AN UNUSUAL SPECIES FROM THE REACTION OF THE UNSATURATED ANION [Re$_3$(μ-H)$_4$(CO)$_{10}$]$^-$ WITH Me$_3$NO. SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION OF THE ADDUCT ANION [Re$_3$(μ-H)$_3$(CO)$_9$(μ_3-O $\cdots$ H $\cdots$ NMe$_3$)]$^-$, AND CRYSTAL AND MOLECULAR STRUCTURE OF ITS TETRAETHYLAMMONIUM SALT

TIZIANA BERINGHELLI, GIUSEPPE D'ALFONSO*, MARIA FRENI,

Dipartimento di Chimica Inorganica e Metallorganica, Via G. Venezian 21, 20133 Milano (Italy)

GIANFRANCO CIANI*

Istituto di Chimica Strutturistica Inorganica, Via G. Venezian 21, 20133 Milano (Italy)

and HENRIETTE MOLINARI

Dipartimento di Chimica Organica e Industriale, Via Golgi 19, 20133 Milano (Italy)

Summary

The reactions of the unsaturated cluster anion [Re$_3$(μ-H)$_4$(CO)$_{10}$]$^-$ with Me$_3$NO, in a solvent of low donor ability, such as acetone or tetrahydrofuran, give three products, in a ratio which depends on the reaction conditions: two of them, the unsaturated [Re$_3$(μ-H)$_4$(CO)$_9$(NMe$_3$)]$^-$ and [Re$_3$(μ-H)$_4$(CO)$_9$(ONMe$_3$)]$^-$ species, have been characterized spectroscopically. The third has been isolated and characterized by X-ray single crystal analysis as an adduct formed by hydrogen bonding between Me$_3$N and the triangular cluster anion [Re$_3$(μ-H)$_3$(CO)$_9$(μ_3-OH)]$^-$. The crystals are monoclinic, space group $P2_1/m$, with a 8.576(3), b 20.442(4), c 8.748(3) Å, β 108.08(4)°, $Z = 2$. The structure was solved by Patterson and Fourier methods by use of 2085 unique reflections and refined to a final R value of 0.026. The mean Re–Re and Re–O(OH) bond lengths are 2.979 and 2.126 Å, respectively. The O · H · N hydrogen bond is short and almost linear (O $\cdots$ N 2.502(10) Å). Various experiments have demonstrated that the triply bridging OH group can, according to the reaction conditions, come either from a water molecule (present in the commercial amine oxide) or by attack of a hydridic ligand on the oxygen of a coordinated amine oxide molecule. The same adduct has been obtained starting from the dianion [Re$_3$(μ-H)$_3$(CO)$_9$(μ_3-O)]$^{2-}$, directly by reaction with Me$_3$NHCl or in a two step sequence by protonation to [Re$_3$(μ-H)$_3$(CO)$_9$(μ_3-OH)]$^-$ and subsequent treatment with Me$_3$N.

Introduction

The unsaturated anion $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ (1) has previously been shown to possess a high reactivity in reactions involving the hydrides of its $Re(\mu\text{-}H)_2Re$ moiety. Owing to their negative polarization these hydrides are readily attacked by a variety of electrophilic reagents such as halogen acids [1], carboxylic acids [2], phenols [3], iodine [4], $C_7H_7^+$ [5], and NO^+ [6]. The hydrides are not the only reactive centres, however, since on the other hand we recently observed during a ^{13}C NMR analysis of compound 1 the occurrence of an unusual selective enrichment in ^{13}CO at the two carbonyl ligands mutually *trans* in the $Re(CO)_4$ unit [7]. The lability of these carbonyls, arising from their competition for π-back-donation, prompted us to attempt selective substitution reactions with other donor species, without affecting the more reactive unsaturated site of the molecule. We accomplished this, obtaining a family of unsaturated derivatives $[Re_3(\mu\text{-}H)_4(CO)_9L]^-$ (e.g. with L = MeCN, PPh$_3$, Py etc.), by decarbonylation of 1 through thermal activation or by reaction with $Me_3NO \cdot 2H_2O$ [8].
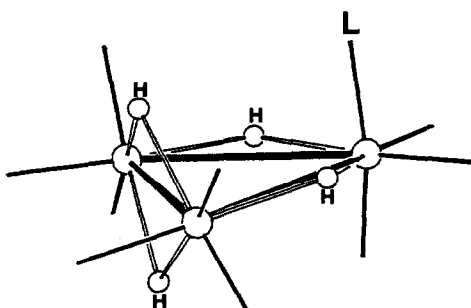

The anions $[Re_3(\mu\text{-}H)_4(CO)_9L]^-$ are of great interest because of the presence of both the reactive $Re(\mu\text{-}H)_2Re$ moiety and a bielectron-donor ligand L, on the third metal, which could be selected to be able to interact with the other molecular site. For instance, if L is an unsaturated neutral organic molecule, a hydride transfer from the basal unit might be expected. However it has so far proved impossible to bind such organic species directly to compound 1, and we are investigating the possibility of doing this by use of a $[Re_3(\mu\text{-}H)_4(CO)_9L]^-$ species in which L is particularly labile. Since nitriles are also too strongly bound to the metal to be displaced by unsaturated hydrocarbons * we have now tried to obtain derivatives containing more labile ligands L by bringing about decarbonylation reaction of 1 with $Me_3NO \cdot 2H_2O$ in solvents of low nucleophilicity such as THF or acetone. We report here the results of these investigations and the characterization and single-crystal X-ray analysis of an unusual product, the adduct $(NEt_4)[Re_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}O \cdots H \cdots NMe_3)]$.

