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SYNTHESIS, SPECTROSCOPIC CHARACTERIZATION AND CRYSTAL AND MOLECULAR STRUCTURE OF μ-(DIMETHYLSTANNADO)-μ-(HYDRIDO)DODECACARBONYLTRIRHENIUM *,**

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Summary

The title compound, $Re_3(\mu\text{-H})(\mu\text{-SnMe}_2)(CO)_{12}$ (I) prepared by treatment of $[(C_6H_5)As]_2[Re_3(\mu\text{-H})(CO)_{12}] \cdot \frac{1}{2} C_4H_8O$ (II) with $(CH_3)_2SnCl_2$ or $(CH_3)_3$-SnCl, has been characterized by IR, Raman, ^{1}H NMR and mass spectra. An absorption due to bridging hydrogen in I has been identified in the Raman at 1680 ($\Delta\nu_{1/2}$ ~ 110) cm^{-1}; this is replaced by an absorption at 1185 ($\Delta\nu_{1/2}$ ~50) cm^{-1} in the deuterated derivative $Re_3(\mu\text{-D})(\mu\text{-SnMe}_2)(CO)_{12}$ (I-d_1).

The crystal and molecular structure of I has been determined by a three-dimensional X-ray diffraction study. The compound crystallizes in the form of yellow-orange platelets in the centrosymmetric space group $P2_1/c$ (C^5_{2h}, No. 14) with a 16.929(5) Å, b 16.968(9) Å, c 16.699(4) Å, $\beta = 114.80(2)°$; $Z = 8$, ρ_{calc} 3.187 and ρ_{obs} 3.19(1) g cm^{-3}. Diffraction data to $2\theta_{max} = 45°$ (Mo-K_α radiation) were collected on a Picker FACS-1 diffractometer equipped with a graphite monochromator. The structure has been solved using direct methods, Fourier, and full-matrix least-squares refinement techniques. The final discrepancy index is $R_F = 0.066$ for 4366 independent observed reflections. The asymmetric unit contains two similar crystallographically independent molecules, and, in each, the three rhenium atoms define an approximately equilateral triangle with the tin atom asymmetrically bridging one edge and essentially coplanar with the Re_3 triangle; Sn—Re(2) 2.87 Å and Sn—Re(3) 2.68 Å. The Me_2Sn-bridged Re—Re distance is 3.15 Å. Each rhenium atom is associated with four terminal carbonyl ligands, of which two can be considered axial and two equatorial. Indirect evidence implies that the hydrido—hydrogen atom bridges the longest Re—Re edge (3.23 Å). The remaining Re—Re distance is 3.01 Å.

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* Taken in part from the dissertations of S.W. Kirtley [1a] and B.T. Huie [1b], preliminary account of the structure study [1c].

** Dedicated to the memory of Professor Paolo Chini.

Introduction

Following our interest in the chemistry of $[Re_3(\mu\text{-}H)(CO)_{12}]^{2-}$ [1a,2] and the well established tendency of transition metals to form robust complexes containing metal—metal bonds to main Group IV elements, especially tin, [3] we were led to attempt the reaction of appropriate salts of the trirhenium dianion with the organotin halides $(CH_3)_2SnCl_2$ and $(CH_3)_3SnCl$. These both yielded, though not in a straightforward manner, the title compound I, in which two of the hydrogen atoms (each bridging a separate side of the Re_3 triangle) of the parent compound $Re_3(\mu\text{-}H)_3(CO)_{12}$ are replaced by a $(CH_3)_2Sn$ group *. Characterization of the product including a structure determination were undertaken to ascertain the consequences of the above-mentioned substitution.

Results

Synthesis

To an acetone solution of $[(C_6H_5)_4As]_2[Re_3(\mu\text{-}H)(CO)_{12}] \cdot \frac{1}{2} C_4H_8O$ (II) [1a] a quantity of solid $(CH_3)_2SnCl_2$ was added resulting in a gradual change of color from deep red to yellow green as the organotin halide dissolved and reacted. A precipitate of one equivalent of Ph_4AsCl is obtained at this point. Work-up of the solution leads to a green oil, insoluble in non-polar solvents. The oil was washed with aliquots of cold ethanol and CCl_4 to remove excess organotin halide and any remaining traces of Ph_4AsCl. Attempts to crystallize the remaining liquid proved unsuccessful. Spectroscopic data on the intermediate oil indicated four principal absorptions in the carbonyl stretching region of the infrared (acetone solution) accompanied by three weaker features [1a] (cm^{-1}): 2096w, 2054s, 2014w (sh), 2004s, 1967s, 1931s, 1908w. ^1H NMR in CD_2Cl_2 solution indicated two principal peaks attributable to phenyl protons of $[Ph_4As]^+$ and to methyl groups on tin (τ 9.22 ppm). Several other minor resonances were observed in the region τ 6 to 10 ppm indicating the substance was not pure and also obscuring the ^{117}Sn and ^{119}Sn satellites of the peak at τ 9.22 ppm. Among the minor peaks the characteristic absorptions of THF introduced as solvent of crystallization of II could also be discerned. At τ 26.02 ppm a sharp singlet was observed indicating hydrogen on a metal cluster. The infrared spectrum of the neat oil as a thin film was obtained in the region 4000—400 cm^{-1}. This contained no significant information other than confirmation of the characteristic absorptions for the groups identified in the ^1H NMR. Attempts to extract the oil with cyclohexane at elevated temperature (ca. 40—50°C) led to isolation of $Re_2(\mu\text{-}H)(\mu\text{-}Cl)(CO)_8$ [5] in approximately 20% yield [1a]. From these data we surmised that the green oil represented in the main some intermediate ionic substance, possibly $[Ph_4As][Re_3(\mu\text{-}H)(CO)_{12} \cdot SnMe_2Cl]$ arising from incomplete displacement of halogen on tin.

We were thus led to attempt the reaction of II with $(CH_3)_3SnCl$ in order to

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* Single crystals of $Re_3(\mu\text{-}H)_3(CO)_{12}$ have thus far eluded us. For a structure determination of the manganese analog. $Mn_3(\mu\text{-}H)_3(CO)_{12}$ see ref. [4c].

produce an intermediate containing an $SnMe_3$ group (i.e. without a hydrolyzable halogen on tin) so that through acidification we might isolate some neutral cluster complex. Accordingly the second synthesis was attempted leading to a second green intermediate oil. This displayed maxima in the carbonyl region (acetone solution, cm^{-1}): 2088w, 2047s, 1995vs, 1953s, 1924s, 1912w, slightly shifted from those observed in the intermediate of the previous reaction. ^1H NMR indicated a sharp singlet at τ 9.69 ppm due to methyl groups in tin whose ^{117}Sn and ^{119}Sn satellites could clearly be seen surrounding the peak at the appropriate relative intensities. These were not well resolved from each other and displayed an average $J(CH_3—Sn)$ of 44 Hz, a value decidedly on the low side of the range observed for organotin derivatives [6], tending towards values observed for methyltin anions (cf. $J(CH_3—Sn)$ 14 Hz in Me_3SnLi [6]). Peaks due to $[Ph_4As]^+$ as well as cluster hydrogen (τ 26.3 ppm) were [illegible] observed, as were those due to the small amount of THF present in the starting material (II). IR spectrum of a thin film of the neat oil in the range 4000—400 cm^{-1} yielded no significant information beyond confirmation of the groups mentioned above. From these data we postulate constitution of the second intermediate oil as $[Ph_4As][Re_3(\mu\text{-}H)(CO)_{12}\cdot SnMe_3]$. This material did not yield any $Re_2(\mu\text{-}H)(\mu\text{-}Cl)(CO)_8$ upon warming in cyclohexane.

