

STRUCTURAL STUDIES ON RUTHENIUM CARBONYL HYDRIDES

X *. CRYSTAL STRUCTURE OF $(\mu\text{-H})\text{Ru}_3(\text{CO})_{10}(\mu\text{-SEt})$

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Summary

The complex $(\mu\text{-H})\text{Ru}_3(\text{CO})_{10}(\mu\text{-SEt})$ crystallizes in the centrosymmetric orthorhombic space group *Pbca* (No. 61) with *a* 17.361(2), *b* 12.804(4), *c* 17.484(3) Å, *V* 3886.5(14) Å³ and *Z* = 8. Diffraction data (*Mo-K α* , $2\theta = 4.0\text{--}45.0^\circ$) were collected with a Syntex P2₁ automated diffractometer and the structure was solved and refined to *R* 5.9% for 1800 reflections with $|F_o| > 3\sigma(|F_o|)$ (*R* 4.1% for those 1413 reflections with $|F_o| > 6\sigma(|F_o|)$). The complex contains a triangular cluster of ruthenium atoms in which Ru(2) and Ru(3) are each linked to three terminal carbonyl ligands while Ru(1) is linked to four. Additionally Ru(2) and Ru(3) are bridged by a SEt ligand [Ru(2)–S 2.389(4), Ru(3)–S 2.391(4) Å and Ru(2)–S–Ru(3) 73.0(1)°] and a hydride ligand. The di-bridged Ru–Ru linkage (Ru(2)–Ru(3) 2.843(1) Å is slightly longer than the non-bridged bonds (Ru(1)–Ru(2) 2.831(2) and Ru(1)–Ru(3) 2.825(1) Å).

Introduction

We have for some time been concerned with the molecular geometry of polynuclear ruthenium carbonyl hydrides [1–9] and osmium carbonyl hydrides [10]. The chemistry of the osmium complexes is perhaps better developed, owing (at least in part) to the availability of the easily synthesized stable precursor $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$. A number of structural studies of complexes of the type $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-X})$ including those with X = Br [11], Cl [12], SEt [13], CHCH₂PMe₂Ph [14], CHCH=NEt₂ [15], NHSO₂(*p*-tol) [16], NHN=CPh₂ [17], N = N(*p*-tol) [18] and OMe [19] have been carried out. There have been far fewer structural studies of

* Ref. 1–9 should be considered to be previous parts of this series.

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simple (unsubstituted) $(\mu\text{-H})\text{Ru}_3(\text{CO})_{10}(\mu\text{-X})$ derivatives, although crystallographic studies of $(\mu\text{-H})\text{Ru}_3(\text{CO})_{10}(\mu\text{-CNMe}_2)$, [8], $(\mu\text{-H})\text{Ru}_3(\text{CO})_{10}(\mu\text{-COMe})$ [5] and $(\mu\text{-H})\text{Ru}_3(\text{CO})_{10}(\mu\text{-Br})$ [20] have previously appeared.

The complex $(\mu\text{-H})\text{Ru}_3(\text{CO})_{10}(\mu\text{-SEt})$ was initially synthesized in 1969 [21]. Although it has been reported to be isomorphous with $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-SEt})$ [13], no complete crystallographic study has appeared; furthermore, it should be noted that the structural study of $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-SEt})$ is, itself, of limited accuracy, with e.s.d.'s of $\sim 0.04\text{--}0.06$ Å on Os–C and $\sim 0.05\text{--}0.07$ Å on C–O distances.

We have therefore undertaken a single-crystal X-ray diffraction study on $(\mu\text{-H})\text{Ru}_3(\text{CO})_{10}(\mu\text{-SEt})$. Our results appear below.

Experimental

The sample used for the X-ray structural analysis was isolated as a byproduct during investigation of the reactions of $(\mu\text{-H})_3\text{Ru}_3(\mu_3\text{-CSEt})(\text{CO})_9$.

