—O(21)	1·16 (2)
Ru(3)—C(32)	1·898 (14)	C(22)—O(22)	1·14 (2)
Ru(3)—C(33)	1·878 (14)	C(31)—O(31)	1·17 (2)
		C(32)—O(32)	1·12 (2)
		C(33)—O(33)	1·15 (2)

Ru(3)—Ru(1)—Ru(2)	58·95 (3)	Ru(2)—Ru(3)—Ru(1)	62·73 (3)
Ru(1)—Ru(2)—Ru(3)	58·32 (3)		
Ru(2)—Ru(1)—S	51·61 (7)	Ru(3)—Ru(1)—C(12)	97·6 (4)
Ru(2)—Ru(1)—P(1)	94·20 (7)	S—Ru(1)—P(1)	102·9 (1)
Ru(2)—Ru(1)—C(11)	109·1 (3)	S—Ru(1)—C(11)	150·1 (4)
Ru(2)—Ru(1)—C(12)	149·7 (4)	S—Ru(1)—C(12)	99·7 (4)
Ru(3)—Ru(1)—S	53·15 (7)	P(1)—Ru(1)—C(11)	100·9 (4)
Ru(3)—Ru(1)—P(1)	151·09 (7)	P(1)—Ru(1)—C(12)	103·0 (4)
Ru(3)—Ru(1)—C(11)	98·3 (3)	C(11)—Ru(1)—C(12)	92·2 (5)
Ru(1)—Ru(2)—S	52·00 (7)	Ru(3)—Ru(2)—C(22)	96·7 (4)
Ru(1)—Ru(2)—P(2)	93·34 (7)	S—Ru(2)—P(2)	98·8 (1)
Ru(1)—Ru(2)—C(21)	109·2 (4)	S—Ru(2)—C(21)	148·8 (4)
Ru(1)—Ru(2)—C(22)	148·5 (4)	S—Ru(2)—C(22)	98·4 (5)
Ru(3)—Ru(2)—S	52·96 (7)	P(2)—Ru(2)—C(21)	107·8 (4)
Ru(3)—Ru(2)—P(2)	147·90 (8)	P(2)—Ru(2)—C(22)	103·1 (4)
Ru(3)—Ru(2)—C(21)	96·6 (4)	C(21)—Ru(2)—C(22)	91·3 (6)
Ru(1)—Ru(3)—S	54·00 (7)	Ru(2)—Ru(3)—C(33)	100·4 (4)
Ru(1)—Ru(3)—C(31)	93·4 (4)	S—Ru(3)—C(31)	139·6 (4)
Ru(1)—Ru(3)—C(32)	97·8 (4)	S—Ru(3)—C(32)	107·5 (4)
Ru(1)—Ru(3)—C(33)	159·9 (4)	S—Ru(3)—C(33)	107·8 (4)
Ru(2)—Ru(3)—S	53·39 (7)	C(31)—Ru(3)—C(32)	99·2 (5)
Ru(2)—Ru(3)—C(31)	92·6 (4)	C(31)—Ru(3)—C(33)	98·6 (6)
Ru(2)—Ru(3)—C(32)	157·9 (4)	C(32)—Ru(3)—C(33)	96·2 (6)
Ru(1)—P(1)—C(1)	110·4 (3)	Ru(2)—P(2)—C(1)	111·0 (3)
Ru(1)—P(1)—C(111)	116·9 (3)	Ru(2)—P(2)—C(211)	119·9 (3)
Ru(1)—P(1)—C(121)	118·6 (3)	Ru(2)—P(2)—C(221)	117·1 (3)
Ru(1)—S—Ru(2)	76·40 (9)	Ru(1)—S—C(5)	142·0 (5)
Ru(1)—S—Ru(3)	72·85 (8)	Ru(2)—S—C(5)	134·5 (5)
Ru(2)—S—Ru(3)	73·65 (9)	Ru(3)—S—C(5)	129·7 (4)
C(1)—P(1)—C(111)	106·7 (5)	C(1)—P(2)—C(211)	103·4 (4)
C(1)—P(1)—C(121)	99·2 (4)	C(1)—P(2)—C(221)	101·1 (5)
C(111)—P(1)—C(121)	103·2 (5)	C(211)—P(2)—C(221)	102·0 (4)
P(1)—C(1)—P(2)	119·3 (5)		
Ru(1)—C(11)—O(11)	178·3 (10)	Ru(3)—C(31)—O(31)	177·6 (11)
Ru(1)—C(12)—O(12)	178·8 (11)	Ru(3)—C(32)—O(32)	178·8 (10)
Ru(2)—C(21)—O(21)	177·0 (12)	Ru(3)—C(33)—O(33)	175·9 (13)
Ru(2)—C(22)—O(22)	177·3 (12)		

