

# Synthesis and Characterization of a New Family of Unsaturated Triangular Rhenium Cluster Anions of Formula $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_9\text{L}]^-$ (L = Neutral Two-electron Donor Ligand). X-Ray Crystal and Molecular Structures of the Tetraethylammonium Salts of the Anions with L = Triphenylphosphine and Pyridine†

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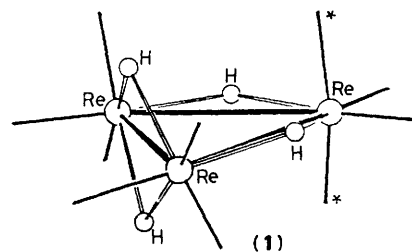
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The unsaturated triangular cluster anion  $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_{10}]^-$  can undergo selective substitution of one of the axial carbonyl ligands of the  $\text{Re}(\text{CO})_4$  vertex by neutral two-electron donor ligands L, giving unsaturated  $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_9\text{L}]^-$  derivatives. The anions with L = NCMe,  $\text{PPh}_3$ , and pyridine (py) have been synthesized either by thermal activation or, more effectively, by carbonyl elimination using  $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$ . X-Ray single-crystal analyses of the  $\text{PPh}_3$  and py derivatives, as  $[\text{NEt}_4]^+$  salts, have been performed. Both species crystallize in the monoclinic system, space group  $P2_1/n$ , with  $a = 11.448(2)$ ,  $b = 25.311(6)$ ,  $c = 13.596(3)$  Å,  $\beta = 94.00(2)^\circ$ , and  $Z = 4$  for the  $\text{PPh}_3$  derivative, and  $a = 11.087(1)$ ,  $b = 15.951(2)$ ,  $c = 17.598(4)$  Å,  $\beta = 104.84(2)^\circ$ , and  $Z = 4$  for the py derivative. The geometries of the two anions are similar to that of the parent anion, with the  $\text{PPh}_3$  or the py ligand co-ordinated in an axial position with respect to the  $\text{Re}_3$  triangle, which presents a short Re-Re bond (close to 2.80 Å) doubly bridged by hydrides. The MeCN derivative is the most reactive member of this new family, containing two active centres: the labile nitrile and the unsaturated moiety. Its reaction with methanol, leading to the anion  $[\text{Re}_3(\mu\text{-H})_3(\text{CO})_9(\mu_3\text{-OMe})]^-$ , exemplifies the possibility of new reaction paths involving both the active sites of this molecule.

We are currently investigating the reactivity of the triangular cluster anion  $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_{10}]^-$  (1), which possesses only 46 valence electrons.<sup>1</sup> Its unsaturation is localized on the  $\text{Re}(\mu\text{-H})_2\text{Re}$  moiety, whose hydrides are the main protagonists of the wide variety of reactions of this compound. A <sup>13</sup>C n.m.r. analysis revealed the occurrence of an unusual process of selective enrichment in <sup>13</sup>CO at the two carbonyl ligands mutually *trans* in the  $\text{Re}(\text{CO})_4$  unit [marked with an asterisk in structure of (1)].<sup>1</sup>

Since all the other carbonyl ligands of the anion are *trans* to hydrides, this phenomenon was easily rationalised in terms of the mutual ligand labilization due to the competition for  $\pi$  back-donation. The lability of these carbonyls suggested to us the possibility of performing selective substitutions with other donor species, without affecting the more reactive unsaturated site of the molecule, *i.e.* the  $\text{Re}(\mu\text{-H})_2\text{Re}$  moiety. We found that this can be accomplished and we report here on the synthetic routes by which a whole family of unsaturated anions of general formula  $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_9\text{L}]^-$  can be prepared. The complete results of the X-ray single-crystal analyses of the triphenylphosphine and pyridine (py) derivatives, as  $[\text{NEt}_4]^+$  salts, are also reported and discussed.



## Results and Discussion

The substitution of one of the labile carbonyl ligands of compound (1) by a nitrile molecule seemed to be the most interesting goal, because of the synthetic versatility that such a derivative should exhibit.

Thermal activation and oxidation by trimethylamine *N*-oxide are the methods most widely used to promote substitution of carbonyl ligands. In the present case both methods proved effective, leading to substitution with high selectivity.

In fact, the treatment of an acetonitrile solution of the parent anion (1) ( $[\text{NEt}_4]^+$  salt used throughout) with the stoichiometric amount of  $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$ , at room temperature, led quantitatively to a species which was formulated as the expected anion  $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_9(\text{NCMe})]^-$  (2) on the basis of its <sup>1</sup>H n.m.r. spectrum and reactivity (see below).

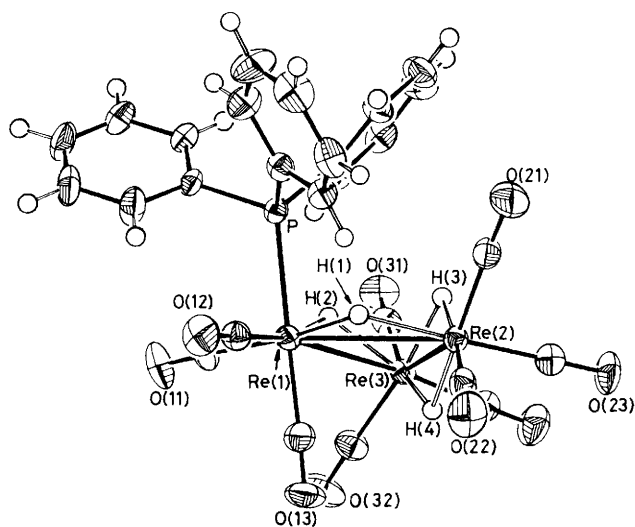
The thermal route proved less straightforward. Refluxing compound (1) in acetonitrile solution for 4 h afforded a mixture, containing *ca.* 65% of compound (2) as determined by the integration of the hydridic *vs.* the cationic signals in the <sup>1</sup>H n.m.r. spectrum. The main by-product was a species responsible for a hydridic resonance at  $\delta -14.95$  p.p.m. (present in a concentration of *ca.* 25%, assuming it to be a dihydride). On

† 1,2; 1,3; 2,3; 2,3-Tetra- $\mu$ -hydrido-1-triphenylphosphine- and 1,2; 1,3; 2,3; 2,3-tetra- $\mu$ -hydrido-1-pyridine-triangulo-tris[tricarbonylrhenate-(1-)] respectively.

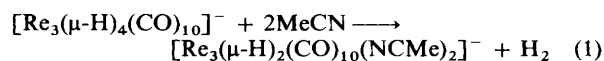
Supplementary data available (No. SUP 56633, 8 pp.): thermal parameters, remaining H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii-xx. Structure factors are available from the editorial office.