A plate-like orange-yellow crystal of approximate dimensions $0.30 \times 0.25 \times 0.03$ mm³ was selected for the crystallographic analysis. The crystal was mounted under nitrogen in a thin-walled glass capillary and was accurately aligned and centered on a Syntex P2₁ automated four-circle diffractometer. Set-up operations (i.e., de-

TABLE 1
EXPERIMENTAL DATA FOR THE X-RAY DIFFRACTION STUDY OF $(\mu\text{-H})\text{Ru}_3(\text{CO})_{10}(\mu\text{-SEt})$

(A) Crystallographic parameters at 21°C (294 K)

| | |
|---|---|
| Crystal system: orthorhombic | Formula: C ₁₂ H ₆ O ₁₀ Ru ₃ S |
| Space group: <i>Pbca</i> (<i>D</i> _{2h} ¹⁵ ; No. 61) | MW 645.5 |
| <i>a</i> 17.361(2) Å | <i>Z</i> = 8 |
| <i>b</i> 12.804(4) Å | <i>D</i> (calcd.) 2.21 g cm ⁻³ |
| <i>c</i> 17.484(3) Å | μ (Mo- <i>K</i> _α) 23.9 cm ⁻¹ |
| <i>V</i> 3886.5(14) Å ³ | |

(B) Collection of X-ray diffraction data

Diffractometer: Syntex P2₁

Radiation: Mo-*K*_α (λ 0.710730 Å)

Monochromator: highly orientated (pyrolytic) graphite, $2\theta_{\text{max}}$ 12.160° for 002 reflection, equatorial mode, assumed to be 50% perfect/50% ideally mosaic for polarization correction.

Reflections measured: + *h*, + *k*, + *l* for $2\theta = 4.0\text{--}45.0^\circ$; 2556 reflections measured and merged to 1800 unique data with $|F_0| > 3.0\sigma(|F_0|)$ (filename RUS1)

Scan type: coupled $\theta(\text{crystal})\text{--}2\theta(\text{counter})$

Scan width: $[2\theta(\text{Mo-}K_{\alpha_1})\text{--}0.9] \rightarrow [2\theta(\text{Mo-}K_{\alpha_2})\text{+}0.9]^\circ$

Scan speed: 4.0° min⁻¹

Background measurement: stationary-crystal and stationary counter at each end of the 2θ scan; each for one-half total scan time

Standards: 3 approximately mutually orthogonal check reflections were remeasured after each batch of 97 reflections; no significant fluctuations nor decay was observed.

Absorption correction: empirical (see text); min/max transmission factor = 0.751.

termination of accurate unit cell parameters, the crystal's orientation matrix, the Laue group and systematic absences) and data collection were carried out as described previously [22]; details appear in Table 1. The observed diffraction symmetry (D_{2h} , mmm) and systematic absences ($0kl$ for $k = 2n + 1$, $h0l$ for $l = 2n + 1$, $hk0$ for $h = 2n + 1$) uniquely indicated the centrosymmetric orthorhombic space group $Pbca$. Following data collection we collected ψ -scans of three reasonably intense close-to-axial reflections (at well spaced 2θ values) and used these to provide the basis for an empirical absorption correction (interpolating both in 2θ and ϕ) for all intensity data. The resulting unique data set was corrected for Lorentz and polarization factors and was converted to a set of approximately absolute $|F_0|$ values by means of a Wilson plot.

Solution and refinement of the structure

All calculations were performed on the SUNY-Buffalo modified version of the Syntax XTL system. The analytical form of the appropriate neutral atom scattering

TABLE 2
FINAL POSITIONAL PARAMETERS FOR THE $(\mu\text{-H})\text{Ru}_3(\text{CO})_{10}(\mu\text{-SEt})$ MOLECULE