The Ru—Ru distances in (1) are 2·842 (1) Å for the pair bridged by the dppm ligand, 2·868 (1) Å for the pair bridged by the thiolate S and the hydride and 2·809 (1) Å for the unbridged atoms. In comparison, the parent $[Ru_3(CO)_{12}]$ shows an average Ru—Ru bond length of 2·854 (5) Å (Churchill, Hollander & Hutchinson, 1977). $[Ru_3(CO)_{11}(PPh_3)]$ (Forbes, Goodhand, Jones & Hamor, 1979) and $[Ru_3(CO)_{11}\{P(C_6H_{11})_3\}]$ (Bruce, Matisons, Skelton & White, 1983) show a lengthening of the Ru—Ru bond *cis* to the phosphine but this trend does not appear to continue to the polysubstituted phosphines and phosphites (Lavigne, Lugan & Bonnet, 1982; Bruce *et al.*, 1983; Bruce, Matisons, Patrick, White & Willis, 1985). In (1) the dppm-bridged bond is ~0·03 Å longer than the unbridged bond and in (2) it is ~0·11 Å longer [2·879 (1) *cf.* 2·757 (1) and 2·775 (1) Å]. The latter no doubt arises more from the lengthening effect of the hydride than from the phosphine. By contrast, the bridged bonds in $[Ru_3(CO)_8(dppm)_2]$ are ~0·02 Å *shorter* than the unsupported bond (Lavigne *et al.*, 1982). The Ru—Ru bond bridged by S and H in (1) is a little longer than that in $[Ru_3H(SCH_2COOH)(CO)_{10}]$- [2·839 (4) Å] (Jeannin, Jeannin & Lavigne, 1978).

The Ru—P distances in (1) are equal [2·318 (1) and 2·321 (1) Å], even though the P atoms are *trans* to radically different atoms, whereas they are significantly different in (2) [2·338 (1) and 2·373 (3) Å] in which they have identical neighboring atoms. An even more extreme example of the latter is $[Ru_3(CO)_{10}\text{-}\{P(OMe)_3\}_2]$ (Bruce *et al.*, 1983).

Ru—S distances in (1) are comparable with those found for $[Ru_3H(SCH_2COOH)(CO)_{10}]$ (Jeannin *et al.*, 1978) and $[Os_3H(SEt)(CO)_{10}]$ (after allowing for the larger covalent radius of Os) (Allen *et al.*, 1977). The μ_3-$S(C_4H_9)$ ligand of (2), however, gives Ru—S bonds which are ~0·07 Å shorter than this, but slightly longer than the average of 2·273 (1) Å found for $[Ru_3\{\mu_3\text{-}S(C_4H_9)\}(\mu_3\text{-}C_7H_7)(CO)_6]$ (Howard, Kennedy & Knox, 1979). These values are intermediate between those found for $Fe_3(\mu_3\text{-}SR)$ and $Os_3(\mu_3\text{-}S)$ systems (Bau *et al.*, 1975; Winter *et al.*, 1982; Johnson, Lewis, Pippard & Raithby, 1978; Johnson, Lewis, Pippard, Raithby, Sheldrick & Rouse, 1979).

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References

ALLEN, V. F., MASON, R. & HITCHCOCK, P. B. (1977). *J. Organomet. Chem.* **140**, 297–307.

BAU, R., DON, B., GREATREX, R., HAINES, R. J., LOVE, R. A. & WILSON, R. D. (1975). *Inorg. Chem.* **14**, 3021–3025.

BRUCE, M. I., MATISONS, J. G., PATRICK, J. M., WHITE, A. H. & WILLIS, A. C. (1985). *J. Chem. Soc. Dalton Trans.* pp. 1223–1227.

BRUCE, M. I., MATISONS, J. G., SKELTON, B. W. & WHITE, A. H. (1983). *J. Chem. Soc. Dalton Trans.* pp. 2375–2384.

BUSING, W. R. & LEVY, H. A. (1964). *Acta Cryst.* **17**, 142–146.

CHURCHILL, M. R., HOLLANDER, F. J. & HUTCHINSON, J. P. (1977). *Inorg. Chem.* **16**, 2655–2659.

DAVIES, E. K. (1983). *CHEMGRAF User Guide.* Chemical Crystallography Laboratory, Univ. of Oxford, England.

FORBES, E. J., GOODHAND, N., JONES, D. L. & HAMOR, T. A. (1979). *J. Organomet. Chem.* **182**, 143–154.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

HIRSHFELD, F. L. (1976). *Acta Cryst.* A**32**, 239–244.

