Reactivity of the Unsaturated Anion Decacarbonyltetra-μ-hydrido-trirhenate(1 −) toward Phenols. Crystal and Molecular Structures of the Tetraethylammonium Salts of the Triangular Cluster Anion $[Re_3(\mu\text{-}H)_3(\mu\text{-}OC_6F_5)(CO)_{10}]^-$ and of the Binuclear Anion $[Re_2(\mu\text{-}OC_6H_5)_3(CO)_6]^-$†

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The reactions of $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ with phenols have been investigated under different conditions. The acidity of phenols is sufficient to abstract one hydride of the $Re(\mu\text{-}H)_2Re$ system leading to compounds $[Re_3(\mu\text{-}H)_3(\mu\text{-}OC_6R_5)(CO)_{10}]^-$ (R = H or F) or, under a CO atmosphere, to neutral $[Re_3(\mu\text{-}H)_3(CO)_{12}]$. The NEt_4^+ salt of the pentafluorophenoxide derivative has been investigated by *X*-ray analysis. The crystals are monoclinic, space group $P2_1/c$, with a = 9.304(1), b = 19.357(3), c = 18.063(3) Å, β = 94.72(1)°, and Z = 4. The structure was solved and refined on the basis of 3 897 significant counter data, to a final R 0.028. The anion contains an isosceles triangle of Re atoms, with two longer hydride-bridged edges [3.215(1) and 3.243(1) Å] and one shorter edge [2.975(1) Å] doubly bridged by a hydride and the phenoxide ligand [Re–O 2.176(5) Å]. Reaction of $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ with an excess of phenol at high temperature leads to cluster degradation, with formation of the binuclear anion $[Re_2(\mu\text{-}OC_6H_5)_3(CO)_6]^-$. The NEt_4^+ salt of the latter has been studied by single-crystal *X*-ray analysis: orthorhombic, space group $Pc2_1n$ (non-standard setting of $Pna2_1$), with a = 9.568(1), b = 18.865(3), c = 18.948(3) Å, and Z = 4. The structure solution and refinements were based on 2 168 significant counter data, the final R value being 0.031. The anion contains two $Re(CO)_3$ units, joined through three phenoxide bridges. The mean Re–O bond length is 2.14 Å, and the non-bonding Re $\cdots$ Re contact is 3.154(1) Å. Pyrolysis in n-heptane of $[Re_3(\mu\text{-}H)_3(\mu\text{-}OC_6H_5)(CO)_{10}]^-$ gives selectively $[Re_3(\mu\text{-}H)_3(\mu_3\text{-}OC_6H_5)(CO)_9]^-$, in a reaction that is readily reversed under CO at room temperature.

The $Re(\mu\text{-}H)_2Re$ system present in the unsaturated cluster anion $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ (1)[1] represents a highly reactive site toward electrophilic reagents.[2–7] Species HX give mainly two types of reactions, in accordance with their acidity: (*i*) halogen[3] and carboxylic[4] acids react with (1) at room temperature, causing H_2 evolution and replacement of one of the two hydrides bridging the shortest Re–Re edge by the X^- ligand [equation (1)], and the rate of the reaction increases with the

$$[Re_3(\mu\text{-}H)_4(CO)_{10}]^- + HX \longrightarrow [Re_3(\mu\text{-}H)_3(\mu\text{-}X)(CO)_{10}]^- + H_2 \quad (1)$$

strength of the acid; (*ii*) alcohols[5] and mercaptans[6] react only at high temperature, giving both H_2 and CO evolution and leading to products with the X^- group μ_3-co-ordinated to the cluster [equation (2)].

$$[Re_3(\mu\text{-}H)_4(CO)_{10}]^- + HX \longrightarrow [Re_3(\mu\text{-}H)_3(\mu_3\text{-}X)(CO)_9]^- + H_2 + CO \quad (2)$$

We have therefore investigated the reactivity of compound (1) toward species exhibiting an acidity intermediate between acids and alcohols, such as phenols, in order to verify the preferred reaction path. We report here the results of these studies which led us to the isolation and characterization of species containing bridging phenoxide. The complete results of the *X*-ray investigations on the $[NEt_4]^+$ salts of the anionic products $[Re_3(\mu\text{-}H)_3(\mu\text{-}OC_6F_5)(CO)_{10}]^-$ and $[Re_2(\mu\text{-}OC_6H_5)_3(CO)_6]^-$ are also reported and discussed.