| Atom | x | y | z | B_{iso} |
|-------|-------------|-------------|-------------|------------------|
| Ru(1) | 0.32931(6) | 0.30294(9) | 0.30325(7) | |
| Ru(2) | 0.40159(6) | 0.21511(9) | 0.43340(6) | |
| Ru(3) | 0.49016(6) | 0.26967(8) | 0.30262(6) | |
| S | 0.48265(19) | 0.36477(28) | 0.42008(19) | |
| O(11) | 0.31224(73) | 0.3908(11) | 0.14095(67) | |
| O(12) | 0.31209(61) | 0.07339(88) | 0.24631(72) | |
| O(13) | 0.35754(66) | 0.53042(91) | 0.35406(68) | |
| O(14) | 0.16269(62) | 0.2956(10) | 0.36117(71) | |
| O(21) | 0.28347(71) | 0.32301(89) | 0.53628(69) | |
| O(22) | 0.50142(78) | 0.1152(11) | 0.55740(65) | |
| O(23) | 0.30582(67) | 0.01573(94) | 0.42498(68) | |
| O(31) | 0.65449(63) | 0.1872(10) | 0.32087(69) | |
| O(32) | 0.46679(63) | 0.14370(86) | 0.15573(56) | |
| O(33) | 0.52296(80) | 0.46748(86) | 0.21272(62) | |
| C(1) | 0.57223(73) | 0.3474(11) | 0.47418(71) | |
| C(2) | 0.63163(77) | 0.4263(13) | 0.44798(78) | |
| C(11) | 0.31776(87) | 0.3570(13) | 0.2006(10) | |
| C(12) | 0.32129(85) | 0.1570(14) | 0.26783(88) | |
| C(13) | 0.34822(86) | 0.4463(13) | 0.34137(94) | |
| C(14) | 0.22356(86) | 0.3022(12) | 0.34014(91) | |
| C(21) | 0.32730(93) | 0.2831(11) | 0.49706(91) | |
| C(22) | 0.4667(10) | 0.1530(14) | 0.51120(92) | |
| C(23) | 0.33866(83) | 0.0928(12) | 0.42636(89) | |
| C(31) | 0.59446(78) | 0.2202(12) | 0.31542(66) | |
| C(32) | 0.47473(79) | 0.1880(11) | 0.20995(84) | |
| C(33) | 0.51273(84) | 0.3935(13) | 0.24533(82) | |
| H | 0.4445 | 0.1646 | 0.3499 | 6.0 |
| H(1A) | 0.5914 | 0.2788 | 0.4659 | 6.0 |
| H(1B) | 0.5622 | 0.3571 | 0.5271 | 6.0 |
| H(2A) | 0.6778 | 0.4169 | 0.4762 | 6.0 |
| H(2B) | 0.6125 | 0.4949 | 0.4562 | 6.0 |
| H(2C) | 0.6417 | 0.4166 | 0.3950 | 6.0 |

TABLE 3

FINAL ANISOTROPIC THERMAL PARAMETERS FOR $(\mu\text{-H})\text{Ru}_3(\text{CO})_{10}(\mu\text{-SEt})$

(These are in standard Syntex XTL format and enter the expression for the calculated structure factor in the form: $\exp[-\frac{1}{4}(h^2a^*{}^2B_{11} + \dots 2hka^*b^*B_{12} + \dots)]$.)

| Atom | B_{11} | B_{22} | B_{33} | B_{12} | B_{13} | B_{23} |
|-------|-----------|-----------|-----------|------------|------------|------------|
| Ru(1) | 2.895(49) | 3.375(55) | 4.045(56) | 0.379(43) | -0.512(45) | -0.772(52) |
| Ru(2) | 3.037(48) | 3.078(54) | 3.248(48) | -0.432(41) | 0.246(44) | -0.262(49) |
| Ru(3) | 2.795(46) | 2.768(50) | 2.954(46) | 0.014(40) | 0.131(40) | -0.202(45) |
| S | 3.19(16) | 3.29(17) | 3.49(16) | -0.57(13) | -0.01(13) | -0.33(14) |
| O(11) | 8.69(84) | 8.23(87) | 5.99(67) | 1.66(66) | -1.45(65) | 1.49(66) |
| O(12) | 5.72(63) | 4.12(56) | 8.67(74) | 0.48(50) | -1.31(55) | -2.92(59) |
| O(13) | 6.44(68) | 4.09(58) | 8.28(74) | 0.37(54) | -1.57(55) | -1.32(59) |
| O(14) | 3.24(50) | 9.29(87) | 10.05(83) | 0.08(58) | 1.12(56) | -3.78(72) |
| O(21) | 8.43(70) | 5.02(65) | 7.98(69) | 0.38(59) | 3.99(62) | -1.41(57) |
| O(22) | 10.10(91) | 8.25(85) | 5.89(68) | -0.65(70) | -2.66(65) | 2.66(65) |
| O(23) | 7.32(68) | 5.11(64) | 8.20(73) | -2.02(57) | 0.62(59) | -0.11(62) |
| O(31) | 3.74(54) | 8.84(81) | 9.19(80) | 1.82(56) | 0.41(56) | 0.40(70) |
| O(32) | 7.03(65) | 5.76(66) | 3.77(48) | -0.94(52) | 0.01(47) | -2.16(50) |
| O(33) | 12.8(10) | 3.82(57) | 5.83(64) | -2.26(63) | 0.68(66) | 0.83(51) |
| C(1) | 3.15(64) | 5.23(82) | 3.21(61) | -0.34(60) | 0.25(53) | 0.46(61) |
| C(2) | 2.85(63) | 7.4(10) | 4.69(78) | -0.87(68) | -1.09(60) | -0.52(76) |
| C(11) | 4.44(80) | 4.29(84) | 5.82(89) | 0.80(65) | 0.71(79) | -0.82(81) |
| C(12) | 4.05(78) | 6.0(10) | 4.85(83) | 0.65(76) | -0.57(65) | -0.94(78) |
| C(13) | 3.94(80) | 4.19(85) | 6.12(91) | -0.21(70) | -1.09(68) | 1.08(79) |
| C(14) | 3.66(75) | 4.54(84) | 6.66(86) | 0.99(70) | -0.02(69) | -1.88(75) |
| C(21) | 5.37(85) | 3.03(76) | 5.96(86) | -1.60(70) | 0.54(72) | -0.21(72) |
| C(22) | 6.3(10) | 5.8(10) | 4.71(84) | -3.50(82) | -0.47(74) | 0.98(79) |
| C(23) | 4.07(72) | 3.40(77) | 6.18(90) | -1.02(63) | 1.63(70) | -1.14(73) |
| C(31) | 3.05(62) | 5.04(81) | 3.00(57) | -0.20(60) | 0.45(57) | -1.47(64) |
| C(32) | 3.90(69) | 3.17(71) | 4.83(80) | 1.33(58) | -0.18(63) | 1.00(64) |
| C(33) | 4.45(77) | 4.91(84) | 2.92(61) | 0.92(70) | 0.52(59) | -0.84(66) |

