Synthesis and Characterization of a Family of Nitrile-substituted Triangular Hydridocarbonyl Rhenium Clusters, [Re$_3$(μ-H)$_3$(CO)$_{12-n}$(NCMe)$_n$] (n = 1–3). X-Ray Crystal Structures of [Re$_3$(μ-H)$_3$(CO)$_{11}$(NCMe)] and [Re$_3$(μ-H)$_3$(CO)$_9$(NCMe)$_3$]

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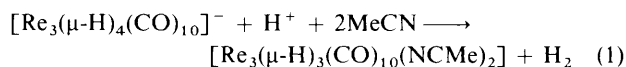**Gianfranco Ciani,* Massimo Moret, and Angelo Sironi**
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Different routes to the new family of cluster compounds [Re$_3$(μ-H)$_3$(CO)$_{12-n}$(NCMe)$_n$] (n = 1—3), containing substitution labile nitrile ligands, are described. The interconversions within the members of the family have been investigated and the stepwise replacement of the MeCN groups with CO has been demonstrated. The reaction of [Re$_3$(μ-H)$_3$(CO)$_{12}$] with Me$_3$NO in controlled ratios (1:1 or 1:2) for progressive decarbonylation, in the presence of nitrile, is found not to be selective, and leads to mixtures of substituted derivatives. On the contrary, with a 1:3 ratio the trisubstituted derivative is obtained quantitatively. The crystal structures of the derivatives with n = 1 **(1)** and 3 **(3)** are reported. Compound **(1)** crystallizes in the monoclinic space group $P2_1/n$, with a = 8.417(2), b = 15.282(4), c = 16.540(4) Å, β = 97.70(2)°, and Z = 4. Compound **(3)** gives triclinic crystals, space group $P\bar{1}$, with a = 8.761(2), b = 9.403(2), c = 15.079(3) Å, α = 92.45(2), β = 94.02(2), γ = 108.38(2)°, and Z = 2. The structures were solved by Patterson and Fourier methods, and refined by full-matrix least squares on the basis of 1 121 **(1)** and 3 129 **(3)** significant counter data, to final values of the conventional R index of 0.035 **(1)** and 0.019 **(3)**, respectively. Both structures contain an almost equilateral Re$_3$ triangle, with all the edges bridged by hydride ligands. The mean values of the Re–Re bonds are 3.258 and 3.284 Å for compounds **(1)** and **(3)**, respectively. The acetonitrile ligands always occupy axial positions. N.m.r. data in solution have shown the presence of only one isomer for each compound.

Much of the current interest in metal cluster complexes arises from their potential role as models of metallic surfaces in catalysis.[1] The peculiar activity of such surfaces being related to their co-ordinative unsaturation, the cluster species more suitable as models are either the unsaturated ones or those containing substitution labile ligands. In the field of rhenium hydridocarbonyl clusters, we have been studying the chemistry of unsaturated species[2,3] for a long time and have recently reported the synthesis of a whole family of unsaturated triangular cluster anions [Re$_3$(μ-H)$_4$(CO)$_9$L]$^-$ (L = two-electron donor ligand).[4] We present here the synthesis of another series of triangular hydridocarbonyl rhenium clusters, the neutral complexes [Re$_3$(μ-H)$_3$(CO)$_{12-n}$(NCMe)$_n$] [n = 1—3, **(1)**—**(3)**, respectively] in which the presence of the labile acetonitrile ligands provides a great synthetic versatility. Some preliminary work has already been published,[5] including the structural characterization of the bis(acetonitrile) derivative **(2)**.
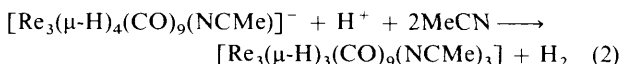
Results and Discussion

Treatment of the unsaturated (46 valence electrons, v.e.s) anion [Re$_3$(μ-H)$_4$(CO)$_{10}$]$^-$ **(4)** with 1 equivalent of the strong, non-co-ordinating acid CF$_3$SO$_3$H, in acetonitrile, results in H$_2$ evolution, with co-ordination of two solvent molecules in *trans* diaxial positions on two vertices of the triangular metal cluster [reaction (1)].[5] This reaction was rationalized as a two-step

$$[\text{Re}_3(\mu\text{-H})_4(\text{CO})_{10}]^- + \text{H}^+ + 2\text{MeCN} \longrightarrow$$
$$[\text{Re}_3(\mu\text{-H})_3(\text{CO})_{10}(\text{NCMe})_2] + \text{H}_2 \quad (1)$$

process: (*i*) attack of the strong acid on one of the hydrides of the unsaturated Re(μ-H)$_2$Re moiety, with H$_2$ evolution and formation of a 'superunsaturated' species 'Re$_3$(μ-H)$_3$(CO)$_{10}$' (44 v.e.s); (*ii*) stabilization of this species by co-ordination of two solvent molecules. In accord with this mechanism, the compounds [Re$_3$(μ-H)$_3$(CO)$_{10}$L$_2$] or [Re$_3$(μ-H)$_3$(μ-X)-(CO)$_{10}$]$^-$ were obtained by this route in the presence of donor groups L or X$^-$, respectively.

We have recently synthesized the unsaturated anion [Re$_3$-(μ-H)$_4$(CO)$_9$(NCMe)]$^-$ **(5)**[4] by treatment of **(4)** with 1 equivalent of trimethylamine oxide in acetonitrile. In this complex a solvent molecule has replaced one of the mutually *trans* CO ligands on the Re(CO)$_4$ unit of the parent anion **(4)**. Compound **(5)** not only contains the labile MeCN ligand, but still retains the unsaturation of **(4)**. It is therefore expected to show a reactivity at the Re(μ-H)$_2$Re unsaturated site comparable with that of the parent anion **(4)**.