**Table 1.** Bond distances (Å) and angles (°) in the anion  $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_9(\text{PPh}_3)]^-$  (3)

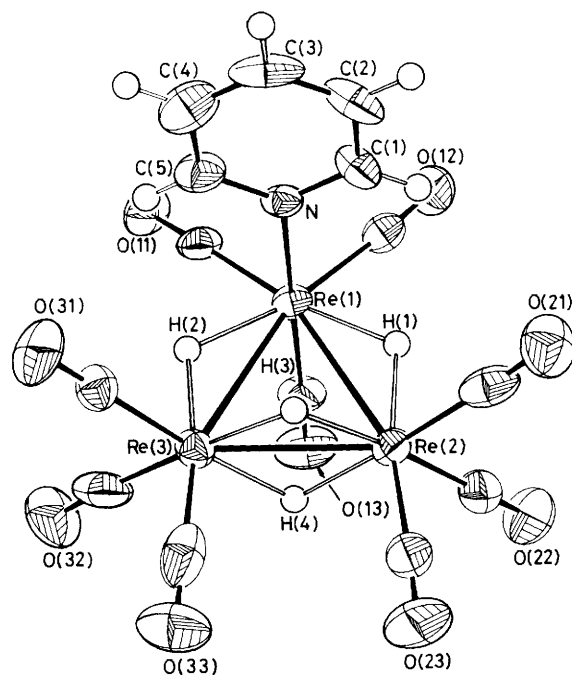
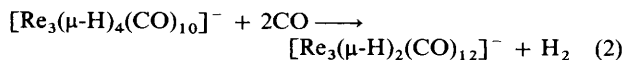
Re(1)–Re(2)	3.234(1)	Re(2)–C(21)	1.898(9)	Re(3)–H(2)	1.90(7)	C(23)–O(23)	1.162(9)
Re(1)–Re(3)	3.193(1)	Re(2)–C(22)	1.917(10)	Re(3)–H(3)	1.86(7)	C(31)–O(31)	1.140(9)
Re(2)–Re(3)	2.797(1)	Re(2)–C(23)	1.899(9)	Re(3)–H(4)	1.80(7)	C(32)–O(32)	1.140(9)
Re(1)–C(11)	1.934(9)	Re(2)–H(1)	1.97(7)	C(11)–O(11)	1.134(9)	C(33)–O(33)	1.147(10)
Re(1)–C(12)	1.904(9)	Re(2)–H(3)	1.90(7)	C(12)–O(12)	1.150(9)	P–C(P11)	1.837(7)
Re(1)–C(13)	1.958(10)	Re(2)–H(4)	1.77(7)	C(13)–O(13)	1.151(9)	P–C(P21)	1.819(8)
Re(1)–P	2.481(2)	Re(3)–C(31)	1.922(9)	C(21)–O(21)	1.168(9)	P–C(P31)	1.825(8)
Re(1)–H(1)	1.65(7)	Re(3)–C(32)	1.932(9)	C(22)–O(22)	1.155(10)	C–C(phenyl)	1.34(1)–1.42(1)
Re(1)–H(2)	1.88(7)	Re(3)–C(33)	1.908(10)				mean 1.38
Re(2)–Re(1)–C(11)	152.4(2)	H(2)–Re(1)–C(12)	165(2)	H(4)–Re(2)–C(21)	169(2)	H(3)–Re(3)–C(31)	92(2)
Re(2)–Re(1)–C(12)	114.0(2)	H(2)–Re(1)–C(13)	107(2)	H(4)–Re(2)–C(22)	99(2)	H(3)–Re(3)–C(32)	171(2)
Re(2)–Re(1)–C(13)	82.4(3)	H(2)–Re(1)–P	79(2)	H(4)–Re(2)–C(23)	88(2)	H(3)–Re(3)–C(33)	97(2)
Re(2)–Re(1)–P	95.82(5)	H(1)–Re(1)–H(2)	93(3)	H(1)–Re(2)–H(3)	90(3)	H(4)–Re(3)–C(31)	169(2)
Re(3)–Re(1)–C(11)	100.9(2)	Re(1)–Re(2)–C(21)	109.8(3)	H(1)–Re(2)–H(4)	96(3)	H(4)–Re(3)–C(32)	99(2)
Re(3)–Re(1)–C(12)	161.2(2)	Re(1)–Re(2)–C(22)	98.5(2)	H(3)–Re(2)–H(4)	79(3)	H(4)–Re(3)–C(33)	85(2)
Re(3)–Re(1)–C(13)	79.1(2)	Re(1)–Re(2)–C(23)	158.9(2)	Re(1)–Re(3)–C(31)	110.6(3)	H(2)–Re(3)–H(3)	74(3)
Re(3)–Re(1)–P	105.54(5)	Re(3)–Re(2)–C(21)	131.9(3)	Re(1)–Re(3)–C(32)	92.6(3)	H(2)–Re(3)–H(4)	104(3)
C(11)–Re(1)–C(12)	92.0(3)	Re(3)–Re(2)–C(22)	136.1(3)	Re(1)–Re(3)–C(33)	158.2(3)	H(3)–Re(3)–H(4)	79(3)
C(11)–Re(1)–C(13)	89.9(4)	Re(3)–Re(2)–C(23)	96.5(2)	Re(2)–Re(3)–C(31)	133.9(2)	Re(1)–P–C(P11)	113.1(3)
C(11)–Re(1)–P	94.9(3)	C(21)–Re(2)–C(22)	91.3(4)	Re(2)–Re(3)–C(32)	133.9(3)	Re(1)–P–C(P21)	114.3(3)
C(12)–Re(1)–C(13)	87.4(4)	C(21)–Re(2)–C(23)	88.3(4)	Re(2)–Re(3)–C(33)	97.2(3)	Re(1)–P–C(P31)	119.0(2)
C(12)–Re(1)–P	86.7(3)	C(22)–Re(2)–C(23)	91.7(4)	C(31)–Re(3)–C(32)	90.8(4)	Re(1)–H(1)–Re(2)	126(4)
C(13)–Re(1)–P	172.6(3)	H(1)–Re(2)–C(21)	89(2)	C(31)–Re(3)–C(33)	90.8(4)	Re(1)–H(2)–Re(3)	115(3)
H(1)–Re(1)–C(11)	174(2)	H(1)–Re(2)–C(22)	86(2)	C(32)–Re(3)–C(33)	91.5(4)	Re(2)–H(3)–Re(3)	96(3)
H(1)–Re(1)–C(12)	89(2)	H(1)–Re(2)–C(23)	177(2)	H(2)–Re(3)–C(31)	79(2)	Re(2)–H(4)–Re(3)	103(3)
H(1)–Re(1)–C(13)	96(2)	H(3)–Re(2)–C(21)	91(2)	H(2)–Re(3)–C(32)	98(2)	Re–C–O	174.3(8)–178.9(8)
H(1)–Re(1)–P	79(2)	H(3)–Re(2)–C(22)	176(2)	H(2)–Re(3)–C(33)	166(2)		
H(2)–Re(1)–C(11)	85(2)	H(3)–Re(2)–C(23)	92(2)				