HOWARD, J. A. K., KENNEDY, F. G. & KNOX, S. A. R. (1979). *J. Chem. Soc. Chem. Commun.* pp. 839–840.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

JEANNIN, S., JEANNIN, Y. & LAVIGNE, G. (1978). *Inorg. Chem.* **17**, 2103–2110.

JOHNSON, B. F. G., LEWIS, J., PIPPARD, D. & RAITHBY, P. R. (1978). *Acta Cryst.* B**34**, 3767–3770.

JOHNSON, B. F. G., LEWIS, J., PIPPARD, D., RAITHBY, P. R., SHELDRICK, G. M. & ROUSE, K. D. (1979). *J. Chem. Soc. Dalton Trans.* pp. 616–618.

LARSON, A. C. & GABE, E. J. (1978). *Computing in Crystallography,* edited by H. SCHENK, R. OLTHOF-HAZEKAMP, H. VAN KONINGSVELD & G. C. BASSI, pp. 81–89. Delft Univ. Press.

LAVIGNE, G., LUGAN, N. & BONNET, J. J. (1982). *Acta Cryst.* B**38**, 1911–1916.

MEULENAER, J. DE & TOMPA, H. (1965). *Acta Cryst.* **19**, 1014–1018.

RAITHBY, P. R. (1980). *Transition Metal Clusters,* edited by B. F. G. JOHNSON, pp. 5–192. Chichester: John Wiley.

ROSENFIELD, R. E., TRUEBLOOD, K. N. & DUNITZ, J. D. (1978). *Acta Cryst.* A**34**, 828–829.

TELLER, R. G. & BAU, R. (1981). *Struct. Bonding (Berlin),* **44**, 1–82.

TRUEBLOOD, K. N. (1978). *Acta Cryst.* A**34**, 950–954.

WATKIN, D. J. & CARRUTHERS, J. R. (1981). *CRYSTALS User Guide.* Chemical Crystallography Laboratory, Univ. of Oxford, England.

WINTER, A., ZSOLNAI, L. & HUTTNER, G. (1982). *Chem. Ber.* **115**, 1286–1304.

Acta Cryst. (1986). C**42**, 793–796

Two New Ruthenium(II) Complexes involving Two Different Chelation Modes of Partially Chlorinated 2-(Benzylthio)azobenzene

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Abstract. Complex A, [RuCl($C_{19}H_{16}N_2S$)($C_{19}H_{14.75}Cl_{0.25}N_2S$)], mean $M_r = 752{\cdot}9$, triclinic, $P\bar{1}$, $a = 16{\cdot}116\,(3)$, $b = 10{\cdot}519\,(8)$, $c = 10{\cdot}416\,(4)$ Å, $\alpha = 74{\cdot}91\,(4)$, $\beta = 95{\cdot}19\,(2)$, $\gamma = 83{\cdot}44\,(3)°$, $V = 1680{\cdot}4$ Å^3, $Z = 2$, $D_x = 1{\cdot}49$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 6{\cdot}87$ cm^{-1}, $T = 295$ K, $F(000) = 768{\cdot}0$, $R = 0{\cdot}051$ for 3966 [$I > 2\sigma(I)$] reflections. Complex B, [Ru($C_{19}H_{15}N_2S$)($C_{19}H_{14.70}Cl_{0.30}N_2S$)], mean $M_r = 718{\cdot}2$, triclinic, $P\bar{1}$, $a = 9{\cdot}831\,(3)$, $b = 10{\cdot}217\,(2)$, $c = 16{\cdot}349\,(5)$ Å, $\alpha = 78{\cdot}81\,(2)$, $\beta = 77{\cdot}43\,(3)$, $\gamma = 88{\cdot}23\,(2)°$, $V = 1572{\cdot}2$ Å^3, $Z = 2$, $D_x = 1{\cdot}52$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 6{\cdot}47$ cm^{-1}, $T = 295$ K, $F(000) = 733{\cdot}6$, $R = 0{\cdot}061$ for 2901 [$I > 2\sigma(I)$] reflections. The metal coordination spheres are complex A $RuClCN_2S_2$ (N,N and S,S pairs are *cis–cis*); and complex B $RuC_2N_2S_2$ (N,N and S,S pairs *trans–cis*). Both coordination spheres are distorted octahedral. The Ru—C bond exerts a dominant *trans* effect. The N=N distances [1·272 (8)–1·300 (10) Å] suggest the presence of substantial Ru-azo π back bonding.

Introduction. Structural studies on ruthenium complexes of azo ligands have been sparse. The available data have revealed the presence of interesting features such as strong π back bonding (Seal & Ray, 1984) and unusual hydrogen bonding (Chakravarty, Chakravorty,

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