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* The saturated reactive species $Re_3(\mu\text{-}H)_3(CO)_{10}(NCMe)_2$ gives many substitution derivatives, but no stable products with simple olefines or dienes [9].

Results and discussion

The reactions of the anion $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ (**1**), carried out at room temperature with a slight excess of $Me_3NO \cdot 2H_2O$, are rather slow. Monotoring by IR spectroscopy showed that compound **1** completely disappeared in ca. 1.5 h in acetone and in ca. 6 h in tetrahydrofuran solution. The ^1H NMR spectra of the reaction mixtures showed in all cases, independent of the solvent used, four signals in the hydridic region. The relative intensities and the chemical shift values of three of them (δ $-7.05(1)$, $-8.31(1)$ and $-9.08(2)$) are immediately indicative of a new member of the above mentioned [8] family of unsaturated anions $[Re_3(\mu\text{-}H)_4(CO)_9L]^-$. The L group in this case (responsible for a singlet in the ^1H NMR spectrum at δ 2.86, with intensity 9 with respect to the two hydridic signals of lower intensity) is a Me_3N molecule, formed by reduction of Me_3NO by a carbonyl ligand of compound **1**:

$$[Re_3(\mu\text{-}H)_4(CO)_{10}]^- + Me_3NO \rightarrow [Re_3(\mu\text{-}H)_4(CO)_9(NMe_3)]^- + CO_2$$
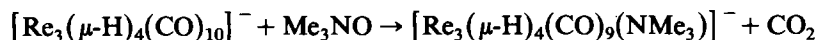
The formation of this species was not observed when the reaction was performed in acetonitrile solution or in the presence of good donor molecules, such as PR_3 or pyridine. The coordination of the amine in the present case confirms that the acetone and THF solvents have very weak donor properties, and therefore might provide the good leaving group that we need. Unfortunately, however, it is impossible by this method to obtain derivatives containing L ligands of lower donor ability than Me_3N.

The concentration of the anion $[Re_3(\mu\text{-}H)_4(CO)_9(NMe_3)]^-$ (**2**) in the various reaction mixtures was in the range 40–60%, as judged from the NMR data. The only other hydridic product present in significant concentration (15–30%) was a species responsible for a high field signal, at chemical shifts which varied somewhat from sample to sample (δ $-12.25/-12.50$). Selection of the low field resonances associated with this species was not possible, and so separation of products by crystallization of the reaction mixture was attempted. The cream crystals obtained were shown by X-ray analysis to contain an unusual adduct involving a hydrogen bond between Me_3N and the triangular cluster anion $[Re_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}OH)]^-$ (**3**).

Two sequences can be suggested to account for the formation of the triply-bridging hydroxyl group:
(1) The water present in the reagent $Me_3NO \cdot 2H_2O$ could give a $[Re_3(\mu\text{-}H)_4(CO)_9(OH_2)]^-$ species, by replacement of the labile amine in compound **2**. The coordination would increase the acidic character of the hydrogen atoms of the water molecule, making them able to react with one of the hydrides bridging the opposite Re–Re edge of the triangle, having a H^- polarization in the parent compound **1**. In this process hydrogen would be evolved, and the oxygen atom would become triply-bridging. A similar process has been previously observed for a closely related system [8]:

$$[Re_3(\mu\text{-}H)_4(CO)_9(NCMe)]^- + MeOH \rightarrow$$
$$[Re_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}OMe)]^- + H_2 + MeCN$$
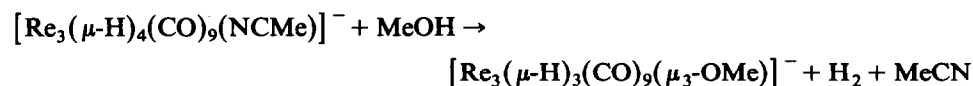
(2) The reagent Me_3NO, if present in excess, could occupy the coordination site left by the oxidized carbonyl ligand. Such a process was observed by Brown in the study

of the reaction of $Re_2(\mu\text{-}H)(\mu\text{-}NC_5H_4)(CO)_8$ with Me_3NO, and the derivative containing the coordinated amine oxide was characterized by X-ray analysis [10]. In our case the nitrogen of such ligand could be attacked by one of the hydrides bridging the opposite Re–Re edge, resulting in insertion of H into the very polarized N–O bond.