**Figure 1.** A view of the anion  $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_9(\text{PPh}_3)]^-$  (3). The CO groups are indicated by the numbering of their oxygen atoms. The numbering of the phenyl carbons of the phosphine ligand is omitted for clarity

performing the reaction under  $\text{H}_2$  flow, this by-product completely disappeared and the yield of compound (2) increased to ca. 90%. A reasonable explanation is the formulation of the by-product as the anion  $[\text{Re}_3(\mu\text{-H})_2(\text{CO})_{10}(\text{NCMe})_2]^-$ , formed in reaction (1) analogous to that occurring under high CO



pressure:<sup>1</sup> reaction (2). The presence of  $\text{H}_2$  could inhibit this

**Figure 2.** A view of the anion  $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_9(\text{py})]^-$  (4)

process; indeed the reaction with CO proved to be reversible, under high pressure of  $\text{H}_2$ .

As expected, the nitrile ligand was found to be rather labile, susceptible to substitution by a variety of neutral two-electron donor species. On bubbling CO into an acetone solution of (2), the parent anion (1) was readily restored. Analogously, addition of the stoichiometric amount of  $\text{PPh}_3$  or pyridine led selectively, at room temperature, to the corresponding substitution

**Table 2.** Bond distances (Å) and angles (°) in the anion  $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_9(\text{py})]^-$  (4)

Re(1)–Re(2)	3.180(1)	Re(2)–C(21)	1.88(2)	C(12)–O(12)	1.13(2)	C(33)–O(33)	1.20(3)
Re(1)–Re(3)	3.184(1)	Re(2)–C(22)	1.90(2)	C(13)–O(13)	1.17(1)	N–C(1)	1.31(2)
Re(2)–Re(3)	2.802(1)	Re(2)–C(23)	1.94(2)	C(21)–O(21)	1.19(2)	N–C(5)	1.30(2)
Re(1)–C(11)	1.91(2)	Re(3)–C(31)	1.93(2)	C(22)–O(22)	1.17(2)	C(1)–C(2)	1.39(2)
Re(1)–C(12)	1.95(2)	Re(3)–C(32)	1.92(3)	C(23)–O(23)	1.15(2)	C(2)–C(3)	1.34(3)
Re(1)–C(13)	1.85(1)	Re(3)–C(33)	1.88(3)	C(31)–O(31)	1.13(2)	C(3)–C(4)	1.36(3)
Re(1)–N	2.21(1)	C(11)–O(11)	1.14(1)	C(32)–O(32)	1.15(2)	C(4)–C(5)	1.35(2)
Re(2)–Re(1)–C(11)	160.4(5)	C(11)–Re(1)–C(13)	93.5(7)	Re(3)–Re(2)–C(21)	136.4(5)	Re(2)–Re(3)–C(31)	134.3(5)
Re(2)–Re(1)–C(12)	109.5(5)	C(11)–Re(1)–N	92.7(5)	Re(3)–Re(2)–C(22)	132.9(6)	Re(2)–Re(3)–C(32)	135.1(6)
Re(2)–Re(1)–C(13)	81.6(5)	C(12)–Re(1)–C(13)	91.9(7)	Re(3)–Re(2)–C(23)	96.2(5)	Re(2)–Re(3)–C(33)	94.8(6)
Re(2)–Re(1)–N	91.0(3)	C(12)–Re(1)–N	93.0(5)	C(21)–Re(2)–C(22)	90.0(8)	C(31)–Re(3)–C(32)	89.7(8)
Re(3)–Re(1)–C(11)	108.6(5)	C(13)–Re(1)–N	172.1(6)	C(21)–Re(2)–C(23)	88.6(8)	C(31)–Re(3)–C(33)	89.8(8)
Re(3)–Re(1)–C(12)	161.8(5)	Re(1)–Re(2)–C(21)	108.1(6)	C(22)–Re(2)–C(23)	91.5(7)	C(32)–Re(3)–C(33)	93.5(8)
Re(3)–Re(1)–C(13)	85.2(5)	Re(1)–Re(2)–C(22)	99.6(6)	Re(1)–Re(3)–C(31)	108.3(5)	Re–C–O	175(2)–177(2)
Re(3)–Re(1)–N	88.2(3)	Re(1)–Re(2)–C(23)	159.8(6)	Re(1)–Re(3)–C(32)	98.8(6)		
C(11)–Re(1)–C(12)	89.5(7)			Re(1)–Re(3)–C(33)	158.1(6)		

**Table 3.** Comparison of some (mean) bond parameters in the unsaturated triangular anions  $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_9\text{L}]^-$ 

Parameter <sup>a</sup>	(1) (L = CO)	(3) (L = PPh <sub>3</sub> )	(4) (L = py)
Re(1)–Re(2,3)	3.190	3.214	3.182
Re(2)–Re(3)	2.789(1)	2.797(1)	2.802(1)
Re(1)–C(E)	1.95	1.92	1.93
Re(1)–C(A)	2.00	1.96(1)	1.85(1)
Re(2,3)–C(E)	1.92	1.90	1.91
Re(2,3)–C(D)	1.91	1.92	1.91
Re(2,3)–Re(1)–C(E)( <i>trans</i> )	159.5	156.8	161.1
Re(2,3)–Re(1)–C(E)( <i>cis</i> )	108.3	107.5	109.1
Re(2,3)–Re(1)–C(A)	86.3	80.8	83.4
Re(2,3)–Re(1)–L	—	100.7	89.6
Re(1)–Re(2,3)–C(E)	161.0	158.6	159.0
Re(1)–Re(2,3)–C(D)	102.2	110.2 <sup>b</sup>	108.2 <sup>b</sup>
		95.6	99.2

<sup>a</sup> E = Equatorial, A = axial, D = diagonal. <sup>b</sup> CO Groups on the same side of the triangle bearing the L ligand.

derivatives, whose X-ray structural characterization (see below) provided further support to the formulation of compound (2).

An alternative, more direct, route to the unsaturated anions  $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_9(\text{PPh}_3)]^-$  (3) and  $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_9(\text{py})]^-$  (4) was provided by treatment of the parent anion (1) with  $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$ , in the presence of a slight excess of  $\text{PPh}_3$  or pyridine, at room temperature.