We therefore treated compound **(5)**, in acetonitrile solution, with 1 equivalent of CF$_3$SO$_3$H. The evolution of H$_2$ was recognized by gas chromatographic analysis and the spectroscopic characterization of the reaction product confirmed the expected formation of [Re$_3$(μ-H)$_3$(CO)$_9$(NCMe)$_3$], **(3)**, according to reaction (2). In its ^{1}H n.m.r. spectrum two hydridic

$$[\text{Re}_3(\mu\text{-H})_4(\text{CO})_9(\text{NCMe})]^- + \text{H}^+ + 2\text{MeCN} \longrightarrow$$
$$[\text{Re}_3(\mu\text{-H})_3(\text{CO})_9(\text{NCMe})_3] + \text{H}_2 \quad (2)$$

resonances were present (ratio 1:2, see Table 4), both at δ values quite close to that found[5] for the hydride bridging two

$Re(CO)_3(NCMe)$ moieties in $[Re_3(\mu-H)_3(CO)_{10}(NCMe)_2]$. Two resonances were also present (ratio 3:6) attributable to the methyl groups of the acetonitrile ligands. The C_s symmetry indicated in solution by the n.m.r. data is in accordance with the ligand stereochemistry found in the solid state by a single-crystal X-ray investigation (Figure 2, see below), with the three acetonitrile molecules co-ordinated in axial positions, one on each rhenium atom.

Under CO, in a solvent different from acetonitrile, compound (3) was easily converted (1 h at room temperature) into the bis(acetonitrile) derivative (2). This, in turn, was converted more slowly (about 24 h) into the monoacetonitrile derivative (1). The substitution of the last nitrile molecule by carbon monoxide was still more difficult and was better accomplished under CO pressure (5—10 atm, ca. 5×10^5—10^6 Pa), leading finally to the neutral species $[Re_3(\mu-H)_3(CO)_{12}]$, (6). Both statistical and electronic factors co-operate in determining the relevant decrease in the rates of the successive substitution steps, in the sequence (3) $\longrightarrow$ (2) $\longrightarrow$ (1) $\longrightarrow$ (6).

The ability of Me_3NO to promote substitution of a carbonyl ligand by an acetonitrile molecule suggested to us the possibility of an alternative stepwise synthesis of the series of $[Re_3(\mu-H)_3(CO)_{12-n}(NCMe)_n]$ complexes, using as starting material $[Re_3(\mu-H)_3(CO)_{12}]$ (6), which is more easily available than compound (4).[6] The addition of n equivalents of trimethylamine oxide to compound (6) is expected to cause the progressive substitution of n carbonyl ligands with n acetonitrile molecules: if a selectivity comparable with that observed in the carbonylation of (3) is operative, the stepwise synthesis (6) $\longrightarrow$ (1) $\longrightarrow$ (2) $\longrightarrow$ (3) would be obtained. This approach however failed. Mixtures of compounds (1), (2), and (3) were obtained using 1 or 2 equivalents of trimethylamine oxide, as shown by n.m.r. analyses. Using 1 equivalent, for instance, only ca. 40% of the monosubstituted derivative (1) was obtained, the other component of the mixture being the starting compound (6) and the disubstituted derivative (2), in comparable amount, plus a few per cent of (3). Analogously, in the mixture obtained using 2 equivalents of the oxidizing agent, only ca. 70% of (2) was present, together with equal amounts of (1) and (3). On the other hand, with 3 equivalents the synthesis of compound (3) was quantitative, while the use of an excess of Me_3NO did not cause any further substitution.

The above results indicate that the presence of a co-ordinated acetonitrile molecule prevents the attack of the amine oxide on the carbonyls bound to the same rhenium atom, very likely because of electronic factors: a donor nitrile not only raises the electron density on the metal, but also replaces one axial carbonyl, which is more positively polarized, thus making more difficult the nucleophilic attack by Me_3NO. The rate of this attack is affected only slightly by the presence of MeCN groups on adjacent vertices.

In this way it is therefore possible to synthesize in good yields only compound (3) according to reaction (3), which goes to

$$[Re_3(\mu-H)_3(CO)_{12}] + 3Me_3NO + 3MeCN \longrightarrow$$
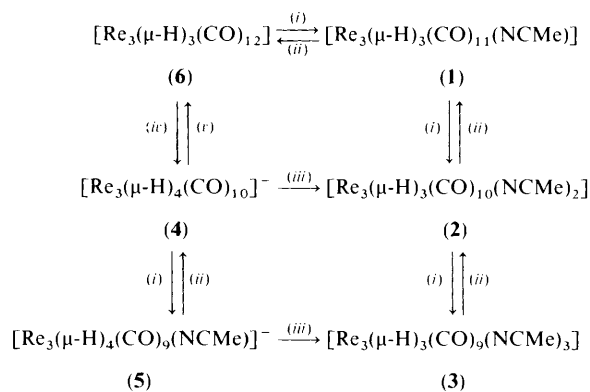$$[Re_3(\mu-H)_3(CO)_9(NCMe)_3] + 3CO_2 + 3NMe_3 \quad (3)$$

completion in about 1 h, at room temperature. Care must be taken to avoid the presence of moisture, because compound (3) shows some reactivity toward water. The nature of this reaction is at present under investigation.

In the related reaction of $[Os_3(CO)_{12}]$ with Me_3NO in acetonitrile, only the mono- and bis-acetonitrile derivatives could be obtained.[7] The failure to obtain $[Os_3(CO)_9(NCMe)_3]$ was explained in terms of the decreased tendency of the carbon atoms of the $Os(CO)_4$ group to undergo nucleophilic attack after the introduction of two donor acetonitrile molecules. In the case of the rhenium complexes, the three hydride ligands

could accept electron density from the nitriles, making the C atoms of the $Re(CO)_4$ moiety of (2) still susceptible to nucleophilic attack.

Taking into account that the unsaturated anion (4) can be synthesized from (6), in a two-step process,[2] the reactions described here can be summarized as in the Scheme.

$$[Re_3(\mu-H)_3(CO)_{12}] \underset{(ii)}{\overset{(i)}{\rightleftharpoons}} [Re_3(\mu-H)_3(CO)_{11}(NCMe)]$$

(6)   (1)

$(iv) \Big\updownarrow (v)$ $(i) \Big\updownarrow (ii)$

$$[Re_3(\mu-H)_4(CO)_{10}]^- \overset{(iii)}{\longrightarrow} [Re_3(\mu-H)_3(CO)_{10}(NCMe)_2]$$

(4)   (2)

$(i) \Big\updownarrow (ii)$ $(i) \Big\updownarrow (ii)$

$$[Re_3(\mu-H)_4(CO)_9(NCMe)]^- \overset{(iii)}{\longrightarrow} [Re_3(\mu-H)_3(CO)_9(NCMe)_3]$$

(5)   (3)