factor was corrected for both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion [23]. The function minimized during least-squares refinement was $\Sigma w(|F_0| - |F_c|)^2$, where $w = [(\sigma|F_0|)^2 + (0.02|F_0|)^2]^{-1}$.

The structure was readily solved using direct methods (MULTAN). The positions of the three ruthenium atoms were located from an E -map. All remaining non-hydrogen atoms were located from a series of difference-Fourier syntheses. The model was refined by full-matrix least-squares techniques using anisotropic thermal parameters for all non-hydrogen atoms. Convergence (with $\Delta/\sigma < 0.05$ for all parameters) was achieved with $R_F = 5.9\%$, $R_{wF} = 5.2\%$ and GOF = 1.27 for 1800 reflections with $|F_0| > 3.0\sigma(|F_0|)$ refined against 235 variables (R_F 4.1%, R_{wF} 4.3% for those 1413 reflections with $|F_0| > 6.0\sigma(|F_0|)$). The μ -hydride was included in a calculated position 1.76 Å from each ruthenium atom, while the other (organic) hydrogen atoms were placed in calculated positions of the appropriate idealized geometry with $d(\text{C-H})$ 0.95 Å [24].

Final positional and thermal parameters are collected in Tables 2 and 3.

Description of the structure

The crystal consists of discrete molecule units of $(\mu\text{-H})\text{Ru}_3(\text{CO})_{10}(\mu\text{-SEt})$ which are mutually separated by normal Van der Waals' distances; there are no unusually