The two methods outlined above allow the preparation of a wide family of unsaturated anions of general formula  $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_9\text{L}]^-$ . The direct synthesis of compounds (3) and (4) *via* thermal activation was also attempted, but the yields were rather low, due to the formation, as often observed under these conditions, of other products not yet characterized. The related unsaturated species  $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}]$  gives isoelectronic monosubstituted derivatives  $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_9\text{L}]$  (L =  $\text{PMe}_2$ , Ph or  $\text{PPh}_3$ ),<sup>2</sup> but *via* a different reaction mechanism, in two steps, involving firstly the formation of an addition intermediate  $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}(\text{PR}_3)]$ , which can subsequently undergo thermal decarbonylation. This route, leaving unaffected the  $\text{Os}(\text{CO})_4$  moiety, leads to a product with a ligand arrangement different from that of the rhenium species described above.

**Description of the Structure of Compounds (3) and (4).**—The structures of the substituted anions  $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_9(\text{PPh}_3)]^-$  (3) and  $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_9(\text{py})]^-$  (4) are shown in Figures 1 and 2 respectively. Their stereochemistry is considered repre-

sentative for the whole  $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_9\text{L}]^-$  family. Bond distances and angles are given in Tables 1 and 2. Both structures derive from that of the parent anion (1) by substitution of one axial carbonyl ligand on Re(1).

A comparison of corresponding bond parameters in the three unsaturated species (1), (3), and (4) is reported in Table 3. The Re–Re bond lengths are comparable and only small effects on these parameters due to the replacement of one CO with ligands of increasing bulk are observed. The short Re(2)–Re(3) edge bridged by two hydrides, formally a metal–metal double bond, remains almost unchanged: 2.789(1), 2.797(1), and 2.802(1) Å, in anions (1), (3), and (4), respectively.

The bond parameters involving the substituent ligands  $\text{PPh}_3$  and py are normal. The Re(1)–P bond in (3), 2.481(2) Å, is slightly longer than the corresponding bond, 2.42(1) Å, in  $[\text{Re}_3(\mu\text{-H})_3(\text{CO})_{11}(\text{PPh}_3)]$ , where the phosphine is co-ordinated in an equatorial position;<sup>3</sup> the Re(1)–N bond in (4), 2.21(1) Å, compares well with the mean Re–N bond length, 2.22 Å, in  $[\text{Re}_3(\mu\text{-H})_3(\text{CO})_{10}(\text{py})_2]$ .<sup>4</sup> In compound (4) the plane of the py ring is almost normal to the  $\text{Re}_3$  plane and parallel to the Re(2)–Re(3) edge, in order to minimize the intramolecular non-bonding repulsions.

The family exhibits a Re(1)–C interaction in the axial direction which follows a regular trend, dependent on the *trans* competition for the metal-to-ligand  $\pi$  back-donation; this bond contact decreases on passing from anion (1) (2.00 Å, CO *trans* to CO) to anion (3) [1.96(1) Å,  $\text{PPh}_3$  *trans* to CO], to anion (4) [1.85(1) Å, py *trans* to CO]. The hydride ligands have been directly located in compound (3) only: the Re–H bonds are in the range 1.65(7)–1.97(7) Å, mean 1.84 Å, and the Re–H–Re angles have mean values of 121° for the bridges on the long Re–Re edges and 100° for those on the short edge.

The main effect on the overall stereochemistry of the replacement of one CO group on Re(1) by ligands of greater steric hindrance is a displacement of the carbonyl ligands on Re(2) and on Re(3) away from the bulky group: the Re(1)–Re(2,3)–C(diagonal) angles are increased for the CO groups lying on the same side of the  $\text{Re}_3$  plane bearing the substituent and are decreased for those on the opposite side, with respect to the values in the parent anion (1) (see Table 3). The effect is, as expected, more marked for  $\text{PPh}_3$  than for py.

**Spectroscopic Data of the Anions  $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_9\text{L}]^-$ .**—The substitution of one of the axial carbonyls of the  $\text{Re}(\text{CO})_4$  group of compound (1) by a ligand L lowers the whole (idealized) symmetry of the anion from  $C_{2v}$  to  $C_s$  (in solution). In fact three signals (relative intensities 1:1:2) are observed in the hydridic region of the <sup>1</sup>H n.m.r. spectra of the anions (2), (3),

**Table 4.** Comparison of the hydridic chemical shifts ( $\delta$ ) in some triangular rhenium carbonyl clusters

Compound	L	M( $\mu$ -H) <sub>2</sub> M <sup>a</sup>	M( $\mu$ -H)ML	M'( $\mu$ -H)ML <sup>b</sup>	LM( $\mu$ -H)ML	Ref.
[Re <sub>3</sub> ( $\mu$ -H) <sub>4</sub> (CO) <sub>10</sub> ] <sup>-</sup>	CO	-8.50	-13.35			1
[Re <sub>3</sub> ( $\mu$ -H) <sub>4</sub> (CO) <sub>9</sub> (NCMe)] <sup>-</sup>	NCMe	-7.96, -8.33	-10.46			
[Re <sub>3</sub> ( $\mu$ -H) <sub>4</sub> (CO) <sub>9</sub> (PPh <sub>3</sub> )] <sup>-</sup>	PPh <sub>3</sub>	-7.78, -8.93	-12.25			
[Re <sub>3</sub> ( $\mu$ -H) <sub>4</sub> (CO) <sub>9</sub> (py)] <sup>-</sup>	py	-7.76, -8.70	-9.20			
[Re <sub>3</sub> ( $\mu$ -H) <sub>2</sub> (CO) <sub>12</sub> ] <sup>-</sup>	CO			-17.2		c
[Re <sub>3</sub> ( $\mu$ -H) <sub>3</sub> (CO) <sub>12</sub> ]	CO			-17.1		d
[Re <sub>3</sub> ( $\mu$ -H) <sub>3</sub> (CO) <sub>11</sub> (NCMe)]	NCMe			-14.56 <sup>e</sup>		f
[Re <sub>3</sub> ( $\mu$ -H) <sub>3</sub> (CO) <sub>10</sub> (NCMe) <sub>2</sub> ]	NCMe			-14.52	-12.0	f
[Re <sub>3</sub> ( $\mu$ -H) <sub>3</sub> (CO) <sub>10</sub> (dppm)]	dppm <sup>g</sup>			-16.43	-15.5	h
[Re <sub>3</sub> ( $\mu$ -H) <sub>3</sub> (CO) <sub>10</sub> (py) <sub>2</sub> ]	py			-13.00	-9.24	4

<sup>a</sup> M = Re(CO)<sub>3</sub>, <sup>b</sup> M' = Re(CO)<sub>4</sub>. <sup>c</sup> M. R. Churchill, P. H. Bird, H. D. Kaesz, R. Bau, and B. Fontal, *J. Am. Chem. Soc.*, 1968, **90**, 7135. <sup>d</sup> M. A. Andrews, S. W. Kirtley, and H. D. Kaesz, *Inorg. Synth.*, 1977, **17**, 66. <sup>e</sup> For this species there is also a resonance at  $\delta$  -17.26, due to a hydride bridging two Re(CO)<sub>4</sub> moieties. <sup>f</sup> G. Ciani, A. Sironi, G. D'Alfonso, P. Romiti, and M. Freni, *J. Organomet. Chem.*, 1983, **254**, C37. <sup>g</sup> dppm = Bis(diphenylphosphino)methane. <sup>h</sup> D. W. Prest, M. J. Mays, P. R. Raithby, and A. G. Orpen, *J. Chem. Soc., Dalton Trans.*, 1982, 737.