To decide between these two sequences, the following experiments were performed:

(a) Anhydrous Me_3NO was prepared by vacuum sublimation of the commercial hydrate and added in large excess to compound 1 in anhydrous THF. The NMR spectrum of the reaction mixture showed the predominant presence (about 90%) of a new unsaturated anion (three hydridic resonances at δ $-7.62(1)$, $-7.82(1)$ and $-8.58(2)$). It was identified as the intermediate $[Re_3(\mu\text{-}H)_4(CO)_9(ONMe_3)]^-$ (4), postulated in the second sequence, on the basis of the following evidence: (i) a singlet is present in the NMR spectrum, at δ 3.12 (cf. the signal at δ 3.11 in $Re_2(\mu\text{-}H)(\mu\text{-}NC_5H_4)(CO)_7(Me_3NO)$, ref. 10), in the correct intensity ratio with respect to the hydridic resonances; (ii) the formation of this species occurs with carbon dioxide evolution, so the formulation as an unsaturated species with L = $C(O)ONMe_3$ (the first intermediate usually postulated in the oxidation of carbonyl ligands by Me_3NO) can be excluded; (iii) treatment of compound 2 with Me_3NO affords this compound quantitatively and immediately, indicating that again in this case, as with the related $Re_2(\mu\text{-}H)(\mu\text{-}NC_5H_4)(CO)_7(Me_3N)$ [10], treatment with an excess of Me_3NO does not lead to the oxidation of a second carbonyl ligand but rather to the replacement of the labile Me_3N ligand.

(b) When a solution of 4 was kept in a sealed NMR tube, 4 was slowly transformed into a species giving a single resonance at δ -12.6, a value very close to that observed for the hydrides in the adduction between 3 and Me_3N. In this case the presence of an excess of amine oxide suggests that the triply-bridging OH of compound 3, formed as postulated in the second sequence, interacts with a Me_3NO molecule. In this process evolution of a small amount of H_2 was observed, and this can be associated with formation of decomposition products, caused by the presence of the large excess of amine oxide (the integrated NMR spectra provided evidence for the formation of non-hydridic derivatives).

(c) When the reaction was carried out in anhydrous deuteroacetone in a NMR tube, using the exact stoicheiometric amount of anhydrous Me_3NO only compound 2 (together with some compound 4 in the intermediate stages of the reaction) was observed. Even after 48 h only a very small amount of the adduct of compound 3 was present (see Fig. 1a).

(d) The reaction was also performed using a slight deficiency of $Me_3NO \cdot 2H_2O$ in undried deuteroacetone. Besides a little amount of unreacted 1 and some intermediate compound 4, compound 2 and the adduct of compound 3 were formed. Subsequent monitoring by NMR (Fig. 1b) revealed a decrease in the concentration of compound 2, accompanied by an increase of the concentration of the (μ_3-OH)-containing species. In addition there was significant H_2 evolution.

The observations in (a)–(c) provide strong support for the second proposed reaction sequence, while that in (d) is in accord with the first. Although definitive conclusions would require isotopic labelling experiments, we think that the results strongly suggest that both mechanisms can operate. Their relative significance is probably related to the ratio of water to amine oxide.
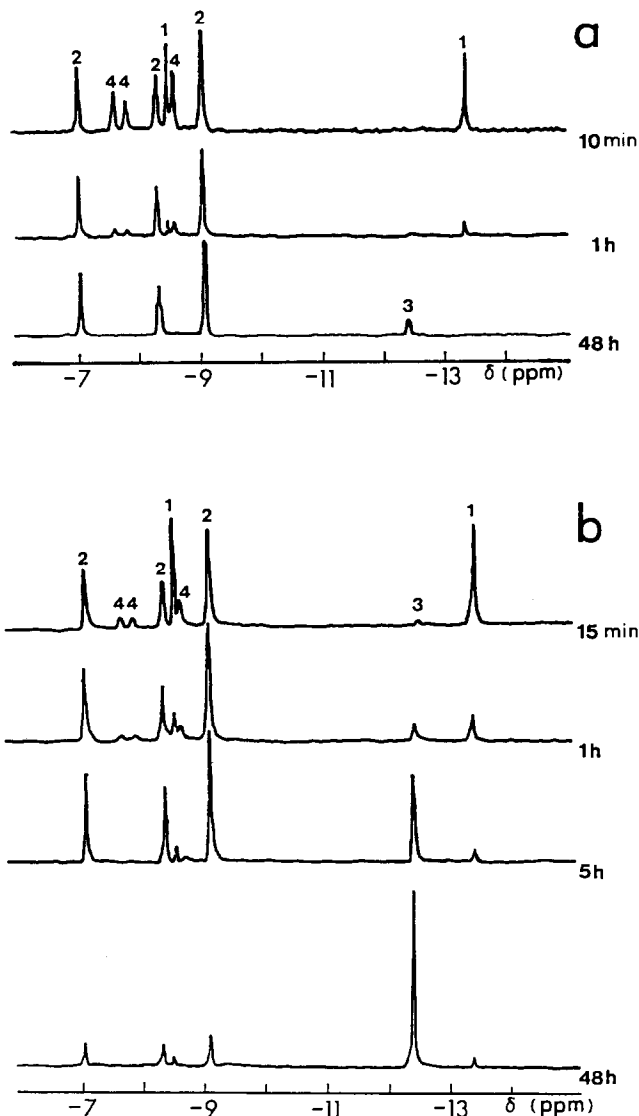
Fig. 1. (a) Monitoring by NMR spectroscopy of the progress of the reaction between $[Re_3(\mu\text{-H})_4(CO)_{10}]^-$ and stoicheiometric anhydrous Me_3NO, in anhydrous deuteroacetone (selected times). Only the hydridic region is depicted and each resonance is marked by the number of the corresponding compound. (b) The same as (a), in non-anhydrous conditions.