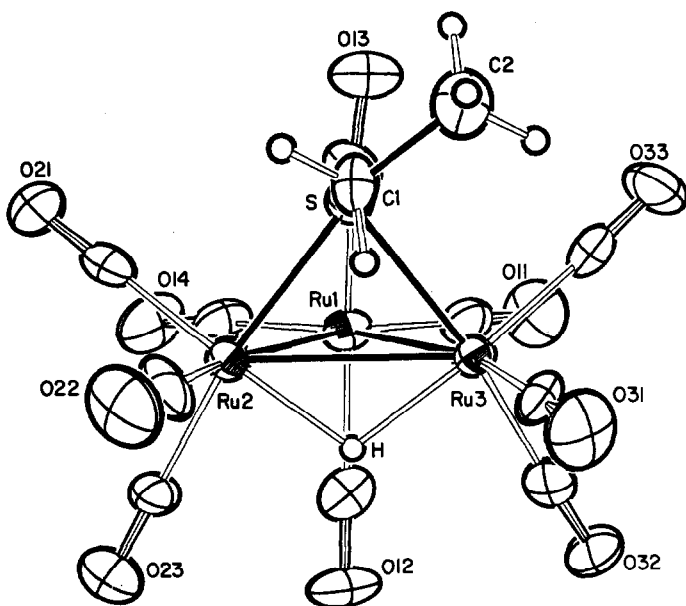


Fig. 1. Labelling of atoms in the $(\mu\text{-H})\text{Ru}_3(\text{CO})_{10}(\mu\text{-SEt})$ molecule. [ORTEP-II diagram, with all hydrogen atoms in calculated positions.] Carbon atoms of the carbonyl groups are labelled with the same number as the attached oxygen. Note the C_s symmetry of the $(\mu\text{-H})\text{Ru}_3(\text{CO})_{10}[\mu\text{-S-C}(1)]$ portion of the molecule.

short intermolecular contacts. The overall molecular geometry and the scheme used for labelling atoms are illustrated in Fig. 1. A stereoscopic view of the $(\mu\text{-H})\text{Ru}_3(\text{CO})_{10}(\mu\text{-SEt})$ molecule is provided by Fig. 2. Interatomic distances and angles are collected in Tables 4 and 5.

The $(\mu\text{-H})\text{Ru}_3(\text{CO})_{10}(\mu\text{-SEt})$ molecule contains a triangular array of ruthenium atoms. Ru(2) and Ru(3) are each linked to three terminal carbonyl ligands while Ru(1) is linked to four. Ru(2) and Ru(3) are additionally bridged by a SEt ligand

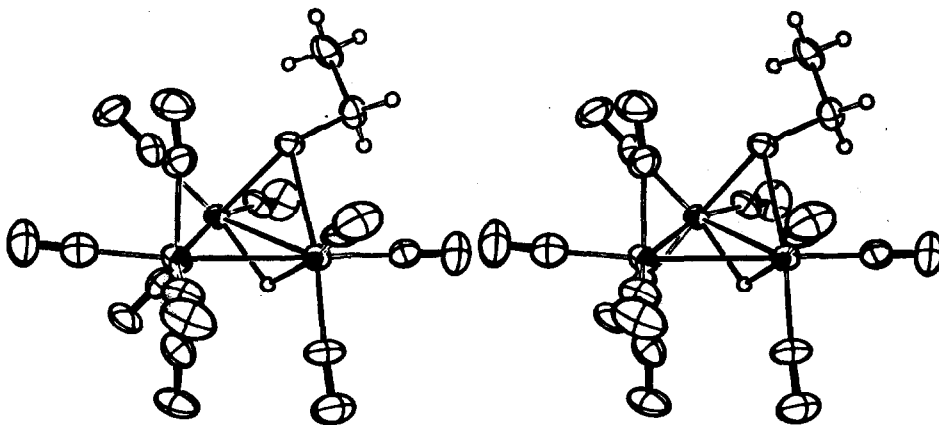


Fig. 2. A stereoscopic view of the $(\mu\text{-H})\text{Ru}_3(\text{CO})_{10}(\mu\text{-SEt})$ molecule.

TABLE 4
 INTERATOMIC DISTANCES (Å) FOR $(\mu\text{-H})\text{Ru}_3(\text{CO})_{10}(\mu\text{-SEt})$

| <i>Ruthenium-ruthenium and ruthenium-sulfur distances</i> | | | |
|---|-----------|-------------|-----------|
| Ru(1)-Ru(2) | 2.831(2) | Ru(2)-S | 2.389(4) |
| Ru(1)-Ru(3) | 2.825(1) | Ru(3)-S | 2.391(4) |
| Ru(2)-Ru(3) | 2.843(1) | | |
| <i>Ru-Co and C-O distances</i> | | | |
| Ru(1)-C(11) | 1.934(17) | C(11)-O(11) | 1.133(21) |
| Ru(1)-C(12) | 1.974(18) | C(12)-O(12) | 1.145(21) |
| Ru(1)-C(13) | 1.980(17) | C(13)-O(13) | 1.111(21) |
| Ru(1)-C(14) | 1.946(15) | C(14)-O(14) | 1.122(19) |
| Ru(2)-C(21) | 1.913(16) | C(21)-O(21) | 1.145(20) |
| Ru(2)-C(22) | 1.940(17) | C(22)-O(22) | 1.117(21) |
| Ru(2)-C(23) | 1.913(15) | C(23)-O(23) | 1.141(19) |
| Ru(3)-C(31) | 1.931(14) | C(31)-O(31) | 1.128(18) |
| Ru(3)-C(32) | 1.947(15) | C(32)-O(32) | 1.113(18) |
| Ru(3)-C(33) | 1.916(16) | C(33)-O(33) | 1.119(19) |
| <i>S-C and C-C distances within the SEt ligand</i> | | | |
| S-C(1) | 1.834(13) | C(1)-C(2) | 1.515(20) |