and (4). The chemical shifts are downfield of those usually found for unsubstituted saturated rhenium carbonyl clusters (Table 4). Some general features can be observed. (a) The resonances of the hydrides of the Re( $\mu$ -H)<sub>2</sub>Re moiety are mainly affected by the presence of the unsaturation. Indeed the values at *ca.*  $\delta$  -8 p.p.m. are typical of other unsaturated rhenium clusters and do not appear substantially modified by the presence of different ligands L in the Re(CO)<sub>3</sub>L moiety (see Table 4). (b) The chemical shifts of the hydrides bridging the lateral edges are affected (in a nearly additive way) both by the nature of the ligand L and by the presence of the unsaturation. A downfield shift (up to 4 p.p.m.) is observed on going from strong to poor  $\pi$ -acceptor ligands and this can be related to a change in the paramagnetic contribution to the shielding. The presence of the unsaturation is responsible for a downfield shift of *ca.* 4 p.p.m. as indicated by the comparison of the chemical shifts of the hydrides bridging the lateral edges in (2), (3), and (4) with those of saturated rhenium clusters containing the same ligands (Table 4).

There is no structural or spectroscopic evidence which could lead to the unambiguous assignment of the two low-field resonances (intensity 1) to the hydride *syn* or *anti* with respect to L. In the case of compounds (3) and (4) only one of these two hydrides shows a coupling with the hydrides of the lateral edges. At present we cannot suggest any explanation for this behaviour and work is in progress to study the coupling properties in a series of analogous compounds.

The carbonyl region of the i.r. spectra of compounds (2), (3), and (4) appears at first glance to be simpler than that of compound (1), in spite of the lower symmetry, probably because the strong absorption at lower frequency, being very broad, includes more bands. It is worth noting, in all these spectra, the disappearance of the weak band at *ca.* 2 100 cm<sup>-1</sup> that is typical, in monoanionic and neutral triangular rhenium clusters, of the presence of a Re(CO)<sub>4</sub> moiety. The course of the substitution of CO by L is indeed monitored on the basis of the decreasing intensity of this band.

**Reactivity of the Anions [Re<sub>3</sub>( $\mu$ -H)<sub>4</sub>(CO)<sub>9</sub>L]<sup>-</sup>.**—This family of unsaturated anions is expected to show a reactivity at the Re( $\mu$ -H)<sub>2</sub>Re moiety comparable with that of the parent anion (1), which has been widely investigated.<sup>1</sup> However the substitution of a carbonyl ligand by ligands having weaker  $\pi$ -acceptor and stronger  $\sigma$ -donor ability can give rise to some modification of the electronic charge distribution on the cluster and consequently on the hydride ligands. By varying the nature of L it would therefore be possible to control the reactivity of the hydrides. For instance, the two hydrides bridging the lateral edges of the parent anion exhibit a partial positive charge, one of

them being removed upon treatment with strong bases.<sup>1</sup> Such a reaction is not observed for the pyridine derivative, in agreement with the higher electron density expected on the hydrides of this species.

The acetonitrile derivative contains two activated sites: the labile nitrile and the hydrides of the unsaturated moiety. Besides the simple substitution of the nitrile, reactions involving the hydrides only or involving both the active sites are also possible. A first example of the last class of reactions is observed on dissolving the anion in methanol: at room temperature, in *ca.* 5 h, the anion [Re<sub>3</sub>( $\mu$ -H)<sub>3</sub>(CO)<sub>9</sub>( $\mu$ -OMe)]<sup>-</sup> is formed.<sup>5</sup> The mechanism implies probable co-ordination of the alcohol, by replacement of the nitrile, and subsequent attack of the hydroxylic hydrogen on one hydride of the Re( $\mu$ -H)<sub>2</sub>Re moiety, with H<sub>2</sub> evolution. Alcohols have been shown unable to attack the hydrides of the parent anion; therefore the reaction *via* the acetonitrile derivative is made possible thanks to the increased acidity of the MeOH ligand, due to co-ordination. In a similar way, other organic substrates (containing for instance polarized multiple bonds) could be activated towards the nucleophilic attack of the hydrides, when co-ordinated in place of the nitrile. Further work on this subject is in progress.

## Experimental

The reactions were performed under nitrogen, using the Schlenk technique, and solvents deoxygenated and dried by standard methods; Me<sub>3</sub>NO·2H<sub>2</sub>O was a Fluka product, used as received. [NEt<sub>4</sub>][Re<sub>3</sub>( $\mu$ -H)<sub>4</sub>(CO)<sub>10</sub>] was prepared as previously described.<sup>1</sup> Infrared spectra were recorded on a Perkin-Elmer 781 grating spectrophotometer, in 0.1-mm CaF<sub>2</sub> cells, and were calibrated with polystyrene film absorptions. N.m.r. spectra were recorded on a Bruker WP 80 spectrometer. Elemental analyses were performed by the Microanalytical Laboratory of Milan University.

**Synthesis of [NEt<sub>4</sub>][Re<sub>3</sub>( $\mu$ -H)<sub>4</sub>(CO)<sub>9</sub>(NCMe)].**—(a) A sample (100 mg, 0.102 mmol) of [NEt<sub>4</sub>][Re<sub>3</sub>( $\mu$ -H)<sub>4</sub>(CO)<sub>10</sub>], dissolved in MeCN (3 cm<sup>3</sup>), was heated in an oil-bath at 85 °C, under H<sub>2</sub> flow. The progress of the reaction was monitored by i.r. spectroscopy. After 4 h the solvent was removed under reduced pressure and the residue was analysed by <sup>1</sup>H n.m.r. spectroscopy [showing a yield of compound (2) of 88%]. The reaction mixture was then treated twice with dichloromethane (0.5 cm<sup>3</sup>), leaving a residue of pure [NEt<sub>4</sub>][Re<sub>3</sub>( $\mu$ -H)<sub>4</sub>(CO)<sub>9</sub>(NCMe)] (38 mg, 0.039 mmol, isolated yields 38%).