The ability of the triply-bridging OH ligand of compound 3 to enter into hydrogen bonds with various donor species (amine, amine oxide, water) accounts for the scattered values of chemical shift observed in the various reaction mixtures for the hydrides of compound 3 and also for the low reproducibility of the signals in the "organic" region of the NMR spectrum.

An alternative, more straightforward, route to compound 3 is provided by protonation with strong acids of the dianion $[Re_3(\mu\text{-H})_3(CO)_9(\mu_3\text{-O})]^{2-}$ (5), which

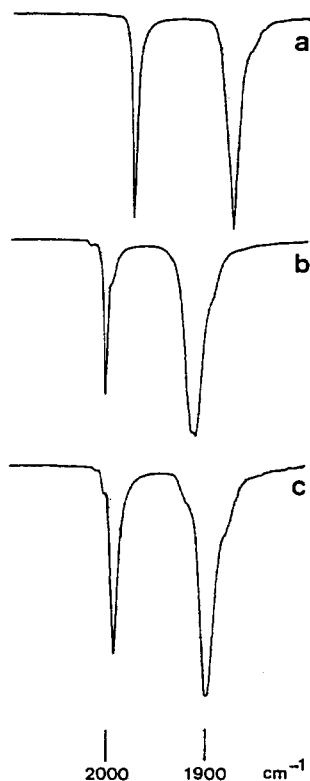Fig. 2. Carbonyl region of the IR spectra, in acetone solution, of (a) $[Re_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}O)]^{2-}$, (b) $[Re_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}OH)]^-$, (c) $[Re_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}O \cdots H \cdots NMe_3)]^-$.

contains a triply-bridging oxygen atom [11]. Treatment of an acetone solution of compound **5** with a stoicheiometric amount of trifluoromethanesulfonic acid immediately causes a shift to higher frequencies (about 35 cm^{-1}) of the two ν(CO) bands in the IR spectrum, in accord with the formation of the protonated compound **3** (see Fig. 2). In the NMR spectrum, the broad signal at δ -12.8 is replaced by a sharper singlet at δ -11.7. The reaction is readily reversed upon treatment with strong bases, such as NEt$_4$OH.

The adduct between compound **3** and trimethylamine exhibits ν(CO) frequencies (Fig. 2), and the δ values for the hydridic resonances are intermediate between those of the dianionic compound **5** and those of its conjugated acid **3**. Both "probes" of the electron density on the clusters thus suggest that the H-bonded adduct can be considered as a resonance hybrid between the two limiting forms $\{[Re_3(\mu_3\text{-}OH)]^- \cdots [NMe_3]\}$ and $\{[Re_3(\mu_3\text{-}O)]^{2-} \cdots [HNMe_3]^+\}$. In agreement with this, the adduct can be prepared in quantitative yields not only by addition of trimethylamine to a solution of compound **3**, but also be treatment of compound **5** with trimethylammonium chloride. In both cases the reactions are fast and quantitative, and the adduct shows a remarkable stability. In very dilute solution partial dissociation to compound **3** and amine is observed, as recognized by the appearance in the IR spectrum of the bands of compound **3**.

Description of the structure of [Re₃(μ-H)₃(CO)₉(μ₃-O · · · H · · · NMe₃)]⁻

Description of the structure of $[Re_3(\mu$-$H)_3(CO)_9(\mu_3$-$O \cdots H \cdots NMe_3)]^-$

The anion, illustrated in Fig. 3, lies on a crystallographic mirror plane; however, the idealized symmetry of the whole adduct is C_{3v}. It contains an equilateral triangle of rhenium atoms, each metal bearing three terminal CO groups. The three hydride ligands, directly located, are in bridging position on the Re_3 triangular edges. The triangle is capped by a μ_3-OH ligand connected through a strong hydrogen bond to a NMe_3 molecule. Bond distances and angles are given in Table 1.

The stereochemistry of the anion is of the type previously found in related species structurally characterized as $[Re_3(\mu$-$H)_3(CO)_9(\mu_3$-$X)]^-$ (X = OEt [12], SBu^t [13]) and the dianion $[Re_3(\mu$-$H)_3(CO)_9(\mu_3$-$O)]^{2-}$ [11], and also present in the anion $[Re_3(\mu$-$H)_3(CO)_9(\mu_3$-$OPh)]^-$ [3].

The Re–Re bond distances, mean 2.979 Å, are very similar to the corresponding values in the related anions containing an oxygen-donor triply-bridging ligand (see Table 2). These metal–metal bonds are determined by the balance between the lengthening effect due to the bridging hydride and the shortening caused by the other bridging group. In the μ_3-SBu^t derivative the larger covalent radius of S allows the attainment of longer Re–Re bonds, mean 3.091 Å [13].