Results and Discussion

Reactivity of Compound (1) *with Phenols.*—Our previous studies showed that the reactions of compound (1) with halogen[3] or carboxylic[4] acids require a large excess of the acids and very long reaction times (up to a week). We have, therefore, tested the reactivity of (1) toward phenols by using phenol itself as solvent, in 1:1 mixture with CH_2Cl_2, at room temperature. Under these conditions an extremely slow reaction took place, evidenced by H_2 evolution and by the appearance, in the ^1H n.m.r. spectrum, of two new signals in the hydridic region, with chemical shifts (δ −8.95 and −13.30 p.p.m., ratio 1:2) typical of $[Re_3(\mu\text{-}H)_3(\mu\text{-}OR)(CO)_{10}]^-$ species (R = Me,[7] δ −9.65 and −13.84; R = H,[8] δ −9.50 and −13.80 p.p.m.). After 1 month, however, only about 15% of the starting compound had reacted. The reaction rate was significantly increased by using molten phenol as solvent, at 50 °C: n.m.r. analysis showed that in only 3 d nearly half of compound (1) was transformed into the new product with high selectivity. After 1 week this species could be isolated in about 70% yield and characterized by elemental analysis, i.r., and ^1H n.m.r. spectra, which confirmed the expected formulation as $[Re_3(\mu\text{-}H)_3(\mu\text{-}OC_6H_5)(CO)_{10}]^-$ (2).

The acidity of phenol is therefore sufficient to promote a reaction of type (1). The trend in reactivity previously observed

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† 1,1,1,2,2,2,3,3,3,3-Decacarbonyl-1,2;1,3;2,3-tri-μ-hydrido-1,2-μ-pentafluorophenoxo-*triangulo*-trirhenate(1 −) and tri-μ-phenoxo-bis-(tricarbonylrhenate)(1 −).

Supplementary data available (No. SUP 56211, 6 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

with other HX species prompted us to use a phenol of higher acidity in order to hasten the reaction. In fact, compound (**1**), dissolved in a 1:1 mixture of CH_2Cl_2 and C_6F_5OH, was converted into the anion $[Re_3(\mu\text{-}H)_3(\mu\text{-}OC_6F_5)(CO)_{10}]^-$ (**3**) in high yields in nearly 2 weeks, at room temperature. Compound (**3**), whose i.r. and n.m.r. spectra are similar to those of (**2**), has been characterized also by *X*-ray structural investigation (see below), thus providing further support for the formulation of (**2**).

We subsequently investigated the possibility that, at higher temperatures, phenols, as alcohols, could give also reactions of type (2). However, on refluxing compound (**1**) in a 1:1 mixture of phenol and acetone, degradation of the cluster occurred: in a few hours compound (**1**) disappeared, giving mainly the new binuclear anion $[Re_2(\mu\text{-}OC_6H_5)_3(CO)_6]^-$ (**4**), characterized also by *X*-ray analysis, together with small amounts of $[Re_3(\mu\text{-}H)_3(CO)_{12}]$ (**5**),[9] identified by i.r., n.m.r., and mass spectroscopy.

Species $[Re_2(\mu\text{-}X)_3(CO)_6]^-$ like (**4**) are very common in rhenium(I) chemistry:[10-12] they are rather unreactive compounds and often represent the final point of mild pyrolysis reactions or cluster degradation.[2]

In order to identify the intermediates of the degradation process we used ^1H n.m.r. spectroscopy to analyse samples taken at different times in the course of the reaction. The only hydride-containing products observed were, besides unreacted (**1**), compound (**2**) and a small amount of (**5**). This suggests that the first attack of phenol leads, as under milder conditions, to replacement of one hydride of the $Re(\mu\text{-}H)_2Re$ system by a phenoxide ligand. At this stage further attack occurs, with both CO and H_2 evolution, and replacement of all the $Re(\mu\text{-}H)Re$ bonds by $Re(\mu\text{-}OC_6H_5)Re$ ones, through intermediates too unstable to be detected. A similar progressive substitution of all the $Re(\mu\text{-}H)Re$ bonds by $Re(\mu\text{-}I)Re$ ones was observed in the reaction of (**1**) with I_2 at room temperature.[2] The small amount of $[Re_3(\mu\text{-}H)_3(CO)_{12}]$ originates, very likely, from the reaction of compound (**1**) with the evolved CO in the presence of an acidic species such as phenol. On treating (**1**) with CO in molten phenol at 50 °C the main product was compound (**5**) [equation (3)].