(b) A sample (100 mg, 0.102 mmol) of [NEt<sub>4</sub>][Re<sub>3</sub>( $\mu$ -H)<sub>4</sub>(CO)<sub>10</sub>], dissolved in MeCN (3 cm<sup>3</sup>) was treated at room temperature with a solution of Me<sub>3</sub>NO·2H<sub>2</sub>O in MeCN (15 mg

Table 5. Final positional parameters for compound (3)

Atom	x	y	z	Atom	x	y	z
Re(1)	-0.043 81(3)	0.082 85(1)	0.285 61(2)	C(P16)	-0.265 6(7)	-0.066 5(3)	0.178 8(6)
Re(2)	-0.113 39(3)	0.196 29(1)	0.189 00(2)	C(P21)	-0.351 1(7)	0.057 5(3)	0.317 1(6)
Re(3)	0.038 46(3)	0.133 45(1)	0.086 74(2)	C(P22)	-0.355 7(7)	0.107 5(3)	0.359 7(6)
P	-0.234 2(2)	0.039 61(8)	0.239 3(2)	C(P23)	-0.447 5(9)	0.121 9(4)	0.412 3(6)
C(11)	0.045 0(8)	0.017 8(3)	0.291 2(6)	C(P24)	-0.538 4(8)	0.086 2(4)	0.426 0(7)
O(11)	0.099 6(6)	-0.019 6(3)	0.292 2(5)	C(P25)	-0.536 0(8)	0.038 3(5)	0.385 2(8)
C(12)	-0.082 0(7)	0.075 6(3)	0.419 0(6)	C(P26)	-0.442 9(8)	0.021 6(4)	0.332 1(7)
O(12)	-0.102 2(6)	0.068 8(3)	0.499 7(4)	C(P31)	-0.301 9(7)	0.049 4(3)	0.115 1(6)
C(13)	0.096 0(8)	0.121 6(4)	0.335 6(6)	C(P32)	-0.241 6(7)	0.033 8(3)	0.037 3(6)
O(13)	0.173 5(6)	0.145 2(3)	0.371 9(5)	C(P33)	-0.293 8(8)	0.037 2(4)	-0.060 0(6)
C(21)	-0.278 7(7)	0.203 8(3)	0.177 7(6)	C(P34)	-0.405 7(8)	0.056 9(4)	-0.075 9(6)
O(21)	-0.379 9(5)	0.210 0(3)	0.167 5(6)	C(P35)	-0.463 3(8)	0.074 8(4)	0.002 3(7)
C(22)	-0.101 8(7)	0.238 0(3)	0.307 1(7)	C(P36)	-0.414 0(7)	0.070 8(4)	0.098 0(6)
O(22)	-0.091 0(7)	0.263 4(3)	0.377 6(5)	N	0.285 6(6)	0.305 6(3)	0.232 2(5)
C(23)	-0.103 4(7)	0.257 4(3)	0.108 9(6)	C(T1)	0.394(1)	0.325 1(5)	0.188 3(9)
O(23)	-0.096 9(6)	0.295 2(2)	0.061 3(5)	C(T2)	0.294(1)	0.325 1(5)	0.336 3(8)
C(31)	0.016 6(7)	0.084 1(4)	-0.020 4(6)	C(T3)	0.178(1)	0.325 9(5)	0.174 9(9)
O(31)	0.002 4(5)	0.056 2(3)	-0.085 9(4)	C(T4)	0.282(1)	0.246 4(5)	0.229 2(8)
C(32)	0.198 0(8)	0.109 8(4)	0.113 7(7)	C(T5)	0.403(1)	0.305 1(6)	0.079(1)
O(32)	0.292 8(6)	0.097 5(3)	0.132 1(6)	C(T6)	0.197(1)	0.308 4(5)	0.398 5(9)
C(33)	0.086 8(8)	0.186 8(4)	-0.001 0(7)	C(T7)	0.172(1)	0.386 7(5)	0.167 1(9)
O(33)	0.113 5(6)	0.218 4(3)	-0.055 6(5)	C(T8)	0.379(1)	0.218 7(5)	0.287 6(9)
C(P11)	-0.229 1(7)	-0.032 6(3)	0.252 9(6)	H(1)	-0.132(6)	0.135(3)	0.276(5)
C(P12)	-0.192 2(9)	-0.052 9(4)	0.343 9(7)	H(2)	-0.038(6)	0.077(3)	0.149(5)
C(P13)	-0.188(1)	-0.106 8(4)	0.357 1(8)	H(3)	-0.120(6)	0.151(3)	0.078(5)
C(P14)	-0.223(1)	-0.140 9(4)	0.283 0(8)	H(4)	0.037(6)	0.186(3)	0.175(5)
C(P15)	-0.262 5(9)	-0.120 9(3)	0.195 1(7)				

Table 6. Final positional parameters for compound (4)

Atom	x	y	z	Atom	x	y	z
Re(1)	0.162 60(5)	0.378 30(4)	-0.051 64(4)	O(31)	0.449(1)	0.134(1)	0.054(8)
Re(2)	0.112 04(6)	0.255 74(4)	-0.198 98(4)	C(32)	0.117(2)	0.154(1)	0.033(1)
Re(3)	0.193 10(6)	0.179 80(5)	-0.051 09(4)	O(32)	0.065(1)	0.137(1)	0.079 2(8)
C(11)	0.193(1)	0.416(1)	0.054 6(8)	C(33)	0.177(2)	0.070(2)	-0.090(1)
O(11)	0.205(1)	0.437 9(8)	0.117 8(6)	O(33)	0.161(1)	-0.000 3(9)	-0.115(1)
C(12)	0.127(1)	0.493(1)	-0.087 8(9)	N(T)	0.139(1)	0.383 2(8)	0.340 8(7)
O(12)	0.109(1)	0.561 4(7)	-0.104 5(7)	C(T1)	0.077(3)	0.294(2)	0.325(2)
C(13)	-0.004(1)	0.356(1)	-0.060(1)	C(T2)	0.164(3)	0.402(2)	0.433(2)
O(13)	-0.109 1(9)	0.346 2(8)	-0.062 4(8)	C(T3)	0.057(2)	0.451(2)	0.293(1)
N	0.361 4(9)	0.388 5(6)	-0.050 9(7)	C(T4)	0.261(2)	0.383(2)	0.316(2)
C(1)	0.396(1)	0.420(1)	-0.110 8(9)	C(T1')	0.148(8)	0.338(6)	0.260(5)
C(2)	0.521(1)	0.426(1)	-0.111(1)	C(T2')	0.214(7)	0.317(5)	0.403(4)
C(3)	0.607(1)	0.399(1)	-0.048(1)	C(T3')	0.019(6)	0.407(4)	0.371(4)
C(4)	0.570(2)	0.368(1)	0.014(1)	C(T4')	0.199(7)	0.474(5)	0.320(4)
C(5)	0.447(1)	0.363(1)	0.010(1)	C(T5)	0.046(3)	0.274(2)	0.237(2)
C(21)	0.188(1)	0.302(1)	-0.274(1)	C(T6)	0.244(2)	0.341(1)	0.487(1)
O(21)	0.243(1)	0.329(1)	-0.317 8(8)	C(T7)	-0.072(2)	0.459(1)	0.310(1)
C(22)	-0.045(2)	0.298(1)	-0.257(1)	C(T8)	0.336(2)	0.460(1)	0.326(1)
O(22)	-0.144(1)	0.325 8(9)	-0.287 4(8)	H(1)*	0.1327	0.3623	-0.1585
C(23)	0.088(2)	0.153(1)	-0.259(1)	H(2)*	0.2129	0.2800	0.0013
O(23)	0.070(2)	0.090 5(9)	-0.293 7(9)	H(3)*	0.2524	0.2108	-0.1357
C(31)	0.354(1)	0.152(1)	0.016 3(9)	H(4)*	0.0482	0.2108	-0.1223