Treatment with aqueous H_3PO_4 and extraction with cyclohexane yielded an orange solid. Recrystallization from CH_2Cl_2 yielded the title compound (I), identified as described below; yield about 15% based on II. Transformation of a trimethyltin starting material into a dimethyltin product parallels the report by Loffredo and Norman [7] of the preparation of dimethylgerma- and dimethylstanna-undecacarboranes in the reaction of $NaB_{10}H_{13}$ with trimethylgermanium or trimethyltin chlorides [7].

Hydrolysis of the green oil isolated from the reaction of II with Me_2SnCl_2 also gives the title compound (I) in somewhat better yield (25%).

Spectroscopic characterization of I

The mass spectrum of a solid sample of I was obtained at 135° C probe temperature and ionizing voltage of 70 eV. The overall spectrum and assignment of multiplets is given in Fig. 1. The average of several scans of the parent ion multiplet together with the calculated intensities are given in Fig. 2 [8]. These data support the molecular formula as indicated for the title compound I.

^1H NMR in CH_2Cl_2 solution showed two principal resonances: a singlet at τ 8.8 ppm due to methyl groups on tin, surrounded by unresolved satellites due to ^{117}Sn and ^{119}Sn ($J(CH_3—Sn)$ 41 Hz). This is on the low side of the range usually observed for this coupling in alkyltin derivatives (50—55 Hz) [6]. Integration of the principal peaks by planimeter, and normalizing to include the satellite peaks, gives a ratio of 5.85 (±0.3)/1, within satisfactory experimental error (including possible differences in T_1 for the different types of protons) of the theoretical ratio of 6/1.

Infrared spectrum in the carbonyl stretching region is shown in Fig. 3; the observed maxima are listed in the caption to that figure. At least ten maxima can be discerned indicating a species of low symmetry. A scan of the region 4000—500 cm^{-1} for a KBr pellet gives no significant information beyond confirmation of the carbonyl stretching modes (off scale), medium peaks in the

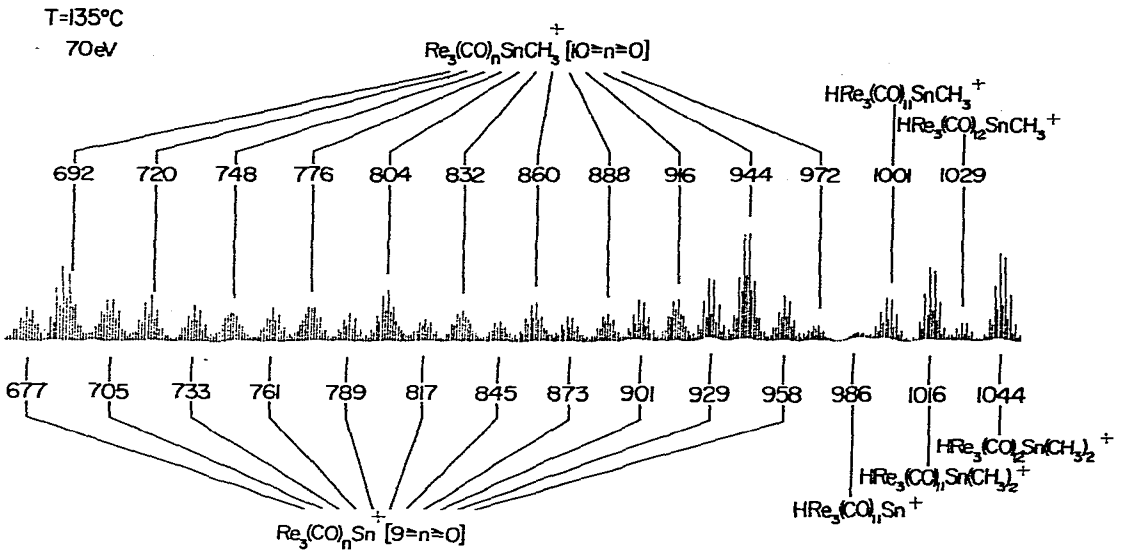

Fig. 1. Mass spectrum and assignment of multiplets for I.

carbonyl deformation region (ca. 600 cm^{-1}) and weak C—H stretching modes due to the CH_3 groups. Raman spectra were obtained for solid samples of I and its deuterated derivative I-d_1 (synthesized from $[Ph_4As]_2[Re_3(\mu\text{-}D)(CO)_{12}]$ [1a] and the appropriate tin halide); the scans for the regions 2200—1100 and 700—300 cm^{-1} are shown in Fig. 4. In addition, a strong CH stretching absorption is

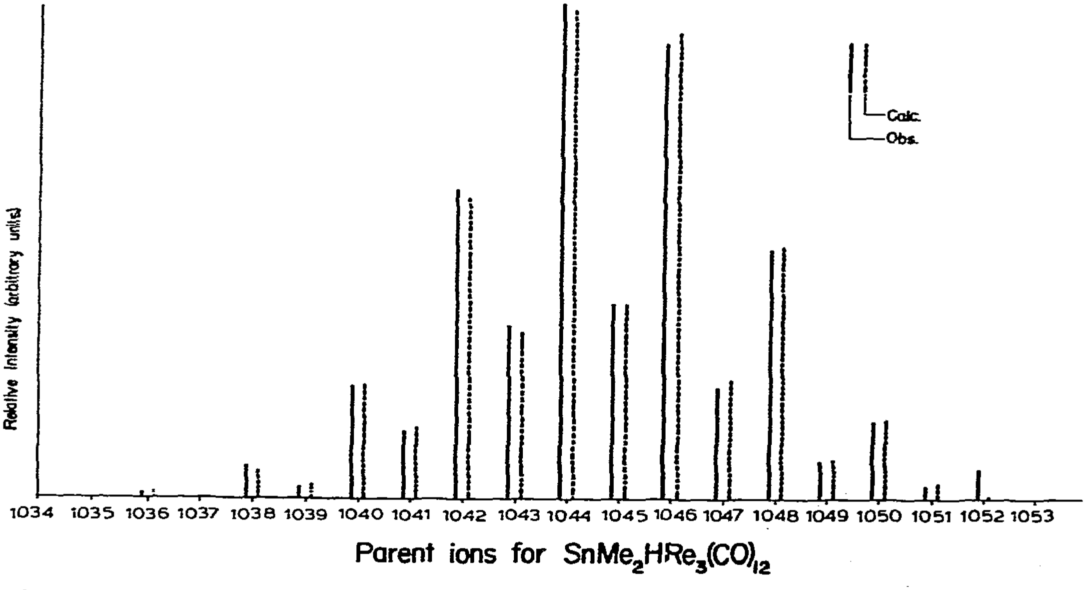

Fig. 2. Calculated [8] and observed intensities for the parent ion multiplet in the mass spectrum of I.