Scheme. (i) Me_3NO, MeCN; (ii) CO, CH_2Cl_2; (iii) CF_3SO_3H, MeCN; (iv) NaOH–EtOH + H_2, 100 atm, 100 °C; (v) CF_3SO_3H, CO

The availability of compounds (1)—(3) will now make possible the selective synthesis of a wide variety of substitution derivatives of $[Re_3(\mu-H)_3(CO)_{12}]$, either with neutral two-electron donors L or with anionic groups X^-. Also cluster-growth reactions will be possible, such as that already accomplished[8] by treatment of compound (2) with the anion $[ReH_2(CO)_4]^-$. However, reactions with unsaturated hydrocarbons, which should be of greater interest in view of the supposed role of these compounds as models of metallic surfaces in catalysis, appear to be quite difficult. The major cause is probably the higher stability, in rhenium carbonyl complexes, of the Re–NCMe bond in comparison with the Re–olefin inter-actions. Significantly, the μ-hydrido-μ-alkenyl-dirhenium octa-carbonyl compounds obtained photochemically by Nubel and Brown[9] were readily transformed into $[Re_2(CO)_8(NCMe)_2]$ by dissolving them in acetonitrile.

Description of the Structures.—The structures of compounds (1) and (3) are illustrated in Figures 1 and 2, respectively; bond distances and angles are given in Tables 1 (1) and 2 (3). Both species, of idealized C_s-m symmetry, contain a triangle of rhenium atoms, with the three edges bridged by hydride ligands. All the metal atoms bear four terminally bonded (CO or MeCN) ligands, so that the co-ordination around each Re atom is nearly octahedral.

The gross structural features are those expected for $[Re_3-(\mu-H)_3(CO)_{12}]$ (6), and observed in the structure of $[Mn_3-(\mu-H)_3(CO)_{12}]$,[10] with replacement of one carbonyl ligand in (1) and of three carbonyl ligands in (3), on different metals, by acetonitrile molecules, which occupy axial co-ordination positions. In (3) two nitriles lie on the same side and the third one on the opposite side of the Re_3 triangle. The structure of the other member of this family, compound (2), was briefly described in a previous paper;[5] it showed a C_2 idealized symmetry, with the two MeCN ligands axially co-ordinated to two rhenium atoms in mutually *trans* direction. Unfortunately the structures of (1) and (2) are not of such a good quality to allow a detailed comparative analysis of the bonding parameters within the family. In Table 3 some mean bond distances are reported.

The values of the Re–N bond lengths, 2.08—2.16 Å within the whole family, fall in the normal range, and the Re–N–C
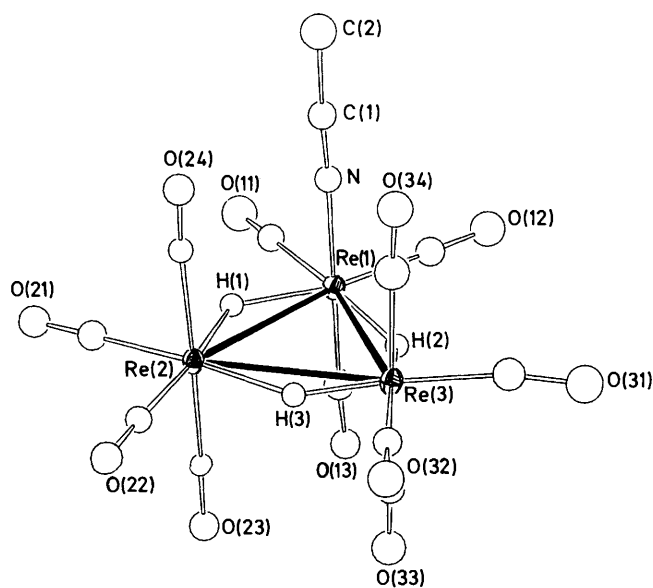
Figure 1. A view of $[Re_3(\mu\text{-H})_3(CO)_{11}(NCMe)]$ (1). The CO groups are indicated by the labels of their oxygen atoms
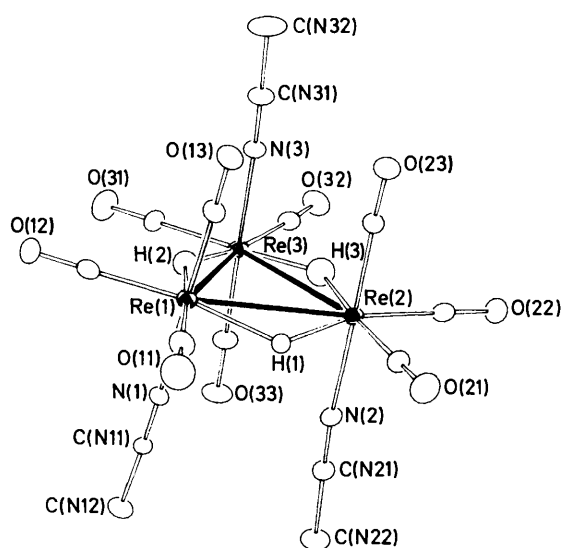

Figure 2. A view of $[Re_3(\mu\text{-H})_3(CO)_9(NCMe)_3]$ (3)

Table 1. Bond distances (Å) and angles (°) within $[Re_3(\mu\text{-H})_3\text{-}(CO)_{11}(NCMe)]$ (1)