\* Hydrides are in calculated positions.

per cm<sup>3</sup>; 0.8 cm<sup>3</sup>, 0.108 mmol). A stream of N<sub>2</sub> was passed through the solution to remove the evolved gases (NMe<sub>3</sub> and CO). After 1 h, the i.r. spectrum in the carbonyl region showed only the bands of [NEt<sub>4</sub>][Re<sub>3</sub>(μ-H)<sub>4</sub>(CO)<sub>9</sub>(NCMe)]. The solvent was removed under reduced pressure and the residue, after analysis by <sup>1</sup>H n.m.r., was submitted to several cycles of dissolution in acetonitrile and evaporation to dryness, until complete elimination of NMe<sub>3</sub>. The residue so obtained was suitable for successive reactions, without further purification (Found: C, 24.05; H, 2.90; N, 3.10. C<sub>19</sub>H<sub>27</sub>N<sub>2</sub>O<sub>9</sub>Re<sub>3</sub> requires C, 23.15; H, 2.75; N, 2.85%; ν<sub>max</sub>(CO) at 2 040w, 2 015s, 2 000vs, and 1 918br vs cm<sup>-1</sup> (acetonitrile); δ<sub>H</sub> [(CD<sub>3</sub>)<sub>2</sub>CO, SiMe<sub>4</sub>

standard] 3.5 (8 H, q, 4CH<sub>2</sub>), 2.38 (3 H, s, CH<sub>3</sub>), 1.4 (12 H, tt, 4CH<sub>3</sub>), -7.96 (1 H, s, ReH), -8.33 (1 H, s, ReH), and -10.46 (2 H, s, ReH). Upon heating, the solid compound decomposes at 140 °C.

*Synthesis of [NEt<sub>4</sub>][Re<sub>3</sub>(μ-H)<sub>4</sub>(CO)<sub>9</sub>L] (L = PPh<sub>3</sub> or py).*—A sample (50 mg, 0.051 mmol) of compound (1), dissolved in acetone (5 cm<sup>3</sup>), was treated at room temperature with PPh<sub>3</sub> (20 mg, 0.075 mmol) or with py (8 μl, 0.1 mmol), and with a solution of Me<sub>3</sub>NO·2H<sub>2</sub>O in acetonitrile (15 mg per cm<sup>3</sup>; 0.4 cm<sup>3</sup>, 0.054 mmol). Dinitrogen was bubbled through the solution for 30 min, then the solvent was removed and the residue analysed by

<sup>1</sup>H n.m.r., showing the quantitative formation (on the basis of the integration with respect to the cationic signals) of the substitution derivative  $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_9\text{L}]^-$ . The product was then isolated by precipitation with n-hexane-diethyl ether from a concentrated acetone solution (isolated yields in the range 85–90%). L = PPh<sub>3</sub>, m.p. 191 °C (decomp.) (Found: C, 34.3; H, 3.15; N, 1.3. C<sub>35</sub>H<sub>39</sub>NO<sub>9</sub>PRE<sub>3</sub> requires C, 34.80; H, 3.25; N, 1.15%).  $\nu_{\text{max}}(\text{CO})$  at 2 033m, 2 005s, 1 997vs, 1 930ms, 1 910vs, and 1 900 (sh) cm<sup>-1</sup> (tetrahydrofuran);  $\delta_{\text{H}}[(\text{CD}_3)_2\text{CO}, \text{SiMe}_4 \text{ standard}]$  7.4 (15 H, m, 3Ph), 3.5 (8 H, q, 4CH<sub>2</sub>), 1.4 (12 H, tt, 4CH<sub>3</sub>), -7.55 [1 H, d,  $J(\text{PH})$  5.5 Hz, ReH], -8.71 [1 H, dt,  $J(\text{PH})$  4,  $J(\text{HH})$  2 Hz, ReH], and -12.18 p.p.m. [2 H, dd,  $J(\text{PH})$  16.2,  $J(\text{HH})$  2 Hz, 2ReH]. L = py, m.p. 160 °C (decomp.) (Found: C, 25.65; H, 2.90; N, 2.85. C<sub>22</sub>H<sub>29</sub>N<sub>2</sub>O<sub>9</sub>Re<sub>3</sub> requires C, 25.80; H, 2.85; N, 2.75%).  $\nu_{\text{max}}(\text{CO})$  at 2 032mw, 2 004s, 1 994vs, 1 916vs, and 1 896 (sh) cm<sup>-1</sup> (tetrahydrofuran);  $\delta_{\text{H}}[(\text{CD}_3)_2\text{CO}, \text{SiMe}_4 \text{ standard}]$  8.8 (2 H, m, H<sup>2,6</sup> of py), 7.9 (1 H, m, H<sup>4</sup> of py), 7.4 (2 H, m, H<sup>3,5</sup> of py), 3.5 (8 H, q, 4CH<sub>2</sub>), 1.4 (12 H, tt, 4CH<sub>3</sub>), -7.76 (1 H, s, ReH), -8.71 [1 H, t,  $J(\text{HH})$  2 Hz, ReH], and -9.18 p.p.m. [2 H, d,  $J(\text{HH})$  2 Hz, 2ReH].

**Reactivity of  $[\text{NEt}_4][\text{Re}_3(\mu\text{-H})_4(\text{CO})_9(\text{NCMe})]$ .**—(a) *Reaction with CO.* Carbon monoxide was bubbled for 30 min into an acetone solution of (2), at room temperature. The i.r. spectrum showed the formation of (1).

(b) *Reaction with PPh<sub>3</sub> or pyridine.* A sample (10 mg, 0.010 mmol) of compound (2) dissolved in CH<sub>2</sub>Cl<sub>2</sub> (3 cm<sup>3</sup>) was treated with PPh<sub>3</sub> (3 mg, 0.011 mmol) or pyridine (1 μl, 0.012 mmol). After 15 min the solvent was removed under reduced pressure and the n.m.r. spectrum showed the quantitative formation of the appropriate substitution derivative.