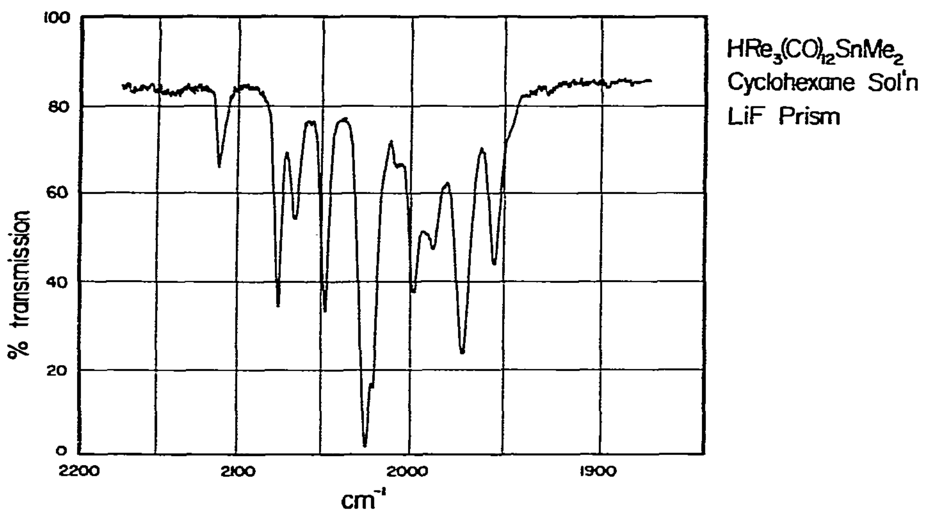

Fig. 3. Infrared absorptions in the carbonyl region for I, cyclohexane solution, Beckman IR4, LiF prism. The maxima are as follows (cm^{-1}): 2112w, 2077m, 2067w, 2048m, 2028vs, 2023(sh), 2007vs, 1995m, 1984m, 1972s, 1953m.

observed at 2910 cm^{-1} accompanied by medium absorptions at 1181 and 1189 cm^{-1} associated with the methyl groups on tin, identical to Raman absorptions in $(CH_3)_2SnCl_2$. In these absorptions and those associated with the carbonyl stretching modes (2100—1800 cm^{-1}) and carbonyl deformation and carbon—metal stretching modes (700—300 cm^{-1}) there is essentially no change between I and I-d_1. By contrast, however, a broad absorption is observed for I, centered at 1680 ($\Delta\nu_{1/2}$ 110) cm^{-1} which disappears in I-d_1 and is replaced by a slightly

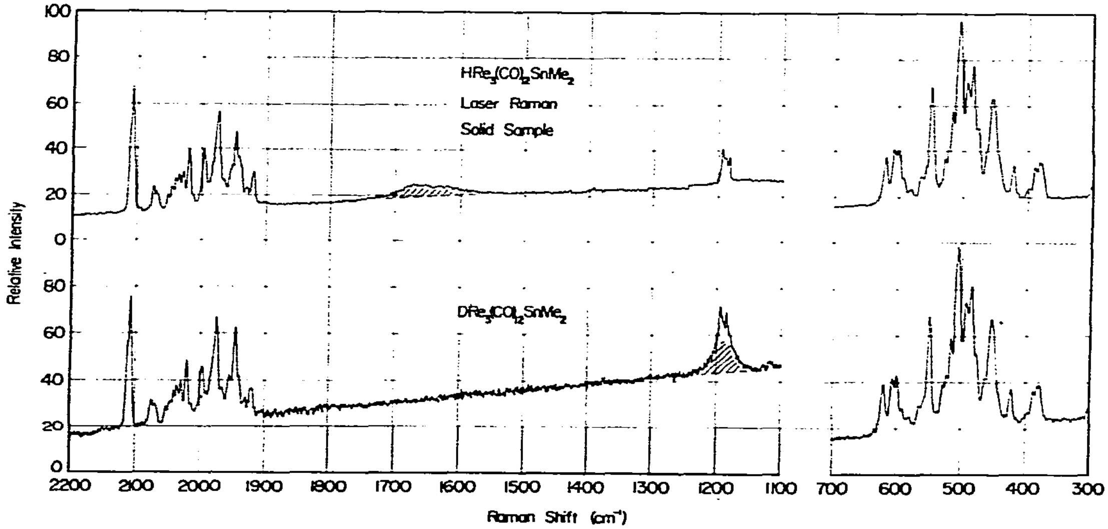

Fig. 4. Raman spectra for powder samples of I (top scan) and I-d_1, lower trace.

less broad feature centered at 1186 ($\Delta\nu_{1/2}$ ~50) cm^{-1}, accidentally coincident with the afore-mentioned CH_3 deformation modes. From the behavior both in the change in band position $\nu(Re—H)/\nu(Re—D) = 1.42$, as well as in the narrowing of line width in going to the deuterium derivative, we can assign this absorption as due unequivocally to hydrogen bridging an edge of the metal cluster [9]. It is however higher than that observed for most bridging hydrogen modes (1100—800 cm^{-1}) [9] which indicates departure from a position equidistant or nearly so with the two metal atoms: the position of the absorption approaches the region associated with terminal M—H stretching modes (2100—1800 cm^{-1}) [9]. A structure containing potentially interesting features was thus indicated and a X-ray study undertaken, as described below.

Experimental

All manipulations were performed under an atmosphere of nitrogen. Solvents were dried and freed from dissolved oxygen, where compatible, by distillation from calcium hydride or by treatment with molecular sieves accompanied by the bubbling of dry nitrogen through a glass frit for 15 to 20 minutes. The organotin halides were purchased from M&T Chemicals and resublimed before use. $Re_2(CO)_{10}$ was purchased from Strem Chemical Co. and utilized without further purification.

Mass spectra were obtained on an AEI-MS9 spectrometer with direct solid sampling probe. IR spectra in the carbonyl stretching region were obtained on a Beckman IR-4 spectrophotometer equipped with LiF prism. Spectra were calibrated against the reference cyclohexane absorption at 2138.5 cm^{-1} or against the water absorption at 1988.5 cm^{-1}. Spectra in the region 4000—500 cm^{-1} were obtained on a Perkin—Elmer 421 Grating spectrophotometer. NMR spectra were obtained at ambient temperature on a Varian A-60D; ppm were measured using tetramethylsilane ($\tau = 10$) as a reference. Raman spectra were obtained on a Cary 81 spectrophotometer equipped with a Spectra-Physics 125 He/Ne laser with an exciting line at 15 803 cm^{-1}, using finely ground solid samples in a parabolic solid sample holder.

Preparation of $[(C_6H_5)_4As]_2[Re_3(\mu\text{-}H)(CO)_{12}] \cdot \frac{1}{2} C_4H_6O$ *(II)*

This compound, first isolated by Fontal [2a] is obtained in a manner analogous to that of salts of $[Re_4(\mu\text{-}H)_6(CO)_{12}]^{2-}$ [10] the primary difference being the reaction time. A slightly improved preparation was developed for this work.

Dirhenium decacarbonyl (5.1 g, 7.7 mmol) is refluxed for 4 h under N_2 in tetrahydrofuran (air free, distilled from CaH_2) with an excess of sodium borohydride (1.25 g, 33 mmol). The initially colorless solution gradually turns yellow and finally red. The borate salts and excess $NaBH_4$ are allowed to settle, and the limpid tetrahydrofuran solution is syringed off under nitrogen. Tetraphenylarsonium chloride (2.0 g, 63 mmol), dried under vacuum for 24 h at 120°C and dissolved in 10 ml of ethanol (dried over molecular sieves, air free) is added to the tetrahydrofuran solution. The mixture, which immediately becomes cloudy, is allowed to stand for several hours and then placed in the refrigerator (—5°C) overnight to aid the formation of red crystals. The solution is syringed off and the crystals washed with cold EtOH; yield (after vacuum drying) 2.0 g (30% based on $Re_2(CO)_{10}$).

The salt is soluble in tetrahydrofuran, dichloromethane, acetonitrile, nitromethane, acetone and somewhat soluble in ether, giving orange to yellow very air sensitive solutions. Conductivity measurements in acetonitrile [2a] indicate a dianion. The infrared spectrum taken in acetone showed four peaks: In the carbonyl region, 2000m, 1965s, 1914m, and 1880m cm^{-1}. ^1H NMR in acetone solution shows a sharp singlet at τ 27.7 ppm corresponding to the metal-bridging hydrogen and a sharp singlet at τ 2.08 ppm due to the hydrogens of the tetraphenylarsonium cation. Area ratios measured by planimeter are 1.0 ± 0.2/40.0 [2a]. The structure of the salt has been determined [1a] and that of the bis(tetraethylammonium) analog recently reported [11].