and by a hydride ligand. Although the bridging hydride ligand was not unequivocally located directly, its approximate position (*trans* to both C(21)-O(21) and C(33)-O(33)) is known definitively by analogy with other $(\mu\text{-H})\text{M}_3(\text{CO})_{10}(\mu\text{-X})$ (M = Ru, Os) systems.

The di-bridged Ru-Ru linkage (Ru(2)-Ru(3) 2.843(1) Å) is slightly longer than the non-bridged Ru-Ru bonds (Ru(1)-Ru(2) 2.831(2) and Ru(1)-Ru(3) 2.825(1); average 2.828 Å). [A similar pattern is found in $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-SEt})$, with Os-Os(di-bridged) = 2.863(2) Å as compared to Os-Os (nonbridged) 2.856(2) and 2.842(2) Å.]

The $\mu\text{-SEt}$ ligand is associated with ruthenium-sulfur distances of Ru(2)-S 2.389(4) and Ru(3)-S 2.391(4) Å and with an acute Ru(2)-S-Ru(3) angle of 73.0(1)°. The Ru(2)-S-Ru(3) plane makes an angle of 103.64° with the Ru(1)-Ru(2)-Ru(3) plane (see Table 6).

The $(\mu\text{-H})\text{Ru}_3(\text{CO})_{10}(\mu\text{-SC})$ portion of the molecule has almost precise $C_s(m)$ symmetry. Possible full molecular C_s symmetry is broken by the orientation of the Et

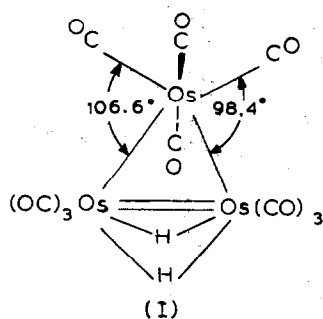


TABLE 5
 INTERATOMIC ANGLES (°) FOR $(\mu\text{-H})\text{Ru}_3(\text{CO})_{10}(\mu\text{-SEt})$