The bond angles at the the Re atoms are quite similar in all three species listed in Table 2 involving a μ_3-O donor ligand: in the present adduct the mean values of the O–Re–C (axial) and of the O–Re–C(equatorial) angles are 167 and 99°, respectively.

The hydride ligands were directly located. Their bonding parameters are normal: the Re–H bonds, range 1.72(7)–1.96(7) Å, have a mean value, 1.83 Å, very close to the corresponding value in $Re_3(\mu$-$H)_3(CO)_{11}(PPh_3)$ [14], established by neutron diffraction. Also the mean Re–H–Re angle, 109°, is normal.
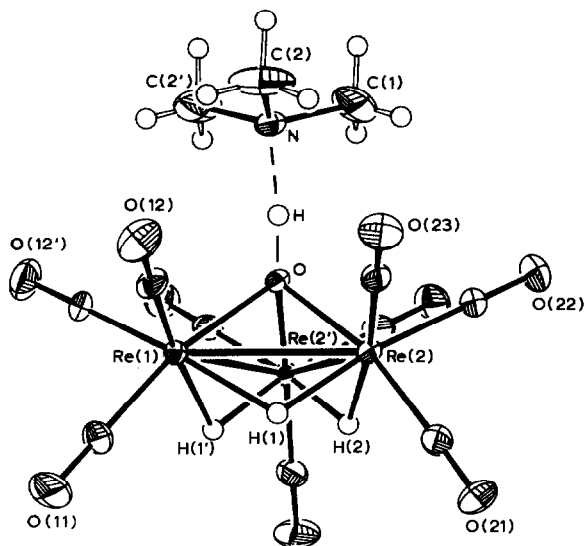
Fig. 3. A view of the anion $[Re_3(\mu$-$H)_3(CO)_9(\mu_3$-$O \cdots H \cdots NMe_3)]^-$. A crystallographic mirror plane passes through Re(1), O, N and the midpoint of the Re(2)–Re(2′) edge. The carbonyls are indicated by the labels of their oxygen atoms.

TABLE 1

BOND DISTANCES (Å) AND ANGLES (°) WITHIN [NEt$_4$][Re$_3$(μ-H)$_3$(CO)$_9$(μ_3-O $\cdots$ H $\cdots$ NMe$_3$)]

Re(1)–Re(2)	2.977(1)	C(11)–O(11)	1.144(13)
Re(2)–Re(2')	2.983(1)	C(12)–O(12)	1.145(10)
Re(1)–O	2.129(6)	C(21)–O(21)	1.156(9)
Re(2)–O	2.125(4)	C(22)–O(22)	1.149(9)
Re(1)–C(11)	1.883(11)	C(23)–O(23)	1.161(10)
Re(1)–C(12)	1.895(8)	O $\cdots$ N	2.502(10)
Re(2)–C(21)	1.899(8)	N–C(1)	1.50(2)
Re(2)–C(22)	1.914(8)	N–C(2)	1.44(1)
Re(2)–C(23)	1.917(9)		
Re(1)–H(1)	1.96(7)	*NEt$_4$$^+$-cation*	
Re(2)–H(1)	1.72(7)	N–C	1.48(2)–1.57(2)
Re(2)–H(2)	1.80(7)	C–C	1.57(2)–1.65(2)
Re(2)–Re(1)–C(11)	125.6(3)	C(21)–Re(2)–C(23)	90.9(4)
Re(2)–Re(1)–C(12)	95.2(3)	C(21)–Re(2)–H(1)	86(2)
Re(2)–Re(1)–C(12')	144.9(2)	C(21)–Re(2)–H(2)	90(3)
Re(1)–Re(2)–C(21)	124.3(2)	C(22)–Re(2)–C(23)	91.2(4)
Re(1)–Re(2)–C(22)	144.2(2)	C(22)–Re(2)–H(1)	169(3)
Re(1)–Re(2)–C(23)	96.4(2)	C(22)–Re(2)–H(2)	97(4)
Re(2')–Re(2)–C(21)	124.2(3)	C(23)–Re(2)–H(1)	99(2)
Re(2')–Re(2)–C(22)	94.9(3)	C(23)–Re(2)–H(2)	172(4)
Re(2')–Re(2)–C(23)	144.3(2)	H(1)–Re(2)–H(2)	73(5)
O–Re(1)–C(11)	168.3(4)	Re(1)–O–Re(2)	88.8(2)
O–Re(1)–C(12)	99.4(3)	Re(2)–O–Re(2')	89.2(2)
O–Re(1)–H(1)	78(2)	Re(1)–O $\cdots$ N	122.9(3)
C(11)–Re(1)–C(12)	88.6(3)	Re(2)–O $\cdots$ N	127.5(2)
C(11)–Re(1)–H(1)	92(2)	Re(1)–C(11)–O(11)	180(1)
C(12)–Re(1)–C(12')	93.0(5)	Re(1)–C(12)–O(12)	178.5(8)
C(12)–Re(1)–H(1)	97(2)	Re(2)–C(21)–O(21)	176.9(8)
C(12)–Re(1)–H(1')	170(2)	Re(2)–C(22)–O(22)	179.4(8)
H(1)–Re(1)–H(1')	74(4)	Re(2)–C(23)–O(23)	179.4(7)
O–Re(2)–C(21)	166.5(3)	Re(1)–H(1)–Re(2)	108(4)
O–Re(2)–C(22)	98.7(3)	Re(2)–H(2)–Re(2')	112(6)
O–Re(2)–C(23)	98.9(3)	O $\cdots$ N–C(1)	104.1(8)
O–Re(2)–H(1)	84(2)	O $\cdots$ N–C(2)	108.9(6)
O–Re(2)–H(2)	79(3)	C(1)–N–C(2)	112(1)
C(21)–Re(2)–C(22)	90.3(3)	C(2)–N–C(2')	111(2)