Preparation of $[(C_6H_5)_4As]_2[Re_3(\mu\text{-}D)(CO)_{12}] \cdot \frac{1}{2} C_4H_6O$ *(II-*d_1*)*

This salt was prepared in a manner analogous to II using $NaBD_4$ in the first step [1a].

Preparation of I. A quantity of II (0.5 g, 0.3 mmol) was stirred in acetone (30 ml) until solution was complete. An excess of dimethyltin dichloride (0.1 g, 0.5 mmol) was added to the resultant red solution which became progressively orange, yellow, and yellow green as the solid dissolved and reacted (apparently instantaneously). A white precipitate of Ph_4AsCl separated from solution at this point and was removed by filtration. Acetone was next removed under vacuum, yielding a light green oil. Separate experiments attempting to characterize this material are described below. For synthesis of I, experiments continue as follows.

To a heterogeneous mixture of the intermediate oil and 50 ml cyclohexane, H_3PO_4 (5 ml, 14.7 *M*) was added and the mixture vigorously stirred for one hour. The cyclohexane layer became yellow and then orange and was syringed off. More cyclohexane was added and the process was repeated until the cyclohexane remained colorless. The combined cyclohexane extracts were evaporated under vacuum. The yellow powder which remained was dissolved in a minimum amount of CH_2Cl_2 and was placed in the refrigerator overnight. The resultant orange crystals were washed with cold cyclohexane and dried under vacuum giving 100 mg of a 25% yield of I (m.p. 165°C (dec.)).

The crystals are air stable and can be stored indefinitely under nitrogen. The compound is soluble in common organic solvents; solutions exposed to oxygen decompose in a matter of hours. Anal. Found (Ms. Heather King. U.C.L.A. and Galbraith Laboratories, Knoxville Tennessee): C, 16.1; H, 0.9; Sn, 9.2. $Re_3C_{14}Sn_2H_7O_{12}$ calcd.: C, 16.1; H, 0.7; Sn, 11.2%.

Preparation of I-d_1. The material is prepared in a manner entirely analogous to I except the starting material is II-d_1; as a precaution, D_3PO_4 in D_2O was used in the acidification step. Further experiments indicated the latter precaution is not necessary. Indeed starting with II and using D_3PO_4/D_2O, no deuterium is introduced into the product. The presence of deuterium in I-d_1 was confirmed by absence of signal at τ 25.7 ppm in the ^1H NMR and by the Raman spectrum (see Fig. 4).

Isolation of $Re_2HCl(CO)_8$ *and* $Re_3DCl(CO)_8$ *from intermediate green oils*

Attempts to purify the intermediate green oil obtained from treatment of II with Me_2SnCl_2 included at one point a cyclohexane extraction. This was carried out at 40°C and repeated until successive portions of cyclohexane no longer revealed carbonyl stretching absorptions in the IR. Evaporation of the cyclohexane extracts leaves a white powder which is recrystallized from CH_2Cl_2 and shown by mass spectra [1a], Raman [1a] and IR, to be $ReHCl(CO)_8$; a four band pattern is observed for the carbonyl stretching modes (cyclohexane solution, cm^{-1}): 2106, 2031, 2013 and 1971 [5].

Green oils produced from similar treatment of II-d_1 with $(CH_3)_2SnCl_2$ yield upon cyclohexane extraction $Re_2DCl(CO)_8$ characterized by IR and Raman spectra [1a]. The characteristic bands for the carbonyl stretching and deformation modes remain essentially unchanged; however, a series of weak, broad bands 1449—1175 cm^{-1} are observed in $Re_2HCl(CO)_8$ which disappear and are replaced by bands in the region 1051—881 cm^{-1} for $Re_2DCl(CO)_8$ [1a] characteristic of bridging hydrogen; or deuterium, respectively.

Crystallographic study

X-ray stable yellow-orange platelets were recrystallized from dichloromethane/hexane solutions. Preliminary X-ray diffraction photographs indicated monoclinic symmetry. From Weissenberg and precession photographs the only systematic absences noted are for reflections $0k0$, $k = 2n + 1$, and for $h0l$, $l = 2n + 1$, indicative of space group $P2_1/c$ (C_{2h}^5, No. 14) [12].

The crystal used for data collection was a fragment bounded by (100), ($\bar{1}02$), (010), centrosymmetrically related faces, ($12\bar{2}$) and ($1\bar{2}\bar{2}$). Crystal dimensions normal to these faces from a point midway between the centrosymmetrically related faces were 0.040, 0.020, 0.098, 0.040, 0.070, 0.098, 0.068, and 0.068 mm, respectively. The crystal, sealed under nitrogen in a capillary, was mounted with b approximately along the ϕ axis of a Picker FACS-1 four circle autodiffractometer equipped with a graphite monochromator (Mo-K_α radiation). Unit cell parameters were determined by a least-squares refinement based on 39 diffractometer-centered reflections in the range $24.8 < 2\theta < 34.3°$ [12]. The lattice parameters at 22°C are listed in Table 1. The numbers given in parentheses here and in succeeding Tables are the estimated standard deviations in the least significant digits.

The intensity data were collected by the θ—2θ scan procedure (Mo-K_α radiation, graphite crystal monochromator set at a 2θ angle of 12.16°, takeoff angle 2.6°, pulse height analyzer set at a 95% window for Mo-K_α radiation). The scan rate was 2°/min with a scan range from 1° below the $K_{\alpha 1}$ peak to 1° above the $K_{\alpha 2}$ peak. Background counts (10 sec) were taken at each end of the scan range. The automatic attenuator mechanism was set to keep the count rate below 10 000 counts/sec. The intensities of two standard reflections were mea-

TABLE 1

CRYSTAL DATA FOR $Re_3(\mu\text{-H})(\mu\text{-SnMe}_2)(CO)_{12}$ [a]

a 16.929(5) Å	mol.wt. 1044.7
b 16.968(9) Å	Space group $P2_1/c$
c 16.699(4) Å	$Z = 8$
β 114.80(2)°	ρ_{obs} [b] 3.19(1) g cm^{-3}
V 4354 Å^3	ρ_{calc} 3.187 g cm^{-3}

[a] Based on Mo-K_α 0.71069 Å. [b] Flotation mixture of $CH_2I_2/CHBr_3$.

sured every fifty reflections. An abrupt 7% loss in intensity was observed late in the course of data collection after a machine malfunction and this data was corrected; no appreciable fluctuations or time-dependent drift occurred. The intensity (I) and estimated standard deviation $\sigma(I)$ were calculated according to the equations

$$I = C_s + 4.5 - (T_s/2t_b)(B_1 + B_2 + 9)$$

$$\sigma(I) = [C_s + (9 + (t_s/2t_b)^2(B_1 + B_2 + 18) + (0.04I)^2]^{1/2}$$

where C_s is the total scan count, B_1 and B_2 are individual background counts, t_s is the scan time (sec) and t_b is the time each background is counted. The values of I and $\sigma(I)$ were corrected for Lorentz and polarization effects. Reflections were considered observed if $I_{hkl} > 3\sigma I_{hkl}$. Of the 5623 reflections measured ($2\theta_{\max} = 45°$), 4366 were considered to be observed. Absorption corrections were made: transmission factors ranged from 0.3327 to 0.5010 ($\mu = 188$ cm^{-1}, Mo-K_α radiation). An average correction (0.4611) was applied to the unobserved reflections.

A Wilson plot was computed in order to obtain normalized structure factors (E) [14]. Phases for 384 reflections with $E \geqslant 1.50$ were obtained by direct methods [15] and were used to calculate an E-map. The six Re atoms and the two Sn atoms were readily located.