(c) *Reaction with methanol.* A sample (10 mg, 0.010 mmol) of compound (2) was dissolved in methanol (3 cm<sup>3</sup>). G.l.c. analysis revealed slow H<sub>2</sub> evolution. After 5 h, the solvent was removed under reduced pressure and the n.m.r. spectrum showed the quantitative formation of  $[\text{Re}_3(\mu\text{-H})_3(\text{CO})_9(\mu_3\text{-OMe})]^-$ .

**X-Ray Analyses of Compounds (3) and (4).**—*Crystal data for (3).* C<sub>35</sub>H<sub>39</sub>NO<sub>9</sub>PRE<sub>3</sub>,  $M = 1\,207.3$ , monoclinic, space group  $P2_1/n$  [non-standard setting of  $P2_1/c$  (no. 14)],  $a = 11.448(2)$ ,  $b = 25.311(6)$ ,  $c = 13.596(3)$  Å,  $\beta = 94.00(2)^\circ$ ,  $U = 3\,930.0$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 2.040$  g cm<sup>-3</sup>,  $F(000) = 2\,272$ , Mo- $K_\alpha$  radiation ( $\lambda = 0.710\,73$  Å),  $\mu(\text{Mo-}K_\alpha) = 94.34$  cm<sup>-1</sup>.

*Crystal data for (4).* C<sub>22</sub>H<sub>29</sub>N<sub>2</sub>O<sub>9</sub>Re<sub>3</sub>,  $M = 1\,024.1$ , monoclinic, space group  $P2_1/n$  [non-standard setting of  $P2_1/c$  (no. 14)],  $a = 11.087(1)$ ,  $b = 15.951(2)$ ,  $c = 17.598(4)$  Å,  $\beta = 104.84(2)^\circ$ ,  $U = 3\,008.4$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 2.261$  g cm<sup>-3</sup>,  $F(000) = 1\,888$ , Mo- $K_\alpha$  radiation ( $\lambda = 0.710\,73$  Å),  $\mu(\text{Mo-}K_\alpha) = 122.53$  cm<sup>-1</sup>.

**Intensity measurements.** Crystal samples of dimensions 0.18 × 0.19 × 0.36 mm for (3) and 0.09 × 0.10 × 0.33 mm for (4) were mounted on glass fibres in air. Intensities for both compounds were collected on an Enraf-Nonius CAD4 automatic diffractometer, using graphite monochromatized Mo- $K_\alpha$  radiation. The setting angles of 25 random intense reflections ( $16 < 2\theta < 25^\circ$ ) were used in each case to determine by least-squares fit accurate cell constants and orientation matrix. The data collections were performed by the  $\omega$ -scan method, within the limits  $3 < \theta < 25^\circ$ . A variable scan speed (from 2 to 20° min<sup>-1</sup>) and a variable scan range of  $(\alpha + 0.35 \tan\theta)^\circ$ , with  $\alpha = 1.0$  for (3) and 0.7 for (4), were used, with a 25% extension at each end of the scan range for background determination. The total numbers of reflections measured were 6 883 for (3) and 5 452 for (4). No significant decay of the crystal sample upon X-ray exposure was observed for compound (3); in the case of compound (4) three standard intense reflections, monitored

every 3 h, revealed a total decay of 13% at the end of the collection, and correction was made. The intensities were corrected for Lorentz and polarization effects. An empirical absorption correction was applied to both data sets, based on  $\psi$ -scans ( $\psi$  0–360° every 10°) of suitable reflections with  $\chi$  values close to 90°; the relative transmission factors had values in the ranges 1.00–0.79 for (3) and 1.00–0.70 for (4), respectively. Two sets of 3 888 [(3)] and 2 018 [(4)] 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)<sup>6</sup> and the physical constants tabulated therein.<sup>7</sup> The structure solutions were based on the deconvolution of three-dimensional Patterson maps, which gave the positions of the Re atoms. Successive difference-Fourier maps showed the locations of all the non-hydrogen atoms. In compound (4) the tetraethylammonium cation was found to be disordered, 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 methods. Anisotropic thermal parameters were assigned to all atoms, except those of the cations, in both compounds. The phenyl hydrogen atoms and the cationic hydrogen atoms in (3) as well as the pyridine hydrogen atoms in (4) were located in their idealized positions ( $C\text{-H } 0.95$  Å,  $B = 5.0$  Å<sup>2</sup>), after each cycle of refinement, but not refined. The cationic hydrogens in compound (4) were ignored because of the disorder present.

The final difference-Fourier maps were rather flat showing residual peaks not exceeding *ca.* 1 e Å<sup>-3</sup> in both cases. For compound (3) four peaks (0.8–0.5 e Å<sup>-3</sup>) were observed, suitable for hydrides in bridging positions. They were refined, with fixed isotropic thermal parameters of 5.0 Å<sup>2</sup>, to convergence, giving acceptable bond parameters. For compound (4), though one or two peaks could be tentatively assigned to bridging hydrides, a complete direct location of these ligands was impossible. We have therefore located them indirectly in computed positions, as previously performed for the parent anion (1).<sup>1</sup> Their mean bond parameters are: Re–H 1.83 Å, Re–H–Re 120° (on the long edges) and 100° (on the short edge). They were included in our model ( $B = 5.0$  Å<sup>2</sup>) but not refined.

Weights were assigned according to the formula  $w = 4F_o^2/\sigma(F_o^2)^2$ , where  $\sigma(F_o^2) = [\sigma(I)^2]^{1/2}/L_p$  ( $I$  and  $L_p$  are the integrated intensity and the Lorentz-polarization correction, respectively);  $p$  was assumed equal to 0.03 in both cases. The final values of the conventional agreement indices  $R$  and  $R'$  were 0.024 and 0.027 for (3) and 0.031 and 0.035 for (4), respectively.

The final positional parameters are given in Tables 5 and 6.

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## References

- 1 T. Beringhelli, G. Ciani, G. D'Alfonso, H. Molinari, and A. Sironi, *Inorg. Chem.*, 1985, **24**, 2666.
- 2 A. J. Deeming and S. Hasso, *J. Organomet. Chem.*, 1976, **114**, 313.
- 3 C. Y. Wei, L. Garlaschelli, R. Bau, and T. F. Koetzle, *J. Organomet. Chem.*, 1981, **213**, 63.
- 4 G. Ciani, G. D'Alfonso, M. Freni, P. Romiti, and A. Sironi, *J. Organomet. Chem.*, 1980, **186**, 353.

- 5 G. Ciani, G. D'Alfonso, M. Freni, P. Romiti, and S. Sironi, *J. Organomet. Chem.*, 1981, **219**, C23.
- 6 B. A. Frenz and Associates, SDP Plus, Version 20, Enraf-Nonius, Delft, Holland, 1982.

- 7 'International Tables for X-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

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