TABLE 2

COMPARISON OF THE MEAN BOND DISTANCES (Å) IN RELATED TRIANGULAR RHENIUM CLUSTERS (see text)

	Present adduct	μ_3-OEt monoanion	μ_3-O dianion	μ_3-SBu monoanion
Re–Re	2.979	2.994	2.968	3.091
Re–O (S)	2.13	2.17	2.12	2.393
Re–C	1.90	1.86	1.88	1.89
C–O	1.15	1.19	1.18	1.17

The mean Re–O bond length, 2.126 Å, is slightly longer than in the μ_3-O dianion but shorter than in the μ_3-OEt monoanion. These data, as well as other parameters reported in Table 2, suggest in accord with the spectroscopic results (see above), that the present adduct has an anionic charge intermediate bewteen one and two on the cluster because of the strong hydrogen bond to the amine.

The O $\cdots$ H $\cdots$ N hydrogen bond is particularly strong and almost linear. The O $\cdots$ N distance of 2.502(10) Å, ca. 0.4 Å less than the sum of the Van der Waals radii, is among the shortest interactions of this kind, and close to the values expected for a symmetric bond. This strong bond accounts for the great stability of the adduct in solution.

Experimental

The reactions were performed under nitrogen by Schlenk techniques, in solvents dried and deoxygenated by standard methods.

[NEt$_4$][Re$_3$(μ-H)$_4$(CO)$_{10}$] and [NEt$_4$]$_2$[Re$_3$(μ-H)$_3$(CO)$_9$(μ_3-O)] were prepared as previously described [7,11]. Me$_3$NO · 2H$_2$O was a Fluka reagent; it was dried (when appropriate - see below) by sublimation under vacuum (0.1 Torr) at about 100°C; the mass of the hydrate salt at first melted, then, after the water was removed, solidified, and finally sublimed. Infrared spectra were recorded on a Perkin–Elmer 781 grating spectrophotometer, in 0.1 mm CaF$_2$ cells, and were calibrated against polystyrene film absorptions. NMR spectra were recorded on a Bruker WP 80 spectrometer. Gas analyses were performed on a Carlo Erba HRGC 5340 instrument, equipped with a 2 m molecular sieve column, with Ar and He, respectively, as carriers for H$_2$ and CO detection. The presence of CO$_2$ was detected by injecting samples of reaction gas into a Carlo Erba HRGC 4000 instrument equipped with a VG Micromass SX 200 quadrupole.

Reactions of [NEt$_4$][Re$_3$(μ-H)$_4$(CO)$_{10}$] with Me$_3$NO · 2H$_2$O

(a) A solution of 20 mg (0.021 mmol) of [NEt$_4$][Re$_3$(μ-H)$_4$(CO)$_{10}$] in ca. 3 ml of the appropriate solvent (acetone or tetrahydrofuran) was treated with 2.5 mg (0.023 mmol) of Me$_3$NO · 2H$_2$O and the suspension was stirred at RT until the IR spectrum showed the complete disappearance of the parent compound (about 1.5 h in acetone and 6 h in THF). The analysis of the evolved gases showed the presence of H$_2$ and CO$_2$. The solvent was removed under reduced pressure and the residue analyzed by ^{1}H NMR spectroscopy, which revealed the presence mainly of compound 2 (40–60%, on the basis of the integration vs. the signals of the cation NEt$_4$$^+$) and of the adduct between NMe$_3$ and compound 3 (ca. 15–30%). The mixture obtained from the reaction in acetone was then crystallized by slow diffusion of diethyl ether into a dichloromethane solution. A small amount of [NEt$_4$][Re$_3$(μ-H)$_3$(CO)$_9$(μ_3-O $\cdots$ H $\cdots$ NMe$_3$)] was obtained as cream crystals. IR: ν(CO) (acetone): 1994s and 1900vs cm^{-1}; ^{1}H NMR (CD$_2$Cl$_2$): δ 2.68 (s, 9H, 3Me), −12.45 (s, 3H, ReH). When the product was heated, decomposition started at about 150°C. (Found: C, 23.65; H, 3.15; N, 2.60. C$_{20}$H$_{33}$N$_2$O$_{10}$Re$_3$ calcd.: C, 23.53; H, 3.23; N, 2.74%). Compound 2: ^{1}H NMR (deuteroacetone): δ 2.86 (s, 9H, 3 Me), −7.05 (s, 1H, ReH), −8.31 (t, 1H, ReH), −9.08 (d, 2H, ReH); J(HH) 2 Hz.