An inner sphere of 3629 observed reflections was used for the solution and early refinement of this structure. One cycle of full-matrix least-squares refinement [13] of the metal positions, individual thermal parameters and scale factor led to a conventional discrepancy factor $R_F = 0.175$, ($R = \Sigma ||F_0| - |F_c||/\Sigma |F_0|$). A combination of difference Fourier and full-matrix least-squares refinement located the 52 carbon and oxygen atoms. Subsequent refinements included the full data set and allowed anisotropic thermal parameters for the metal atoms; the final $R_F = 0.066$. A final difference Fourier synthesis showed no maxima above 1 e^- Å^{-3} except in the immediate vicinity of the Re atoms where maxima of ±3 e^- Å^{-3} were noted *.

Description of the structure and discussion

The asymmetric unit consists of two crystallographically independent molecules, A and B, which show virtually identical conformations and are of course chemically equivalent. Atomic positional parameters and isotropic thermal parameters for the non-metal atoms in each independent molecule are given in Table 2. An overall view and numbering scheme pertaining to both molecules is shown in Fig. 5. The anisotropic thermal parameters for the metal atoms in the two molecules are given in Table 3.

In each molecule the metal atoms form two fused triangles with dihedral angles of 180° in A and 177° in B; both are effectively planar with equatorial carbonyl groups lying very close to the plane defined by the three rhenium atoms, while the axial carbonyl groups are essentially perpendicular to that plane. Displacements from the trirhenium plane are given in Table 4 while the near-planar system together with the carbon atoms of the methyl groups on tin

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* A table of observed and calculated structive factors (11 pages) has been deposited with National Auxiliary Publications Service, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017, U.S.A.

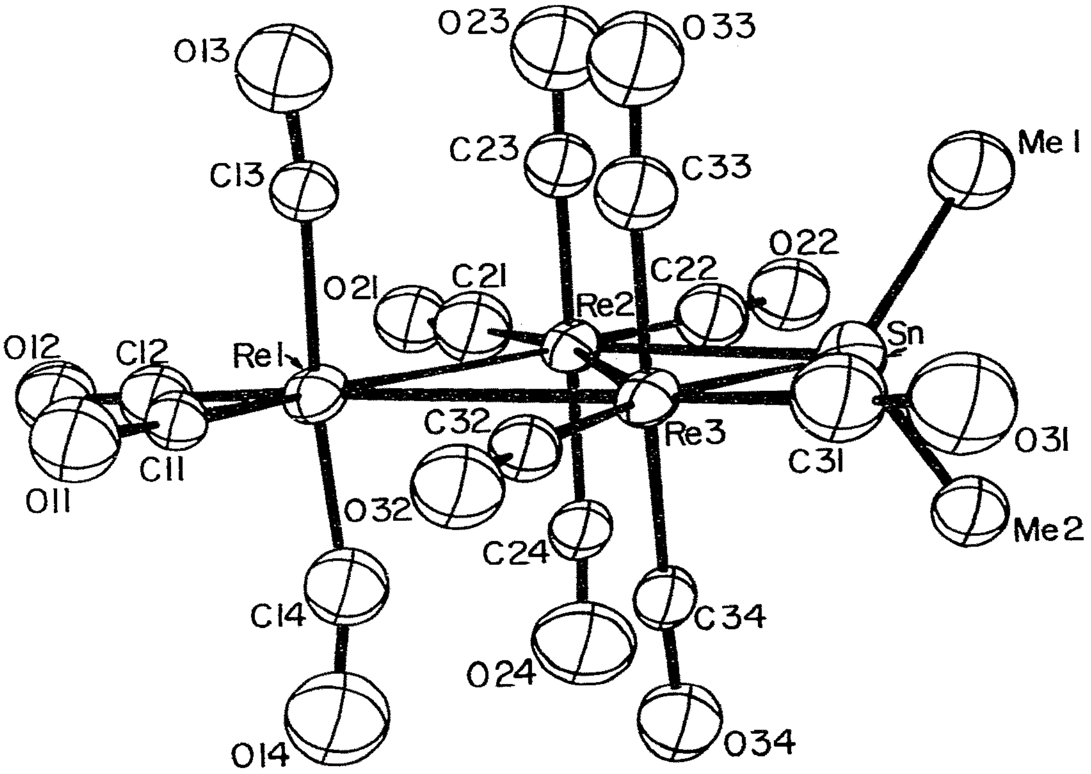

Fig. 5. Molecular structure of I illustrating the numbering scheme. Thermal ellipsoids enclose 50% of the electron density; hydrogen atoms on the methyl groups are omitted for clarity. A hydrogen atom (not located) is believed to be bridging between Re(1) and Re(2), see text.

are shown in Fig. 6; important bond lengths and angles (averaged for the two molecules A and B) are also shown in Fig. 6.

The tetracarbonyl groups are skewed slightly relative to the plane of the three rhenium atoms, the angular values of which are shown at the bottom of Table 4. Similar skewing was observed in $[n\text{-Bu}_4N]_2[Re_4(CO)_{16}]$ [16], but this may not be an inherent property of these planar triangulated polynuclear carbonyls since the tetraethylammonium salt of the $[Re_4(CO)_{16}]^{2-}$ anion possesses a rigorous, crystallographically imposed D_{2h} symmetry [11].

The isotropic temperature factors shown in Table 2 are normal for such a molecule; root mean square thermal displacements [1b] are also normal. No abnormal intermolecular contacts are observed; the shorter contacts given in Table 5 occur between oxygen atoms.

Bond lengths and angles obtained for the two crystallographically independent molecules are given in Tables 6 and 7, respectively. The slight differences in dimensions are not chemically significant. In the discussion which follows, averaged values for these parameters will be cited.

The Re(1)—Re(3) distance of 3.02 Å lies well within that reported for a variety of similar compounds, i.e. 2.96 to 3.06 Å, cf. [11], [16], and Table 5.10 in [1b]. In particular it compares favorably with the unbridged distances of 3.004(2) Å [1b] and of 3.014(3) and 3.018(3) Å [11] in two salts of the dianion $[Re_3(\mu\text{-H})(CO)_{12}]^{2-}$. The Re(1)—Re(2) separation is significantly

(Continued on p. 60)