$$[Re_3(\mu\text{-}H)_4(CO)_{10}]^- + 2CO + C_6H_5OH \longrightarrow [Re_3(\mu\text{-}H)_3(CO)_{12}] + H_2 + C_6H_5O^- \quad (3)$$

Further attempts to obtain a reaction of type (2) on treating compound (**1**) with a stoicheiometric amount of phenol (at reflux in acetone or tetrahydrofuran) led to mixtures of products most of which did not contain the phenoxide ligand. The characterization of these species, probably derived by the reaction of (**1**) with the solvent, is in progress. Similar mixtures of products were obtained also by refluxing compound (**2**) in the same solvents. On the contrary, when compound (**2**) was suspended in an inert solvent like n-heptane and refluxed for 26 h it afforded a species containing the phenoxide group μ_3-co-ordinated to the cluster, $[Re_3(\mu\text{-}H)_3(\mu_3\text{-}OC_6H_5)(CO)_9]^-$ (**6**), according to equation (4). The CO evolved was recognized by gas chromatographic analysis and the compound identified by i.r. and ^1H n.m.r. spectroscopy. Reaction (4) is readily reversed

$$[Re_3(\mu\text{-}H)_3(\mu\text{-}OC_6H_5)(CO)_{10}]^- \underset{}{\overset{\text{Heat}}{\rightleftarrows}} [Re_3(\mu\text{-}H)_3(\mu_3\text{-}OC_6H_5)(CO)_9]^- + CO \quad (4)$$

by treatment of (**6**) with CO at room temperature in acetone. Similar double-bridging (three-electron donor ligand) $\rightleftarrows$ triple-bridging (five-electron donor ligand) interconversions were previously observed in triangular clusters of osmium.[13]

In compound (**6**) the $\mu_3\text{-}OC_6H_5$ ligand is rather labile in solution and attempts to obtain crystals suitable for *X*-ray

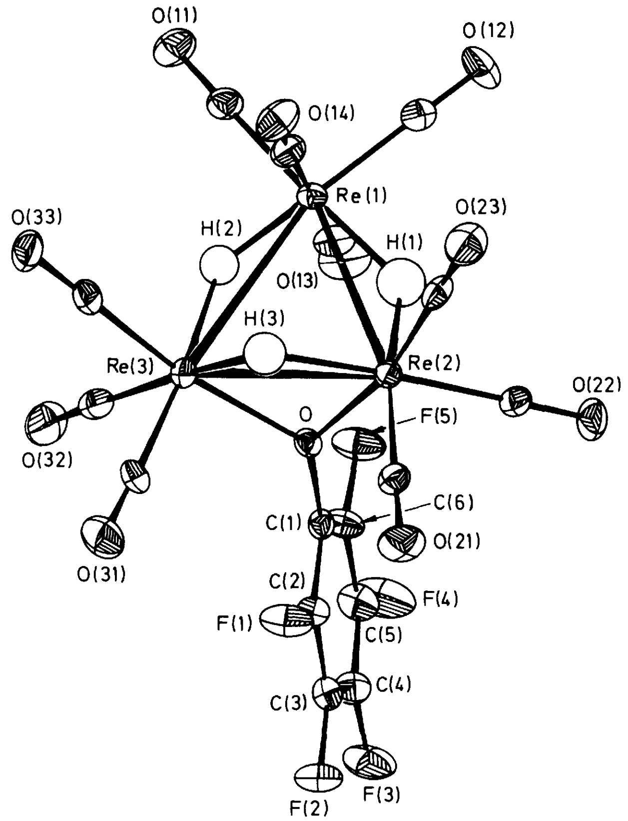

Figure 1. A view of the anion $[Re_3(\mu\text{-}H)_3(\mu\text{-}OC_6F_5)(CO)_{10}]^-$ (**3**). The carbonyl groups are indicated according to their oxygen atoms

analysis were unsuccessful. In particular, in alcohols replacement of the phenoxide by alkoxide was observed.