Re(1)–Re(2)	3.249(2)	Re(3)–C(33)	2.00(4)
Re(1)–Re(3)	3.243(2)	Re(3)–C(34)	1.96(5)
Re(2)–Re(3)	3.281(2)	Re(3)–H(2)	1.64(24)
Re(1)–C(11)	1.90(3)	Re(3)–H(3)	1.58(19)
Re(1)–C(12)	1.86(3)	C(11)–O(11)	1.19(4)
Re(1)–C(13)	1.86(4)	C(12)–O(12)	1.20(3)
Re(1)–N	2.08(3)	C(13)–O(13)	1.16(4)
Re(1)–H(1)	1.77(19)	C(21)–O(21)	1.14(3)
Re(1)–H(2)	1.83(23)	C(22)–O(22)	1.18(3)
Re(2)–C(21)	1.90(3)	C(23)–O(23)	1.16(3)
Re(2)–C(22)	1.89(3)	C(24)–O(24)	1.08(3)
Re(2)–C(23)	2.00(3)	C(31)–O(31)	1.21(4)
Re(2)–C(24)	2.02(3)	C(32)–O(32)	1.16(4)
Re(2)–H(1)	1.88(22)	C(33)–O(33)	1.08(4)
Re(2)–H(3)	1.91(21)	C(34)–O(34)	1.14(4)
Re(3)–C(31)	1.86(4)	N–C(1)	1.16(4)
Re(3)–C(32)	1.88(3)	C(1)–C(2)	1.50(5)
Re(2)–Re(1)–C(11)	102.1(9)	Re(1)–Re(3)–C(31)	103.2(11)
Re(2)–Re(1)–C(12)	164.9(10)	Re(1)–Re(3)–C(32)	161.4(9)
Re(2)–Re(1)–C(13)	91.1(10)	Re(1)–Re(3)–C(33)	89.3(10)
Re(2)–Re(1)–N	87.3(6)	Re(1)–Re(3)–C(34)	89.6(12)
Re(3)–Re(1)–C(11)	162.6(9)	Re(2)–Re(3)–C(31)	162.9(11)
Re(3)–Re(1)–C(12)	104.5(10)	Re(2)–Re(3)–C(32)	101.6(9)
Re(3)–Re(1)–C(13)	90.4(12)	Re(2)–Re(3)–C(33)	88.1(9)
Re(3)–Re(1)–N	87.4(7)	Re(2)–Re(3)–C(34)	91.5(11)
C(11)–Re(1)–C(12)	92.6(13)	C(31)–Re(3)–C(32)	95.5(14)
C(11)–Re(1)–C(13)	92.6(15)	C(31)–Re(3)–C(33)	92.3(15)
C(11)–Re(1)–N	89.4(12)	C(31)–Re(3)–C(34)	87.7(16)
C(12)–Re(1)–C(13)	92.0(14)	C(32)–Re(3)–C(33)	90.3(14)
C(12)–Re(1)–N	89.1(12)	C(32)–Re(3)–C(34)	90.9(16)
C(13)–Re(1)–N	177.8(13)	C(33)–Re(3)–C(34)	178.8(15)
Re(1)–Re(2)–C(21)	105.1(10)	Re(1)–C(11)–O(11)	171(3)
Re(1)–Re(2)–C(22)	161.1(9)	Re(1)–C(12)–O(12)	174(3)
Re(1)–Re(2)–C(23)	86.7(7)	Re(1)–C(13)–O(13)	177(3)
Re(1)–Re(2)–C(24)	91.6(7)	Re(1)–N–C(1)	176(3)
Re(3)–Re(2)–C(21)	164.6(10)	N–C(1)–C(2)	177(4)
Re(3)–Re(2)–C(22)	101.6(9)	Re(2)–C(21)–O(21)	178(3)
Re(3)–Re(2)–C(23)	89.5(7)	Re(2)–C(22)–O(22)	178(2)
Re(3)–Re(2)–C(24)	93.1(7)	Re(2)–C(23)–O(23)	176(3)
C(21)–Re(2)–C(22)	93.7(13)	Re(2)–C(24)–O(24)	176(2)
C(21)–Re(2)–C(23)	89.3(13)	Re(3)–C(31)–O(31)	169(3)
C(21)–Re(2)–C(24)	87.2(13)	Re(3)–C(32)–O(32)	178(3)
C(22)–Re(2)–C(23)	92.2(13)	Re(3)–C(33)–O(33)	177(3)
C(22)–Re(2)–C(24)	90.8(13)	Re(3)–C(34)–O(34)	177(4)
C(23)–Re(2)–C(24)	175.6(12)		

interactions are all linear (range 170—179°). A moderate increase of the mean Re–Re bond length with increasing number of MeCN substituents is observed. However, while in compound (3) the three triangular edges are very similar, in (1) the edge connecting the two $Re(CO)_4$ units, Re(2)–Re(3), is significantly longer [3.281(2) Å] than the other two (mean 3.246 Å). These Re–Re hydrogen-bridged bonds are comparable with the corresponding ones in a number of hydridocarbonyl rhenium clusters, and, in particular, with the values found in the other two structurally characterized neutral species of formula $[Re_3(\mu\text{-H})_3(CO)_{12-n}L_n]$ (L = terminal two-electron donor ligand), namely $[Re_3(\mu\text{-H})_3(CO)_{11}(PPh_3)]$ (mean Re–Re 3.262 Å, with equatorial PPh_3)[11] and $[Re_3(\mu\text{-H})_3(CO)_{10}(py)_2]$ (mean Re–Re 3.292 Å, with diaxial pyridines).[12] Another species strictly related to this family from the viewpoint of the overall stereochemistry is the anion $[Re_3(\mu\text{-H})_3I(CO)_{11}]^-$ (ref. 13), with a mean Re–Re edge of 3.265 Å and the iodide

ligand in axial co-ordination. Also in the species $[Re_3(\mu\text{-H})_3\text{-}(CO)_8\{(EtO)_2POP(OEt)_2\}_2]$ with a mean Re–Re bond length of 3.282 Å,[14] the two chelating diphosphites occupy axial co-ordination sites.

In this family of derivatives of $[Re_3(\mu\text{-H})_3(CO)_{12}]$, therefore, the substituents are generally found to lie in axial positions, the only exception being $[Re_3(\mu\text{-H})_3(CO)_{11}(PPh_3)]$.

It is interesting to compare these results with those for the related species $[M_3(CO)_{12-n}L_n]$ derived from $[M_3(CO)_{12}]$. From a steric viewpoint equatorial substitution positions are considered to be favoured in this family since, in approximately anticuboctahedral arrangements of the ligands, equatorial sites are less sterically hindered than axial sites.[7,15,16] Both equatorial and axial substituted derivatives have been observed. The solid-state structures of $[Ru_3(CO)_{11}(CNBu^t)]$[17] and $[Os_3(CO)_{12-n}(NCMe)_n]$ ($n = 1$ or 2)[18] show axial substitutions, while in $[Os_3(CO)_{11}\{P(OMe)_3\}]$ the phosphite is equatorially bonded.[16] The sterically demanding nature of the substituent can therefore influence the preferred co-ordination.