TABLE 2

ATOMIC POSITIONAL PARAMETERS WITH THEIR STANDARD DEVIATIONS

Atom	x	y	z	B(Å^2) [a]
Molecule A				
Re(1)	−0.11526(8)	0.11303(8)	0.29824(7)	—
Re(2)	−0.00495(8)	0.24396(8)	0.24996(8)	—
Re(3)	0.08100(8)	0.09935(8)	0.37423(7)	—
Sn	0.17693(15)	0.20576(14)	0.33757(14)	—
C(11) [b]	−0.155(2)	0.028(2)	0.347(2)	2.1(6)
C(12)	−0.228(2)	0.141(2)	0.230(2)	3.7(7)
C(13)	−0.108(2)	0.179(2)	0.397(2)	2.6(6)
C(14)	−0.111(2)	0.049(2)	0.206(2)	4.4(8)
C(21)	−0.093(3)	0.313(2)	0.173(2)	4.9(9)
C(22)	0.068(2)	0.317(2)	0.232(2)	3.8(8)
C(23)	0.002(2)	0.302(2)	0.352(2)	3.7(7)
C(24)	−0.010(2)	0.179(2)	0.151(2)	3.1(6)
C(31)	0.193(2)	0.061(2)	0.449(2)	4.6(8)
C(32)	0.038(2)	0.009(2)	0.413(2)	2.3(6)
C(33)	0.086(2)	0.162(2)	0.472(2)	3.9(7)
C(34)	0.077(2)	0.040(2)	0.273(2)	2.9(6)
Me(1)	0.252(2)	0.300(2)	0.429(2)	4.8(8)
Me(2)	0.233(2)	0.187(2)	0.243(2)	3.9(7)
O(11)	−0.183(1)	−0.023(1)	0.375(1)	4.0(5)
O(12)	−0.303(1)	0.157(1)	0.188(1)	4.2(5)
O(13)	−0.112(2)	0.218(2)	0.454(2)	5.8(6)
O(14)	−0.120(2)	−0.005(2)	0.150(2)	6.5(6)
O(21)	−0.149(2)	0.354(1)	0.125(2)	5.1(6)
O(22)	0.109(2)	0.369(2)	0.219(2)	5.6(6)
O(23)	0.007(2)	0.344(2)	0.411(2)	5.6(6)
O(24)	−0.017(2)	0.136(2)	0.091(2)	6.4(6)
O(31)	0.262(2)	0.035(2)	0.494(2)	6.2(6)
O(32)	0.021(1)	−0.049(1)	0.438(1)	3.9(5)
O(33)	0.093(2)	0.203(1)	0.533(2)	5.6(6)
O(34)	0.079(1)	−0.002(1)	0.215(1)	4.6(5)
Molecule B				
Re(1)	0.50468(8)	0.32495(8)	0.12819(8)	—
Re(2)	0.63420(8)	0.32168(8)	0.33657(8)	—
Re(3)	0.55700(8)	0.47744(8)	0.22935(8)	—
Sn	0.17693(15)	0.20576(14)	0.33757(14)	—
C(11)	0.430(2)	0.349(2)	0.009(2)	2.9(6)
C(12)	0.489(2)	0.237(2)	0.099(2)	3.4(7)
C(13)	0.599(3)	0.326(2)	0.095(3)	6.3(9)
C(14)	0.404(3)	0.329(2)	0.158(2)	5.8(9)
C(21)	0.648(2)	0.212(2)	0.352(2)	4.3(8)
C(22)	0.715(2)	0.327(2)	0.455(2)	3.7(7)
C(23)	0.728(2)	0.335(2)	0.299(2)	3.8(7)
C(24)	0.536(3)	0.316(3)	0.366(3)	5.9(13)
C(31)	0.568(2)	0.588(2)	0.248(2)	3.1(6)
C(32)	0.475(2)	0.494(2)	0.106(2)	3.4(7)
C(33)	0.655(2)	0.479(2)	0.191(2)	5.2(8)
C(34)	0.461(3)	0.467(2)	0.264(2)	4.9(9)
Me(1)	0.804(3)	0.521(2)	0.435(3)	5.8(10)
Me(2)	0.638(2)	0.499(2)	0.511(3)	5.1(10)
O(11)	0.387(2)	0.365(1)	−0.066(2)	4.8(5)
O(12)	0.482(2)	0.145(2)	0.083(2)	6.1(6)
O(13)	0.657(2)	0.329(2)	0.073(2)	6.6(7)
O(14)	0.338(2)	0.324(2)	0.166(2)	7.3(7)
O(21)	0.661(2)	0.143(2)	0.365(2)	5.7(6)
O(22)	0.764(2)	0.320(1)	0.531(2)	5.6(6)
O(23)	0.790(2)	0.342(1)	0.283(2)	5.1(6)
O(24)	0.477(2)	0.313(2)	0.389(2)	7.9(8)
O(31)	0.565(2)	0.656(2)	0.251(2)	5.2(6)
O(32)	0.435(1)	0.524(1)	0.037(1)	4.5(5)
O(33)	0.715(2)	0.490(2)	0.177(2)	5.5(6)
O(34)	0.406(2)	0.473(2)	0.291(2)	6.0(7)

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[a] The isotropic temperature parameter B is of the form $\exp[-B \sin^2\theta/\lambda^2]$. [b] Carbonyl groups are numbered to correspond to the metal atoms to which they are bonded.

TABLE 3

ANISOTROPIC THERMAL PARAMETERS ($\times 10^5$)

Atom	β_{11} [a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Molecule A						
Re(1)	302(6)	269(6)	221(6)	8(10)	301(10)	13(9)
Re(2)	317(6)	263(6)	232(6)	21(10)	283(10)	67(9)
Re(3)	298(6)	272(6)	207(6)	40(10)	277(10)	48(9)
Sn	353(12)	344(10)	343(11)	−35(18)	336(18)	110(17)
Molecule B						
Re(1)	317(7)	274(6)	242(6)	−34(10)	264(10)	2(9)
Re(2)	360(7)	278(6)	238(6)	28(10)	313(10)	50(9)
Re(3)	323(7)	254(6)	259(6)	19(10)	317(10)	25(9)
Sn	514(14)	330(10)	261(10)	−48(20)	330(20)	−18(17)

[a] The expression for the anisotropic temperature factor is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

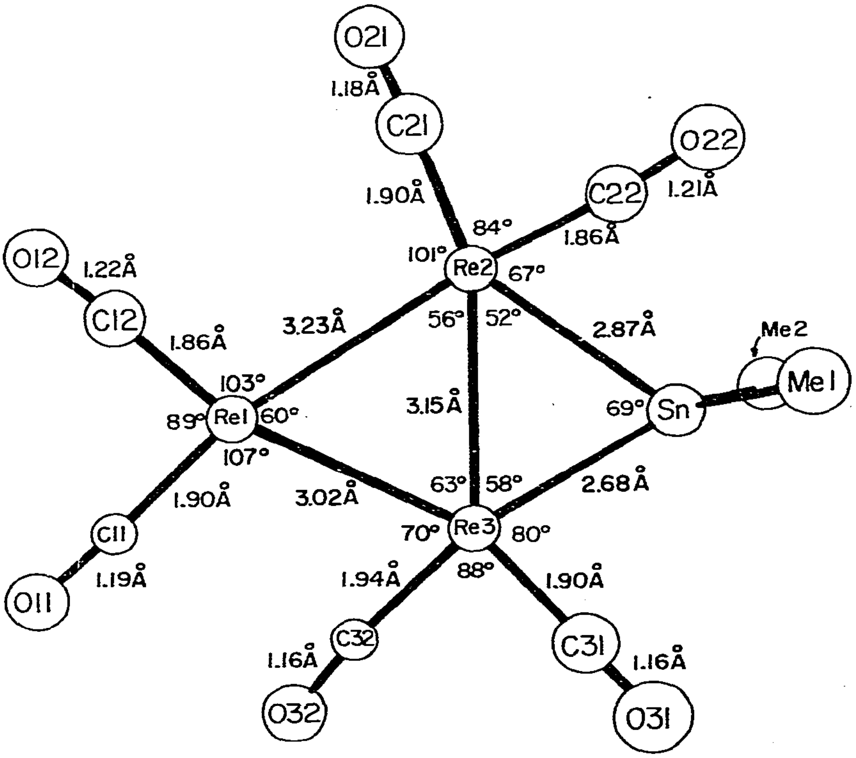


Fig. 6. Projection of I against the plane defined by the three rhenium atoms with average values of selected bond distances and angles observed for the two crystallographically independent molecules in the unit cell; the six axial carbonyl groups above and below the plane of the three rhenium atoms and hydrogen atoms on the two methyl groups have been omitted for clarity. A hydrogen atom (not located) is believed to be bridging between Re(1) and Re(2), see text.