| | | | |
|--|----------|-------------------|-----------|
| <i>Angles within the $\text{Ru}_3(\mu\text{-S})$ system</i> | | | |
| Ru(3)–Ru(1)–Ru(2) | 60.34(4) | Ru(1)–Ru(2)–S | 82.2(1) |
| Ru(1)–Ru(2)–Ru(3) | 59.72(4) | Ru(3)–Ru(2)–S | 53.6(1) |
| Ru(2)–Ru(3)–Ru(1) | 59.94(4) | Ru(1)–Ru(3)–S | 82.3(1) |
| Ru(2)–S–Ru(3) | 73.0(1) | Ru(2)–Ru(3)–S | 53.5(1) |
| <i>Ru–Ru–CO angles</i> | | | |
| Ru(2)–Ru(1)–C(11) | 159.1(5) | Ru(3)–Ru(1)–C(11) | 98.8(5) |
| Ru(2)–Ru(1)–C(12) | 84.7(5) | Ru(3)–Ru(1)–C(12) | 85.7(5) |
| Ru(2)–Ru(1)–C(13) | 91.4(5) | Ru(3)–Ru(1)–C(13) | 88.7(5) |
| Ru(2)–Ru(1)–C(14) | 98.6(5) | Ru(3)–Ru(1)–C(14) | 159.0(5) |
| Ru(1)–Ru(2)–C(21) | 89.3(5) | Ru(1)–Ru(3)–C(31) | 167.4(4) |
| Ru(1)–Ru(2)–C(22) | 170.0(5) | Ru(1)–Ru(3)–C(32) | 87.0(4) |
| Ru(1)–Ru(2)–C(23) | 91.2(5) | Ru(1)–Ru(3)–C(33) | 94.6(5) |
| Ru(3)–Ru(2)–C(21) | 136.1(5) | Ru(2)–Ru(3)–C(31) | 109.5(4) |
| Ru(3)–Ru(2)–C(22) | 110.5(5) | Ru(2)–Ru(3)–C(32) | 117.6(4) |
| Ru(3)–Ru(2)–C(23) | 117.3(5) | Ru(2)–Ru(3)–C(33) | 137.3(5) |
| <i>OC–Ru–CO and Ru–C–O angles</i> | | | |
| C(11)–Ru(1)–C(12) | 92.3(7) | Ru(1)–C(11)–O(11) | 178.2(15) |
| C(11)–Ru(1)–C(13) | 89.9(7) | Ru(1)–C(12)–O(12) | 175.9(14) |
| C(11)–Ru(1)–C(14) | 102.2(7) | Ru(1)–C(13)–O(13) | 171.7(14) |
| C(12)–Ru(1)–C(13) | 174.3(7) | Ru(1)–C(14)–O(14) | 176.0(14) |
| C(12)–Ru(1)–C(14) | 91.9(7) | Ru(2)–C(21)–O(21) | 178.8(14) |
| C(13)–Ru(1)–C(14) | 92.8(7) | Ru(2)–C(22)–O(22) | 176.9(15) |
| C(21)–Ru(2)–C(22) | 99.9(7) | Ru(2)–C(23)–O(23) | 174.5(14) |
| C(21)–Ru(2)–C(23) | 91.4(7) | Ru(3)–C(31)–O(31) | 176.7(12) |
| C(22)–Ru(2)–C(23) | 92.4(7) | Ru(3)–C(32)–O(32) | 177.9(13) |
| C(31)–Ru(3)–C(32) | 92.8(6) | Ru(3)–C(33)–O(33) | 177.1(14) |
| C(31)–Ru(3)–C(33) | 98.1(6) | | |
| C(32)–Ru(3)–C(33) | 92.2(6) | | |
| <i>OC–Ru–S angles</i> | | | |
| C(21)–Ru(2)–S | 95.1(5) | C(31)–Ru(3)–S | 96.8(4) |
| C(22)–Ru(2)–S | 93.1(5) | C(32)–Ru(3)–S | 168.8(4) |
| C(23)–Ru(2)–S | 170.6(5) | C(33)–Ru(3)–S | 92.2(5) |
| <i>Angles involving the SC_2H_5 ligand</i> | | | |
| Ru(2)–S–C(1) | 110.6(4) | S–C(1)–C(2) | 109.9(9) |
| Ru(3)–S–C(1) | 109.6(4) | | |

portion of the $\mu\text{-SEt}$ ligand. Even the equatorial carbonyl ligands are arranged according to strict C_s symmetry, with Ru(2)–Ru(1)–C(14) 98.6(5)° and Ru(3)–Ru(1)–C(11) 98.8(5)°, and with Ru(3)–Ru(2)–C(22) 110.5(5)° and Ru(2)–Ru(3)–C(31) 109.5(4)°. Contrary to one's expectation, this is not always the case. Thus, in $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ [25] the equatorial Os–Os–CO angles at the Os(CO)₄ group vary by 8.2° (see I).

The equatorial carbonyl ligands are all displaced from the triruthenium plane in a direction away from the $\mu\text{-SEt}$ ligand; the smallest displacements for carbon atoms of the CO groups are 0.026(16) for C(14) and 0.067(16) Å for C(11); the largest such displacement is 0.241(14) Å for C(31) (see Table 6).

The individual Ru–CO distances range from 1.913(15) through 1.980(17) Å. The

TABLE 6

IMPORTANT MOLECULAR PLANES AND ATOMIC DEVIATIONS THEREFROM (Å) FOR $(\mu\text{-H})\text{Ru}_3(\text{CO})_{10}(\mu\text{-SEt})$