However, within the two families of derivatives, significant stereochemical differences can be outlined. The presence of edge-

Table 2. Bond distances (Å) and angles (°) within [Re$_3$(μ-H)$_3$(CO)$_9$(NCMe)$_3$] (3)

Re(1)–Re(2)	3.277(1)	Re(3)–N(3)	2.134(5)
Re(1)–Re(3)	3.288(1)	Re(3)–H(2)	1.58(8)
Re(2)–Re(3)	3.286(1)	Re(3)–H(3)	1.70(8)
Re(1)–C(11)	1.916(8)	C(11)–O(11)	1.155(9)
Re(1)–C(12)	1.924(9)	C(12)–O(12)	1.147(9)
Re(1)–C(13)	1.903(7)	C(13)–O(13)	1.159(8)
Re(1)–N(1)	2.136(5)	C(21)–O(21)	1.150(9)
Re(1)–H(1)	1.94(6)	C(22)–O(22)	1.152(9)
Re(1)–H(2)	1.95(8)	C(23)–O(23)	1.139(8)
Re(2)–C(21)	1.914(7)	C(31)–O(31)	1.146(9)
Re(2)–C(22)	1.918(9)	C(32)–O(32)	1.136(9)
Re(2)–C(23)	1.928(7)	C(33)–O(33)	1.146(8)
Re(2)–N(2)	2.142(5)	N(1)–C(N11)	1.144(8)
Re(2)–H(1)	1.70(6)	C(N11)–C(N12)	1.453(9)
Re(2)–H(3)	1.92(8)	N(2)–C(N21)	1.129(8)
Re(3)–C(31)	1.917(7)	C(N21)–C(N22)	1.478(10)
Re(3)–C(32)	1.946(8)	N(3)–C(N31)	1.137(8)
Re(3)–C(33)	1.919(7)	C(N31)–C(N32)	1.478(10)
Re(2)–Re(1)–C(11)	103.8(3)	Re(1)–Re(3)–C(31)	102.8(3)
Re(2)–Re(1)–C(12)	162.4(3)	Re(1)–Re(3)–C(32)	166.5(2)
Re(2)–Re(1)–C(13)	86.6(2)	Re(1)–Re(3)–C(33)	92.2(2)
Re(2)–Re(1)–N(1)	92.1(2)	Re(1)–Re(3)–N(3)	84.8(2)
Re(3)–Re(1)–C(11)	163.4(3)	Re(2)–Re(3)–C(31)	162.4(3)
Re(3)–Re(1)–C(12)	103.0(3)	Re(2)–Re(3)–C(32)	107.2(2)
Re(3)–Re(1)–C(13)	93.8(2)	Re(2)–Re(3)–C(33)	88.6(2)
Re(3)–Re(1)–N(1)	85.0(2)	Re(2)–Re(3)–N(3)	88.6(2)
C(11)–Re(1)–C(12)	93.4(4)	C(31)–Re(3)–C(32)	90.3(4)
C(11)–Re(1)–C(13)	88.7(3)	C(31)–Re(3)–C(33)	89.1(3)
C(11)–Re(1)–N(1)	92.2(3)	C(31)–Re(3)–N(3)	93.0(3)
C(12)–Re(1)–C(13)	90.0(3)	C(32)–Re(3)–C(33)	91.3(3)
C(12)–Re(1)–N(1)	91.1(3)	C(32)–Re(3)–N(3)	91.3(3)
C(13)–Re(1)–N(1)	178.5(3)	C(33)–Re(3)–N(3)	176.7(3)
Re(1)–Re(2)–C(21)	102.6(2)	Re(1)–C(11)–O(11)	178.9(8)
Re(1)–Re(2)–C(22)	166.5(2)	Re(1)–C(12)–O(12)	179.2(6)
Re(1)–Re(2)–C(23)	88.9(2)	Re(1)–C(13)–O(13)	178.7(7)
Re(1)–Re(2)–N(2)	90.5(2)	Re(1)–N(1)–C(N11)	178.4(5)
Re(3)–Re(2)–C(21)	162.6(2)	N(1)–C(N11)–C(N12)	178.1(7)
Re(3)–Re(2)–C(22)	106.6(2)	Re(2)–C(21)–O(21)	178.2(7)
Re(3)–Re(2)–C(23)	90.9(2)	Re(2)–C(22)–O(22)	179.4(7)
Re(3)–Re(2)–N(2)	87.9(2)	Re(2)–C(23)–O(23)	178.1(7)
C(21)–Re(2)–C(22)	90.7(3)	Re(2)–N(2)–C(N21)	175.1(6)
C(21)–Re(2)–C(23)	90.5(3)	N(2)–C(N21)–C(N22)	178.9(9)
C(21)–Re(2)–N(2)	90.7(3)	Re(3)–C(31)–O(31)	178.9(8)
C(22)–Re(2)–C(23)	89.1(3)	Re(3)–C(32)–O(32)	177.0(7)
C(22)–Re(2)–N(2)	91.2(3)	Re(3)–C(33)–O(33)	179.2(7)
C(23)–Re(2)–N(2)	178.7(3)	Re(3)–N(3)–C(N31)	176.8(7)
		N(3)–C(N31)–C(N32)	178.8(10)

Table 3. Mean bond lengths (Å) within the family [Re$_3$(μ-H)$_3$(CO)$_{12-n}$(NCMe)$_n$]

	$n = 1$	$n = 2$	$n = 3$
Re–Re	3.258	3.266	3.284
Re–C[a]	1.94	1.92	
Re–C[b]	1.87	1.87	1.921
C–O	1.15	1.16	1.148
Re–N	2.08	2.13	2.137

[a] Within the Re(CO)$_4$ units. [b] Within the Re(CO)$_3$ moieties.