TABLE 4A

DISPLACEMENT FROM Re—Re—Re PLANE (Å)

Atoms	Molecule A	Molecule B
Re(1)	0	0
Re(2)	0	0
Re(3)	0	0
Sn	0.006(3)	0.115(4)
C(11)	0.09(3)	0.01(4)
C(12)	−0.17(4)	−0.09(4)
C(13)	1.95(3)	1.88(5)
C(14)	−1.89(4)	−1.95(5)
C(21)	−0.02(4)	−0.07(4)
C(22)	0.08(4)	0.13(4)
C(23)	1.93(3)	1.94(4)
C(24)	−1.96(3)	−1.92(6)
C(31)	0.16(4)	0.11(4)
C(32)	−0.09(3)	−0.06(4)
C(33)	1.92(3)	2.00(5)
C(34)	−1.95(3)	−1.94(5)
Me(1)	1.79(4)	2.00(5)
Me(2)	−1.75(4)	−1.53(5)
O(11)	0.15(2)	0.09(3)
O(12)	−0.24(2)	−0.11(3)
O(13)	3.12(3)	3.08(4)
O(14)	−3.14(3)	−3.14(4)
O(21)	−0.05(3)	−0.05(3)
O(22)	0.17(3)	0.15(3)
O(23)	3.12(3)	3.13(3)
O(24)	−3.17(3)	−3.14(4)
O(31)	0.21(3)	0.12(3)
O(32)	−0.19(2)	0.01(3)
O(33)	3.12(3)	3.15(3)
O(34)	−3.14(2)	−3.12(4)

TABLE 4B

ANGULAR DEVIATION FROM PLANARITY: DIHEDRAL ANGLE WITH Re—Re—Re PLANE (°)

Plane	Molecule A	Molecule B
C(11)—Re(1)—C(12)	5.9(11)	2.9(12)
C(21)—Re(2)—C(22)	2.7(13)	4.7(14)
C(31)—Re(3)—C(32)	5.6(12)	3.8(11)
Sn—Re(2)—Re(3)	0.15(8)	2.88(10)

TABLE 5

SHORTER INTERMOLECULAR DISTANCES [a]

First atom	Second atom	Position	Distance (Å)
O(31A)	O(32A)	55504	2.89(4)
O(32A)	O(32A)	55602	2.97(5)
O(22A)	O(32A)	55503	2.98(3)
55504		$-x, \frac{1}{2}+y, \frac{1}{2}-z$	
55602		$-x, -y, 1-z$	
55503		$x, \frac{1}{2}-y, \frac{1}{2}+z$	

[a] Sum of Van der Waals radii: O---O, 2.8 Å [13].

TABLE 6

INTRAMOLECULAR DISTANCES (Å).

Bond	Molecule A	Molecule B
(a) Metal—metal distances		
Re(1)—Re(2)	3.215(2)	3.243(2)
Re(1)—Re(3)	3.028(2)	3.013(2)
Re(1)—Sn	4.965(3)	4.975(3)
Re(2)—Re(3)	3.148(2)	3.152(2)
Re(2)—Sn	2.874(3)	2.868(3)
Re(3)—Sn	2.666(3)	2.684(2)
(b) Metal—carbon distances		
Re(1)—C(11)	1.91(3)	1.89(3)
Re(1)—C(12)	1.83(3)	1.89(3)
Re(1)—C(13)	1.95(3)	1.89(5)
Re(1)—C(14)	1.91(4)	1.96(5)
Re(2)—C(21)	1.92(4)	1.88(4)
Re(2)—C(22)	1.85(4)	1.87(3)
Re(2)—C(23)	1.93(4)	1.95(4)
Re(2)—C(24)	1.96(3)	1.92(6)
Re(3)—C(31)	1.90(3)	1.90(3)
Re(3)—C(32)	1.93(3)	1.96(3)
Re(3)—C(33)	1.92(4)	2.01(5)
Re(3)—C(34)	1.95(3)	1.95(5)
Sn(Me(1)	2.21(3)	2.20(4)
Sn—Me(2)	2.18(4)	2.16(5)
(c) Metal—oxygen distances		
Re(1)—O(11)	3.10(2)	3.08(2)
Re(1)—O(12)	3.01(2)	3.14(3)
Re(1)—O(13)	3.13(3)	3.08(4)
Re(1)—O(14)	3.16(3)	3.14(4)
Re(2)—O(21)	3.09(2)	3.07(3)
Re(2)—O(22)	3.05(3)	3.07(2)
Re(2)—O(23)	3.12(3)	3.14(3)
Re(2)—O(24)	3.17(3)	3.14(4)
Re(3)—O(31)	3.07(3)	3.04(3)
Re(3)—O(32)	3.07(2)	3.10(2)
Re(3)—O(33)	3.12(2)	3.15(3)
Re(3)—O(34)	3.16(3)	3.13(4)
(d) Carbon—oxygen distances		
C(11)—O(11)	1.19(4)	1.19(3)
C(12)—O(12)	1.18(4)	1.25(4)
C(13)—O(13)	1.18(4)	1.19(6)
C(14)—O(14)	1.28(5)	1.19(6)
C(21)—O(21)	1.17(4)	1.19(5)
C(22)—O(22)	1.21(5)	1.21(4)
C(23)—O(23)	1.19(4)	1.19(5)
C(24)—O(24)	1.21(4)	1.22(8)
C(31)—O(31)	1.17(4)	1.15(4)
C(32)—O(32)	1.15(4)	1.17(4)
C(33)—O(33)	1.20(4)	1.15(6)
C(34)—O(34)	1.21(4)	1.20(6)
(e) Non-bonding contacts		
Re(1)—C(32)	3.05(3)	2.91(3)
Sn—C(22)	2.71(3)	2.76(3)
Sn—C(31)	3.01(4)	3.01(3)
C(11)—C(12)	2.64(4)	2.65(4)
C(11)—C(13)	2.70(4)	2.63(5)
C(11)—C(14)	2.76(6)	2.71(6)
C(11)—C(32)	2.99(4)	2.87(4)
C(11)—O(32)	3.03(3)	3.00(4)

TABLE 6 (continued)

Bond	Molecule A	Molecule B
C(12)—C(13)	2.76(4)	2.65(6)
C(12)—C(14)	2.68(6)	2.79(6)
C(13)—C(33)	3.00(4)	2.99(5)
C(14)—C(34)	2.91(5)	2.85(5)
C(21)—C(22)	2.48(6)	2.53(5)
C(21)—C(23)	2.74(5)	2.83(6)
C(21)—C(24)	2.78(5)	2.66(7)
C(22)—C(23)	2.67(6)	2.70(6)
C(22)—C(24)	2.75(5)	2.76(6)
C(23)—C(33)	3.06(4)	2.99(5)
C(31)—C(32)	2.60(5)	2.74(4)
C(31)—C(33)	2.65(6)	2.77(6)
C(31)—C(34)	2.79(4)	2.82(5)
C(32)—C(33)	2.78(4)	2.78(5)
C(32)—C(34)	2.74(5)	2.79(6)

TABLE 7

BOND ANGLES (°)

Atoms	Molecule A	Molecule B
(a) Angles between metal atoms		
Re(2)—Re(1)—Re(3)	60.48(4)	60.38(4)
Re(1)—Re(2)—Re(3)	56.81(5)	56.19(4)
Re(1)—Re(2)—Sn	109.11(7)	108.85(6)
Re(3)—Re(2)—Sn	52.30(6)	52.70(6)
Re(1)—Re(3)—Re(2)	62.71(4)	63.43(5)
Re(1)—Re(3)—Sn	121.26(7)	121.57(7)
Re(2)—Re(3)—Sn	58.56(6)	58.20(6)
Re(2)—Sn—Re(3)	69.14(7)	69.09(6)
(b) Angles at metal atoms		
Re(2)—Re(1)—C(11)	166.9(8)	168.6(9)
Re(2)—Re(1)—C(12)	103.3(12)	102.5(8)
Re(2)—Re(1)—C(13)	89.0(10)	92.2(11)
Re(2)—Re(1)—C(14)	88.3(12)	89.9(10)
Re(3)—Re(1)—C(11)	106.6(8)	108.2(9)
Re(3)—Re(1)—C(12)	163.0(12)	162.7(9)
Re(3)—Re(1)—C(13)	91.3(8)	93.9(12)
Re(3)—Re(1)—C(14)	83.5(10)	84.8(11)
Re(1)—Re(2)—C(21)	102.8(14)	98.9(9)
Re(1)—Re(2)—C(22)	174.5(9)	174.6(12)
Re(1)—Re(2)—C(23)	87.8(11)	86.0(8)
Re(1)—Re(2)—C(24)	89.7(10)	90.5(13)
Re(3)—Re(2)—C(21)	159.6(14)	155.1(9)
Re(3)—Re(2)—C(22)	118.2(10)	120.1(10)
Re(3)—Re(2)—C(23)	88.9(9)	85.6(9)
Re(3)—Re(2)—C(24)	87.9(8)	89.4(14)
Sn—Re(2)—C(21)	148.1(14)	152.2(9)
Sn—Re(2)—C(22)	65.9(10)	67.4(10)
Sn—Re(2)—C(23)	90.7(9)	86.6(10)
Sn—Re(2)—C(24)	87.9(8)	91.2(15)
Re(1)—Re(3)—C(31)	157.5(13)	157.9(8)
Re(1)—Re(3)—C(32)	72.3(8)	67.9(9)
Re(1)—Re(3)—C(33)	87.7(10)	85.7(10)
Re(1)—Re(3)—C(34)	92.6(9)	90.1(11)
Re(2)—Re(3)—C(31)	139.1(12)	138.4(8)