(b) A solution of 16 mg (0.0165 mmol) of [NEt$_4$][Re$_3$(μ-H)$_4$(CO)$_{10}$] in 0.5 ml of deuteroacetone in a NMR tube, was treated under N$_2$ with 1.8 mg (0.0162 mmol) of

Me₃NO · 2H₂O, and the progress of the reaction was monitored by NMR spectroscopy (see Fig. 1b). Initially compound **2** was the main product (75% after 3 h), but at longer times its concentration decreased, while that of the adduct of compound **3** continuously increased, reaching ca. 60% after 48 h. Significant H_2 evolution was detected by GLC. Initially compound **4** was also present (max. 15%).

Reactions of [NEt₄][Re₃(μ-H)₄(CO)₁₀] with anhydrous Me₃NO

(a) An 18 mg (0.019 mmol) sample of [NEt₄][Re₃(μ-H)₄(CO)₁₀] was placed under N_2 in a Schlenk tube and carefully dried, then dissolved in 5 ml of tetrahydrofuran, which was distilled directly into the vessel from sodium benzophenone ketyl. Freshly sublimed Me₃NO (4.6 mg, 0.061 mmol) was added and the mixture was stirred for 2.5 h. Only CO_2 was evolved. The solvent was removed under reduced pressure and the residue was dissolved in CD_2Cl_2 (dried over molecular sieves) and the solution was transferred to an NMR tube, which was then sealed. The NMR spectrum showed that compound **4** was the main component of the mixture (ca. 90%), the other component (ca. 10%) being an adduct of compound **3** with Me₃NO. When the solution was kept at room temperature the concentration of the adduct of compound **3** increased (ca. 60% after one night).

Compound **4**: ¹H NMR (deuteroacetone): δ 3.12 (s, 9H, 3 Me), −7.62 (s, 1H, ReH), −7.82 (t, 1H, ReH), −8.58 (d, 2H, ReH); *J*(HH) 2 Hz.

(b) Freshly sublimed Me₃NO (1 mg, 0.0133 mmol) was dissolved in 0.5 ml of deuteroacetone (dried over molecular sieves) in a NMR tube. The solution was treated with 13 mg (0.0134 mmol) of [NEt₄][Re₃(μ-H)₄(CO)₁₀]. The progress of the reaction was monitored by NMR spectroscopy (Fig. 1a), which showed the formation of compound **2** (90% after 4 h), with the adduct of compound **3** present only in very low concentration (ca. 5% after 48 h). In the intermediate stages of the reaction, compound **4** was also present.

Synthesis of [NEt₄][Re₃(μ-H)₃(CO)₉(μ₃-OH)]

A solution of 22 mg (0.020 mmol) of [NEt₄]₂[Re₃(μ-H)₃(CO)₉(μ₃-O)], in 2 ml of acetone, was treated with 2 μl (0.023 mmol) of CF₃SO₃H and the mixture was stirred at room temperature for 5 min. Water was then added, causing the precipitation of a white powder, which was dried over P₂O₅ under vacuum. IR: ν(CO) 2008s, 1914vs (acetone); NMR δ(hydrides) −11.7 (deuteroacetone).

Synthesis of [NEt₄][Re₃(μ-H)₃(CO)₉(μ₃-O ··· H ··· NMe₃)]

(a) A solution of 20 mg (0.021 mmol) of [NEt₄][Re₃(μ-H)₃(CO)₉(μ₃-OH)], in 3 ml of acetone was treated with a few drops of cold NMe₃. The IR spectrum showed the immediate formation of the adduct [Re₃(μ-H)₃(CO)₉(μ₃-O ··· H ··· NMe₃)]⁻. The addition of a large excess of amine caused no further change in the spectrum. The product was precipitated by addition of n-heptane.

(b) A solution of 20 mg (0.018 mmol) of [NEt₄]₂[Re₃(μ-H)₃(CO)₉(μ₃-O)], in 2 ml of acetone was treated with 2 mg (0.021 mmol) of Me₃NHCl. The IR spectrum showed the immediate formation of the adduct [Re₃(μ-H)₃(CO)₉(μ₃-O ··· H ··· NMe₃)]⁻. The product was precipitated by addition of n-heptane.

X-Ray analysis

Crystal data. $C_{20}H_{33}N_2O_{10}Re_3$, $M = 1020.1$, monoclinic, space group $P2_1/m$ (no. 11), a 8.576(3), b 20.442(4), c 8.748(3) Å, β 108.08(4)°, U 1457.8 Å³, $Z = 2$,

$D_c = 2.324$ g cm^{-3}, $F(000) = 944$, Mo-K_α radiation (λ 0.71073 Å), μ(Mo-K_α) 126.44 cm^{-1}.