Table 4. Spectroscopic properties of the [Re$_3$(μ-H)$_3$(CO)$_{12-n}$(NCMe)$_n$] (n = 0—3) complexes

n	I.r. (toluene) v(CO)	N.m.r. (CD$_3$)$_2$CO
0	2 096m, 2 033s, 2 010ms, 1 982m	−16.92
1	2 113mw, 2 090mw, 2 038m, 2 022s, 2 003vs, 1 971m, 1 936m, 1 921 (sh)	2.61(3), −14.37(2), −17.00(1)
2	2 098mw, 2 039 (sh), 2 028vs, 2 000 (sh), 1 991s, 1 961m, 1 938s, 1 921m	2.53(3), −11.90(1), −14.38(2)
3	2 044mw, 2 021s, 1 940s, 1 932 (sh), 1 903m	2.58(6), 2.45(3), −11.58(1), −11.94(2)

Spectroscopic Data.—The v(CO) bands in the i.r. spectra (Table 4) show on average the expected shift to lower frequency, on increasing substitution of CO by donor MeCN molecules. The pattern of bands of compound (3), significantly different from the quite simple one of compounds of C_{3v} symmetry e.g. [Re$_3$(μ-H)$_3$(μ$_3$-X)(CO)$_9$]$^{n-}$,[21] is in accord with the lower symmetry indicated in the solid by X-ray analysis and in solution by n.m.r. spectra. The presence of two hydridic resonances, in the ratio 2:1, in the n.m.r. spectra of all the three complexes is indicative of C_s symmetry, with a mirror plane perpendicular to the triangle, or of C_2 symmetry, for (2), with the two-fold axis lying in the metal plane. The hypothesis that this symmetry could arise from the rapid rearrangement of the ligands in each Re(CO)$_3$(NCMe) unit is ruled out since this pattern is observed even in compound (3), in which this fluxional behaviour should occur on each metal, giving rise to a single hydridic signal. On the contrary, up to 70 °C in CD$_3$CN two sharp resonances are observed for compound (3).

This implies the presence in solution of only one isomer for all three compounds. According to C_s symmetry, one MeCN ligand in (1) and in (3) must occupy an axial co-ordination site. The solution structure of (1) is therefore unambiguously established, while for (2) and (3) is not possible to discriminate between structures involving two axial or two equatorial symmetry-related nitrile ligands. The chemical evidence discussed above in rationalizing the reactions of (6) with trimethylamine oxide strongly favours a structure analogous to that observed in the solid state. Moreover, solution structures different from the solid state ones usually occur when ligand rearrangements with low activation energy paths are possible. This is not the case for the complexes discussed here, as shown above. A very high interconversion barrier (25 kcal mol^{-1}, ca. 104—106 kJ mol^{-1}) was estimated[22] for [Re$_3$(μ-H)$_3$-(CO)$_{11}$(PPh$_3$)], the only species in this family for which the presence in solution of both axial and equatorial isomers was recognized. The relevance of the kinetic barrier is demonstrated also by the fact that two different isomers of [Re$_3$(μ-H)$_3$(CO)$_{10}$(PPh$_3$)$_2$] could be isolated, on using different synthetic routes: a diaxial one was produced by treatment of (2) with PPh$_3$,[5] while protonation of [Re$_3$(μ-H)$_2$(CO)$_{10}$(PPh$_3$)$_2$]$^-$ led to the equatorial isomer.[20]

bridging hydrides in [Re$_3$(μ-H)$_3$(CO)$_{12-n}$L$_n$] with respect to [M$_3$(CO)$_{12-n}$L$_n$] causes variations in the geometry of the equatorial plane, described in detail by Churchill and De Boer.[19] In particular the lengthening of the M–H–M bonds results in longer intramolecular axial–axial distances.

We think, therefore, that in the series [Re$_3$(μ-H)$_3$(CO)$_{12-n}$-L$_n$] steric factors can play some role in determining the co-ordination sites only in the case of bulky ligands such as PPh$_3$. Equatorial locations have been observed in the solid-state structure of [Re$_3$(μ-H)$_3$(CO)$_{11}$(PPh$_3$)] and also of the related anion [Re$_3$(μ-H)$_2$(CO)$_{10}$(PPh$_3$)$_2$]$^-$ (ref. 20) (but see below). However for this family electronic factors are very probably dominant in orienting the substitution in the axial direction (also from the kinetic point of view). For L ligands which are essentially σ donors co-ordination *trans* to a hydride (equatorial site) is disfavoured with respect to that *trans* to a CO (axial site).

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The trend of the hydridic chemical shifts (Table 4) is in line with the discussion relative to the substitution of CO by MeCN, already reported in ref. 4.

The electron impact (e.i.) mass spectra of compounds (1)—(3) did not show the molecular peak. For compounds (1) and (2) a multiplet of higher molecular weight corresponded to compound (6), indicating that under the mass spectrometer conditions [200 °C, 10^{-7} Torr (ca. 1.33×10^{-5} Pa)] the labile nitriles were immediately lost and substituted by carbon monoxide. The mass spectrum of (3) was completely different, because no peak corresponding to Re_3 clusters was observed. Multiplets of higher intensity corresponded to $[Re_4H_4(CO)_{12}]$ (7)[23] and to fragments obtained by stepwise loss of its 12 CO ligands. Other peaks were present, of higher mass but much lower intensity, attributable to the stepwise loss of 15 CO ligands by a pentanuclear complex $[Re_5H_5(CO)_{15}]$: computer simulation was in excellent agreement with the relative intensities of the components of the molecular peak.

Under e.i. conditions, therefore, the $[ReH(CO)_3]_3$ unit originating by loss of the nitriles did not add CO, but rearranged, mainly to $[\{ReH(CO)_3\}_4]$ (7), and small amounts of the pentamer $[\{ReH(CO)_3\}_5]$. This last species was never synthesized (it would be a superunsaturated, 70 v.e.s, pentanuclear cluster), while the tetramer (7) (which too is a superunsaturated cluster, 56 v.e.s) was obtained[23] by thermal transformation of the trimer $[\{ReH(CO)_4\}_3]$ (6), at 190 °C in boiling decalin (decahydronaphthalene). Using (3) as starting material, the synthesis of (7) could be performed under milder conditions: by refluxing (3) in toluene for 1 h, a red-brown solution was obtained, in which (7), identified by its i.r. and n.m.r. spectra, was the main component.