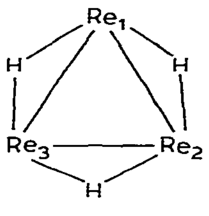
TABLE 7 (continued)

Atoms	Molecule A	Molecule B
Re(2)—Re(3)—C(32)	134.9(8)	131.3(9)
Re(2)—Re(3)—C(33)	88.4(9)	89.6(10)
Re(2)—Re(3)—C(34)	90.0(8)	87.3(11)
Sn—Re(3)—C(31)	80.9(13)	80.2(8)
Sn—Re(3)—C(32)	166.2(8)	170.5(9)
Sn—Re(3)—C(33)	90.5(11)	91.2(9)
Sn—Re(3)—C(34)	87.2(10)	89.8(10)
Re(2)—Sn—Me(1)	111.8(10)	115.2(11)
Re(2)—Sn—Me(2)	111.4(7)	111.2(11)
Re(3)—Sn—Me(1)	124.1(11)	119.0(11)
Re(3)—Sn—Me(2)	124.2(9)	126.3(10)
C(11)—Re(1)—C(12)	89.8(14)	88.9(12)
C(11)—Re(1)—C(13)	88.8(13)	88.1(16)
C(11)—Re(1)—C(14)	92.9(15)	89.3(15)
C(12)—Re(1)—C(13)	93.4(14)	89.3(17)
C(12)—Re(1)—C(14)	91.4(15)	92.9(17)
C(13)—Re(1)—C(14)	174.9(13)	176.5(16)
C(21)—Re(2)—C(22)	82.2(17)	84.9(14)
C(21)—Re(2)—C(23)	91.1(16)	95.1(17)
C(21)—Re(2)—C(24)	91.6(15)	88.9(20)
C(22)—Re(2)—C(23)	89.7(16)	89.8(15)
C(22)—Re(2)—C(24)	92.5(16)	93.5(18)
C(23)—Re(2)—C(24)	176.7(13)	175.0(17)
C(31)—Re(3)—C(32)	85.9(15)	90.3(12)
C(31)—Re(3)—C(33)	87.7(15)	90.1(15)
C(31)—Re(3)—C(34)	91.9(15)	94.3(16)
C(32)—Re(3)—C(33)	92.5(14)	88.7(15)
C(32)—Re(3)—C(34)	90.0(13)	91.0(15)
C(33)—Re(3)—C(34)	177.5(14)	175.6(15)
Me(1)—Sn—Me(2)	107.7(14)	109.1(16)
(c) Re—C—O angles		
Re(1)—C(11)—O(11)	177(2)	177(3)
Re(1)—C(11)—O(12)	176(3)	177(3)
Re(1)—C(11)—O(14)	174(3)	178(3)
Re(1)—C(11)—O(13)	166(3)	171(3)
Re(2)—C(21)—O(21)	178(4)	177(3)
Re(2)—C(21)—O(22)	175(3)	171(3)
Re(2)—C(21)—O(23)	175(3)	175(2)
Re(2)—C(21)—O(24)	176(3)	177(4)
Re(3)—C(31)—O(31)	177(8)	172(2)
Re(3)—C(31)—O(32)	172(3)	163(3)
Re(3)—C(31)—O(33)	176(3)	170(3)
Re(3)—C(31)—O(34)	174(2)	169(3)

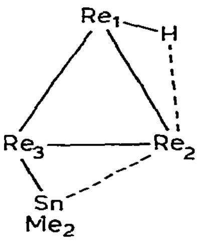
longer, 3.23 Å and falls in the range 3.14 to 3.39 Å recognized to represent a hydrogen bridged edge [9,17]. Specifically this compares favorably with the edges assumed to be hydrogen bridged in the two salts of $[\mathrm{Re}(\mu\text{-H})(\mathrm{CO})_{12}]^{2-}$, namely 3.144(5) Å [1a] and 3.125(3) Å [11]. We return to a discussion of the possible positioning of the hydrogen along the edge Re(1)—Re(3) after a consideration of the Re—Sn separations.

The $\mathrm{Me_2Sn}$ is observed to bridge the Re(2)—Re(3) edge with significant difference in the Re—Sn separations, Re(2)—Sn 2.871(3) Å and Re(3)—Sn 2.675(3) Å. Despite reports of a large number of compounds containing Re—Sn bonds [3] none have as yet been determined crystallographically, so there are no direct comparisons possible. The closest pertinent structure determination is an electron diffraction study of the methyl, silyl, and germyl derivatives of Re-$(CO)_5$ [18]. While the C(sp^3)—Re separation of 2.308 [18] was found to be close to 2.29 Å expected for the sum of the covalent radii, r(C(sp^3)) 0.77 Å [18] and r(Re) 1.52 Å [19], those for Si(sp^3)—Re 2.562(12) and Ge(sp^3)—Re 2.628(6) Å are significantly shorter by 4 and 5% than the sum of the covalent radii, 2.69 and 2.74 Å, respectively, based on r(Si(sp^3)) 1.17 Å and r(Ge(sp^3)) 1.22 Å [19].

With r(Sn(sp^3)) 1.40 Å [19], the sum of covalent radii for Re—Sn comes to 2.92 Å, and a "normal" Re—Sn separation might be anticipated at about 5% less, i.e. 2.77 Å. This is exactly intermediate between the Re(2)—Sn and Re(3)—Sn distances observed in this work; the Sn atom thus seems to be shifted by about 0.1 Å away from Re(2) towards Re(3). With hydrogen presumed to be bridging between Re(1) and Re(2) (see above) it is not possible with a single divalent atom along Re(2)—Re(3) to replace the charge that would normally be delivered by a bridging hydrogen, one each along Re(2)—Re(3) and Re(3)—Re(1), as in the parent hydride $Re_3(\mu\text{-}H)_3(CO)_{12}$ (see structural diagram (a) and remarks in the Introduction). Removal of two of the edge-bridging hydrogen atoms and replacement by a single divalent edge-bridging group such as R_2Sn, thus builds up charge at Re(2) and reduces it at Re(3) unless the divalent group is asymmetrically bridging, with a shorter approach to Re(3), as observed in this work. The asymmetry in the Re—Sn separations in I is thus seen to be a consequence of the need to maintain electroneutrality in the molecule [21]. The asymmetry may also carry over to the placement of hydrogen, as suggested by the relatively high energy of its Raman absorption (see discussion above). Redetermination of the structure of this complex including location of the hydrogen atom [22] thus becomes an interesting and important problem.



(a)



(b)

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