Intensity measurements. A crystal sample of dimensions 0.14 × 0.20 × 0.23 mm was mounted on a glass fibre in the air. The intensities were collected on an Enraf–Nonius CAD4 automatic diffractometer, using graphite-monochromatized Mo-K_α radiation. The setting angles of 25 random intense reflections ($16 < 2\theta < 25°$) were used to determine accurate cell constants and orientation matrix by least-squares. The data collection was performed by the ω-scan method, within the limits $3 < \theta < 26°$. A variable scan-speed (from 2 to 20°/min) and a variable scan-range of $(1.0 + 0.35 \tan \theta)$ were used, with a 25% extension at each end of the scan-range for background determination. The total number of reflections measured was 2961. Three standard intense reflections, monitored every 3 h, revealed a total decay of ca. 4% by the end of the collection. The intensities were corrected for Lorentz, polarization and decay effects. An empirical absorption correction was applied to the data set, based on ω-scans (0–360° every 10°) of suitable reflections with χ values close to 90°; the relative transmission factors had values in the ranges 1.00–0.72. A set of 2085 independent significant reflections, with $I > 3\sigma(I)$, was used in the structure solution and refinements.

Structure solution and refinements. All computations were performed on a PDP 11/34 computer, using the Enraf–Nonius Structure Determination Package (SDP) and the physical constants therein tabulated.

TABLE 3

FINAL POSITIONAL PARAMETERS WITHIN [NEt$_4$][Re$_3(\mu$-H)$_3$(CO)$_9(\mu_3$-O $\cdots$ H $\cdots$ NMe$_3$)]

Atom	x	y	z
Re(1)	0.33850(5)	0.250	0.20279(4)
Re(2)	0.02246(3)	0.17703(2)	0.10598(3)
O	0.1274(7)	0.250	−0.0047(7)
C(11)	0.494(1)	0.250	0.409(1)
O(11)	0.587(1)	0.250	0.535(1)
C(12)	0.4608(9)	0.1827(5)	0.144(1)
O(12)	0.5323(8)	0.1411(4)	0.1087(8)
C(21)	−0.054(1)	0.1248(5)	0.2476(9)
O(21)	−0.1001(9)	0.0955(4)	0.3381(7)
C(22)	−0.186(1)	0.1690(5)	−0.0567(9)
O(22)	−0.3107(8)	0.1636(4)	−0.1543(8)
C(23)	0.103(1)	0.1009(5)	0.0271(9)
O(23)	0.1510(9)	0.0545(3)	−0.0205(8)
N	0.145(1)	0.250	−0.285(1)
C(1)	−0.031(2)	0.250	−0.390(2)
C(2)	0.229(2)	0.1920(7)	−0.308(1)
NT ^{a}	0.500	0.000	0.500
CT(1)	0.510(2)	0.0306(9)	0.342(2)
CT(2)	0.447(2)	0.0508(9)	0.595(2)
CT(3)	0.668(2)	−0.0305(9)	0.602(2)
CT(4)	0.378(2)	−0.0574(9)	0.461(2)
CT(5)	0.566(1)	−0.0211(6)	0.236(1)
CT(6)	0.197(1)	−0.0295(6)	0.354(1)
H(1)	0.190(9)	0.192(4)	0.271(8)
H(2)	−0.02(2)	0.250	0.20(1)

^{a} NT and CT(i) are the cationic atoms.

The structure solution was determined from a three-dimensional Patterson map, which gave the positions of the Re atoms. A subsequent difference-Fourier map showed the locations of all the non-hydrogen atoms. The anion lies on a crystallographic mirror plane containing Re(1), the middle point of the Re(2)–Re(2') edge and the triple bridging O atom; the N atom of the adduct NMe_3 and one of its C atoms also lie in the same plane. The tetraethylammonium cation was found to be disordered, on an inversion centre (1/2,0,1/2), with the methylene carbon atoms doubled to give a distorted cube of half-carbons around the nitrogen atom.

The refinements were carried out by full-matrix least-squares. Anisotropic thermal factors were assigned to all atoms except the cationic ones. The hydrogen atoms of the trimethylammine were located in their idealized positions (C–H 0.95 Å, B 5.0 $Å^2$), after each cycle of refinement, but not refined. The cationic hydrogens, were ignored because of the disorder.

The final difference-Fourier maps were rather flat showing residual peaks not exceeding ca. 1 e $Å^{-3}$. Two peaks were observed at positions appropriate for hydrides in bridging positions. They were refined to convergence, giving acceptable bond parameters. The hydrogen atom of the O $\cdots$ H $\cdots$ N hydrogen bond was not located.

Weights were assigned according to the formula $w = 4F_0^2/\sigma(F_0^2)^2$, where $\sigma(F_0^2) = [\sigma(I)^2 + (pI)^2]^{1/2}/L_p$ (I and L_p being the integrated intensity and the Lorentz-polarization correction, respectively); p was taken as 0.04. The final values of the conventional agreement indices R and R_w were 0.026 and 0.034, respectively.

The final positional parameters are given in Table 3. The final list of observed and calculated structure factors and a Table of thermal parameters can be obtained from the authors.

Acknowledgment

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