Experimental

The reactions were performed under nitrogen, using the Schlenk technique, in solvents deoxygenated and dried by standard methods. Infrared spectra were recorded on a Perkin-Elmer 781 grating spectrophotometer, in 0.1-mm CaF_2 cells, and were calibrated with polystyrene film absorptions. N.m.r. spectra were recorded on a Bruker WP 80 spectrometer, mass spectra on a VG 7070EQ spectrometer. Elemental analyses were performed by the Microanalytical Laboratory of Milan University. Published methods were used for the synthesis of $[NEt_4][Re_3(\mu\text{-}H)_4(CO)_{10}]$ (4),[2] $[NEt_4][Re_3(\mu\text{-}H)_4(CO)_9(NCMe)]$ (5),[4] and $[Re_3(\mu\text{-}H)_3(CO)_{12}]$ (6).[6] Anhydrous trimethylamine oxide was obtained by sublimation of the commercial product $Me_3NO \cdot 2H_2O$, as previously described.[21]

Synthesis of $[Re_3(\mu\text{-}H)_3(CO)_9(NCMe)_3]$ (3).—(a) A sample of $[Re_3(\mu\text{-}H)_3(CO)_{12}]$ (6) (100 mg, 0.111 mmol), suspended in freshly dehydrated acetonitrile (5 cm³), was treated with a 0.067 mol dm⁻³ solution of freshly sublimed Me_3NO (5 cm³, 0.335 mmol) in acetonitrile. After 1 h, the solvent was removed under reduced pressure and the residue dissolved in freshly distilled tetrahydrofuran (3 cm³). Addition of n-heptane (10 cm³) caused the precipitation of a white material, which was washed with 3×3 cm³ portions of n-heptane (76 mg, 0.081 mmol, isolated yield 73°₀ after drying under vacuum) (Found: C, 19.35; H, 1.25; N, 4.60. $C_{15}H_{12}N_3O_9Re_3$ requires C, 19.20; H, 1.30; N, 4.50%). Upon heating, the solid compound decomposes (darkening starts at about 120 °C and melting occurs at 175 °C).

(b) A sample of $[NEt_4][Re_3(\mu\text{-}H)_4(CO)_9(NCMe)]$ (5) (50 mg, 0.051 mmol), dissolved in freshly dehydrated acetonitrile (5 cm³) was treated with CF_3SO_3H (5 µl, 0.057 mmol). The solution became progressively colourless and after 30 min the solvent was removed under reduced pressure. The residue was eluted on a short SiO_2 column, with n-hexane–methylene chloride–acetonitrile (10:10:1, v/v), affording, after evaporation

to dryness, spectroscopically pure $[Re_3(\mu\text{-}H)_3(CO)_9(NCMe)_3]$ (31 mg, 0.033 mmol, isolated yield 65°₀).

Reaction of $[Re_3(\mu\text{-}H)_3(CO)_9(NCMe)_3]$ (3) *with Carbon Monoxide.*—A sample (80 mg, 0.085 mmol) of compound (3) was dissolved in methylene chloride (20 cm³) under CO. Samples were taken at different times, rapidly evaporated to dryness, and analysed by n.m.r. spectroscopy. After 1 h only signals due to $[Re_3(\mu\text{-}H)_3(CO)_{10}(NCMe)_2]$ (2) were observed. After 24 h $[Re_3(\mu\text{-}H)_3(CO)_{11}(NCMe)]$ (1) was mainly present, together with a small amount (ca. 10%) of $[Re_3(\mu\text{-}H)_3(CO)_{12}]$ (6).

X-Ray Analyses of Compounds (1) *and* (3).—*Crystal data.* Compound (1), $C_{13}H_6NO_{11}Re_3$, $M = 910.8$, monoclinic, space group $P2_1/n$ [non-standard setting of $P2_1/c$ (no. 14)], $a = 8.417(2)$, $b = 15.282(4)$, $c = 16.540(4)$ Å, $\beta = 97.70(2)°$, $U = 2\,108.3$ Å³, $Z = 4$, $D_c = 2.869$ g cm⁻³, $F(000) = 1\,616$, Mo-K_α radiation ($\lambda = 0.710\,73$ Å), $\mu(\text{Mo-}K_\alpha) = 174.71$ cm⁻¹.

Compound (3), $C_{15}H_{12}N_3O_9Re_3$, $M = 936.9$, triclinic, space group $P\bar{1}$, (no. 2), $a = 8.761(2)$, $b = 9.403(2)$, $c = 15.079(3)$ Å, $\alpha = 92.45(2)$, $\beta = 94.02(2)$, $\gamma = 108.38(2)°$, $U = 1\,173.2$ Å³, $Z = 2$, $D_c = 2.652$ g cm⁻³, $F(000) = 840$, Mo-K_α radiation ($\lambda = 0.710\,73$ Å), $\mu(\text{Mo-}K_\alpha) = 156.99$ cm⁻¹.

Intensity measurements. Crystal samples of dimensions $0.05 \times 0.14 \times 0.28$ mm (1) and $0.11 \times 0.22 \times 0.34$ mm (3) were mounted on glass fibres in the air. The intensities for both compounds were collected on an Enraf-Nonius CAD4 automated diffractometer, using graphite monochromatized Mo-K_α radiation. The setting angles of 25 random intense reflections ($16 < 2\theta < 25°$) were used in each case to determine by least-squares fit accurate cell constants and the orientation matrix. The crystals of (1) were of notably poorer diffraction quality with respect to those of (3).

Table 5. Final positional parameters within $[Re_3(\mu\text{-}H)_3(CO)_{11}(NCMe)]$ (1)

Atom	x	y	z
Re(1)	0.027 3(2)	0.207 35(8)	0.267 53(7)
Re(2)	−0.231 8(1)	0.093 21(8)	0.148 01(7)
Re(3)	0.043 0(2)	−0.004 53(8)	0.276 22(8)
C(11)	−0.041(4)	0.324(2)	0.242(2)
O(11)	−0.062(3)	0.399(2)	0.225(1)
C(12)	0.187(4)	0.244(2)	0.349(2)
O(12)	0.290(3)	0.276(2)	0.397(2)
C(13)	0.168(4)	0.208(2)	0.190(2)
O(13)	0.261(3)	0.207(1)	0.144(1)
N	−0.131(3)	0.202(2)	0.353(1)
C(1)	−0.222(4)	0.204(2)	0.400(2)
C(2)	−0.334(5)	0.203(3)	0.463(2)
C(21)	−0.363(4)	0.177(2)	0.086(2)
O(21)	−0.437(3)	0.299(1)	0.048(1)
C(22)	−0.341(4)	−0.003(2)	0.095(2)
O(22)	−0.404(3)	−0.066(1)	0.063(1)
C(23)	−0.077(3)	0.099(2)	0.066(1)
O(23)	0.010(2)	0.098(1)	0.017(1)
C(24)	−0.390(3)	0.097(2)	0.229(2)
O(24)	−0.468(2)	0.099(2)	0.276(1)
C(31)	0.214(4)	−0.026(2)	0.357(2)
O(31)	0.335(3)	−0.048(2)	0.400(2)
C(32)	−0.005(4)	−0.123(2)	0.255(2)
O(32)	−0.036(3)	−0.196(2)	0.244(1)
C(33)	0.185(4)	−0.004(2)	0.188(2)
O(33)	0.259(3)	−0.007(2)	0.140(1)
C(34)	−0.095(5)	−0.003(3)	0.362(2)
O(34)	−0.173(3)	−0.005(2)	0.414(1)
H(1)	−0.14(2)	0.20(1)	0.19(1)
H(2)	0.11(2)	0.10(2)	0.28(1)
H(3)	−0.10(2)	0.01(1)	0.20(1)