| <i>The triruthenium plane</i> | | | |
|---|------------|-------|------------|
| $-0.1412X - 0.9162Y - 0.3749Z + 6.3490 = 0$ | | | |
| Ru(1)* | 0.000 | O(14) | 0.115(13) |
| Ru(2)* | 0.000 | C(21) | -1.033(15) |
| Ru(3)* | 0.000 | O(21) | -1.651(12) |
| S | -1.867(4) | C(22) | 0.059(17) |
| C(1) | -2.238(14) | O(22) | 0.115(14) |
| C(2) | -3.138(16) | C(23) | 1.634(16) |
| C(11) | 0.067(16) | O(23) | 2.629(12) |
| O(11) | 0.075(14) | C(31) | 0.241(14) |
| C(12) | 1.964(18) | O(31) | 0.445(13) |
| O(12) | 3.108(11) | C(32) | 1.604(15) |
| C(13) | -1.978(17) | O(32) | 2.498(11) |
| O(13) | -3.071(12) | C(33) | -1.133(16) |
| C(14) | 0.026(16) | O(33) | -1.812(11) |
| <i>The Ru(2)-S-Ru(3) plane</i> | | | |
| $-0.7724X + 0.5236Y - 0.3595Z + 6.6671 = 0$ | | | |
| Ru(2)* | 0.000 | Ru(1) | 2.376(1) |
| Ru(3)* | 0.000 | C(1) | -1.658(13) |
| S* | 0.000 | C(2) | -1.761(15) |
| <i>Dihedral angle</i> | | | |
| Plane A/B | 103.64° | | |

longest Ru-CO bond lengths are for the mutually *trans* Ru(1)-C(12) and Ru(1)-C(13) bonds (1.974(18) and 1.980(17) Å, respectively); the shortest pair of Ru-CO bonds are those *trans* to the μ -hydride ligand (Ru(2)-C(21) 1.913(16) and Ru(3)-C(33) 1.916(16) Å). These results are in keeping with the normally accepted

TABLE 7

BOND LENGTHS (Å) AND ANGLES (deg.) WITHIN $(\mu\text{-H})\text{Ru}_3(\text{CO})_{10}(\mu\text{-X})$ SPECIES

| X | $d(\text{Ru-X})$ | $\angle \text{Ru-X-Ru}$ | $d(\text{Ru-Ru})$ (bridged) | $d(\text{Ru-Ru})$ (non-bridged) | Δ^a |
|-------------------------------|----------------------|-------------------------|--------------------------------|------------------------------------|------------|
| COMe | 1.978(4) 1.991(4) | 90.62(17) | 2.821(1) | 2.816(1) 2.838(1) | -0.006 |
| CNMe ₂ (mol. 1) | 2.039(4) 2.018(4) | 87.27(17) | 2.7997(5) | 2.8288(6) 2.8279(5) | -0.0287 |
| CNMe ₂ (mol. 2) | 2.034(5) 2.037(5) | 87.98(17) | 2.8016(6) | 2.8336(6) 2.8216(6) | -0.026 |
| SEt | 2.389(4) 2.391(4) | 73.0(1) | 2.843(1) | 2.831(2) 2.825(1) | +0.015 |
| Br (mol. A) | 2.559(2) 2.561(2) | 66.80(5) | 2.819(1) | 2.813(1) 2.802(1) | +0.0115 |
| Br (mol. B) | 2.571(2) 2.574(1) | 66.42(4) | 2.818(1) | 2.816(1) 2.811(1) | +0.0045 |

^a $\Delta = d(\text{Ru-Ru, bridged}) - \text{average } d(\text{Ru-Ru, non-bridged})$.

mode of bonding in M–CO linkages, which contains a significant component of $d_{\pi}-\pi^*(\text{CO})$ back donation. All C–O distances lie in the range 1.111(21)–1.145(20) Å.

As Kaesz and coworkers have pointed out previously [20], the geometry of these $(\mu\text{-H})\text{Ru}_3(\text{CO})_{10}(\mu\text{-X})$ species is more easily described if one ignores the direct metal–metal interaction in the di-bridged Ru–Ru bond. The molecule can then be described as containing three octahedrally coordinated ruthenium atoms. In keeping with this we have the *trans* angles C(23)–Ru(2)–S 170.6(5) and C(32)–Ru(3)–S 168.8(4)° to the $\mu\text{-SEt}$ ligand.

Table 7 compares molecular parameters for various $(\mu\text{-H})\text{Ru}_3(\text{CO})_{10}(\mu\text{-X})$ species (X = CNMe₂ [8], COMe [5], SEt and Br [20]). As can quickly be seen, increasing Ru–X distance is associated with decreasing Ru–X–Ru angle; the di-bridged Ru–Ru distance is fairly constant and the parameter Δ (defined in Table 7) increases only slowly with the covalent radius of the bridgehead atom of X.

Additional Material. A table of observed and calculated structure factor amplitudes is available on request from M.R.C.

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