Table 6. Final positional parameters within $[Re_3(\mu\text{-}H)_3(CO)_9(NCMe)_3]$ (3)

Atom	x	y	z
Re(1)	0.218 08(3)	0.158 63(3)	0.752 35(2)
Re(2)	−0.040 54(3)	0.278 45(3)	0.635 25(2)
Re(3)	−0.052 01(3)	0.267 42(3)	0.852 24(2)
C(11)	0.335 3(8)	0.095 8(8)	0.664 3(6)
O(11)	0.405 7(7)	0.055 8(8)	0.611 9(5)
C(12)	0.348 7(9)	0.119 3(7)	0.850 2(6)
O(12)	0.427 7(7)	0.097 7(6)	0.908 7(4)
C(13)	0.364 8(8)	0.357 1(8)	0.752 2(5)
O(13)	0.456 5(6)	0.476 9(5)	0.752 2(4)
N(1)	0.048 5(7)	−0.061 8(5)	0.752 1(4)
C(N11)	−0.041 5(8)	−0.179 8(7)	0.754 0(4)
C(N12)	−0.152(1)	−0.330 9(8)	0.758 7(6)
C(21)	0.013 9(9)	0.255 2(8)	0.516 0(5)
O(21)	0.050 7(8)	0.243 8(7)	0.444 9(4)
C(22)	−0.203 4(9)	0.362 4(7)	0.593 7(5)
O(22)	−0.301 4(7)	0.412 1(6)	0.568 1(4)
C(23)	0.113 2(8)	0.478 1(7)	0.649 5(5)
O(23)	0.202 3(7)	0.597 0(6)	0.655 7(4)
N(2)	−0.211 6(7)	0.056 6(6)	0.622 6(4)
C(N21)	−0.304 5(8)	−0.058 5(7)	0.609 8(5)
C(N22)	−0.428(1)	−0.207 8(9)	0.592 6(8)
C(31)	−0.014(1)	0.227 1(8)	0.973 9(5)
O(31)	0.007(1)	0.201 6(8)	1.046 5(4)
C(32)	−0.215 8(9)	0.354 5(7)	0.885 4(5)
O(32)	−0.307 8(6)	0.407 2(6)	0.908 3(4)
C(33)	−0.209 5(9)	0.071 2(8)	0.833 0(5)
O(33)	−0.304 1(7)	−0.045 8(6)	0.822 6(4)
N(3)	0.129 5(7)	0.482 6(6)	0.866 9(4)
C(N31)	0.232(1)	0.593 9(8)	0.874 9(5)
C(N32)	0.367(1)	0.737(1)	0.885 5(8)
H(1)	0.078(7)	0.168(6)	0.648(4)
H(2)	0.91(9)	0.201(7)	0.845(5)
H(3)	−0.11(1)	0.310(8)	0.750(5)

The data collections were performed by the ω-scan method, within the limits $3 < \theta < 22°$ for (1) and $3 < \theta < 25°$ for (3). A variable scan speed (from 2 to 20° min⁻¹) and a variable scan range of $(\alpha + 0.35\tan\theta)°$, with $\alpha = 0.9$ (1) and 1.0 (3), were used, with a 25% extension at each end of the range for background determination. The total numbers of reflections measured were 2 582 (1) and 4 101 (3). No significant decay of the crystal sample upon X-ray exposure was observed for compound (1), while in the case of (3) three standard intense reflections, monitored every 3 h, revealed a moderate decay (of ca. 7% at the end of the collection). The intensities were corrected for Lorentz and polarization effects. The data for compound (3) were also corrected for decay. An empirical absorption correction was applied to both data sets, based on ψ scans (ψ 0—360° every 10°) of suitable reflections with χ values close to 90°; the relative transmission factors had values in the ranges 1.00—0.46 (1) and 1.00—0.52 (3), respectively. Two sets of 1 121 (1) and 3 129 (3) independent significant reflections, with $I > 3\sigma(I)$, were used in the structure solutions and refinements.

Structure solutions and refinements. All computations were performed on a PDP 11/34 computer, using the Enraf-Nonius structure determination package (SDP) and the physical constants tabulated therein. The structure solutions were based on the deconvolution of three-dimensional Patterson maps, which gave the positions of the metal atoms. Successive Fourier difference maps showed the locations of all the non-hydrogen atoms. The refinements were carried out by full-matrix least squares. Anisotropic thermal parameters were assigned to all atoms in (3), while in compound (1), due to the limited number of significant reflections, only the rhenium atoms were treated anisotropically.

The final Fourier difference maps were rather flat showing

residual peaks not exceeding ca. 1 e Å^{-3} in each case. Three peaks were observed in both structures, appropriate for hydrides in bridging positions on the Re–Re edges. They were refined [with a fixed isotropic thermal parameter of 3.5 Å^2 for compound (1)] leading to convergence. However the resulting bond parameters are widely scattered and offer only a rough indication of the co-ordination of these hydrides. No attempt was made to locate the methyl hydrogens, though in (3) some residual peaks could be tentatively attributed to these atoms.

Weights were assigned according to the formula $w = 4F_o^2/\sigma(F_o^2)^2$, where $\sigma(F_o^2) = [\sigma(I)^2 + (pI)^2]^{\frac{1}{2}}/L_P$ (I and L_P being the integrated intensity and the Lorentz polarization correction, respectively); p was optimized to 0.04 in each case. The final values of the conventional agreement indices R and R' were 0.035 and 0.042 (1) and 0.019 and 0.027 (3), respectively.

The final positional parameters are given in Tables 5 [compound (1)] and 6 [compound (3)].

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters.

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