These results [equation (4)] could suggest that the reaction of (**1**) with alcohols implies the intermediate formation of a labile μ-OR species. However, the rate of formation of μ-X derivatives has been proved to depend strongly on the acidity of the HX reagent. Taking into account the slowness of reaction (1) in molten phenol and the extremely low acidity of alcohols, it seems unlikely that the fast reactions of type (2) follow this pathway. An alternative mechanism could be the substitution of one axial carbonyl in the $Re(CO)_4$ moiety by a solvent molecule and the subsequent abstraction of a H^- ligand by the activated hydroxylic hydrogen. This suggestion is supported by the marked lability of these mutually *trans* carbonyls, as recently observed by ^{13}C n.m.r. spectroscopy.[1b]

Description of the Structures of Compounds (**3**) *and* (**4**).—The structure of the anion $[Re_3(\mu\text{-}H)_3(\mu\text{-}OC_6F_5)(CO)_{10}]^-$ is illustrated in Figure 1. Bond distances and angles are reported in Table 1. The anion consists of an isosceles triangle of rhenium atoms bearing ten terminal CO groups, three edge-bridging hydrides and a pentafluorophenoxide ligand bridging the short Re(2)–Re(3) edge. Neglecting the metal–metal interaction, each rhenium atom shows an almost octahedral co-ordination: Re(1) with four CO groups and two hydrides and Re(2) and Re(3) both with three CO groups, two hydrides, and the phenoxide ligand.

The anion stereochemistry resembles that of other known $[Re_3(\mu\text{-}H)_3(\mu\text{-}X)(CO)_{10}]^-$ species (X = hydride, halide, carboxylate, or benzamide); in particular, it is close to that of the $[Re_3(\mu\text{-}H)_3(\mu\text{-}Cl)(CO)_{10}]^-$ anion.[3]

The two longer triangular edges, Re(1)–Re(2) and Re(1)–

Table 1. Selected bond distances (Å) and angles (°) within the anion $[Re_3(\mu\text{-}H)_3(\mu\text{-}OC_6F_5)(CO)_{10}]^-$ (**3**)

Re(1)–Re(2)	3.215(1)	Re(3)–C(32)	1.92(1)	C(12)–O(12)	1.14(1)	C(2)–C(3)	1.39(1)
Re(1)–Re(3)	3.243(1)	Re(3)–C(33)	1.87(1)	C(13)–O(13)	1.13(1)	C(3)–C(4)	1.37(1)
Re(2)–Re(3)	2.975(1)	Re(2)–O	2.176(5)	C(14)–O(14)	1.12(1)	C(4)–C(5)	1.36(1)
Re(1)–C(11)	1.93(1)	Re(3)–O	2.176(5)	C(21)–O(21)	1.16(1)	C(5)–C(6)	1.38(1)
Re(1)–C(12)	1.94(1)	Re(1)–H(1)	1.79(11)	C(22)–O(22)	1.15(1)	C(6)–C(1)	1.36(1)
Re(1)–C(13)	2.00(1)	Re(1)–H(2)	1.65(9)	C(23)–O(23)	1.15(1)	C(2)–F(1)	1.36(1)
Re(1)–C(14)	1.99(1)	Re(2)–H(1)	1.93(10)	C(31)–O(31)	1.16(1)	C(3)–F(2)	1.35(1)
Re(2)–C(21)	1.90(1)	Re(2)–H(3)	1.84(9)	C(32)–O(32)	1.15(1)	C(4)–F(3)	1.33(1)
Re(2)–C(22)	1.92(1)	Re(3)–H(2)	1.98(8)	C(33)–O(33)	1.17(1)	C(5)–F(4)	1.34(1)
Re(2)–C(23)	1.89(1)	Re(3)–H(3)	1.81(9)	O–C(1)	1.36(1)	C(6)–F(5)	1.34(1)
Re(3)–C(31)	1.91(1)	C(11)–O(11)	1.15(1)	C(1)–C(2)	1.37(1)		

Re(2)–Re(1)–C(11)	157.5(3)	C(12)–Re(1)–C(14)	91.6(5)	C(22)–Re(2)–C(23)	90.0(4)	H(1)–Re(3)–H(3)	98(4)
Re(2)–Re(1)–C(12)	104.7(3)	C(13)–Re(1)–C(14)	179.4(4)	H(1)–Re(2)–H(3)	104(4)	O–Re(2)–C(21)	97.6(3)
Re(2)–Re(1)–C(13)	101.9(3)	H(1)–Re(1)–H(2)	100(5)	Re(1)–Re(3)–C(31)	159.6(3)	O–Re(2)–C(22)	100.3(3)
Re(2)–Re(1)–C(14)	77.5(3)	Re(1)–Re(2)–C(21)	161.7(4)	Re(1)–Re(3)–C(32)	110.5(3)	O–Re(2)–C(23)	168.2(3)
Re(3)–Re(1)–C(11)	105.9(3)	Re(1)–Re(2)–C(22)	108.9(3)	Re(1)–Re(3)–C(33)	94.4(3)	O–Re(3)–C(31)	98.0(3)
Re(3)–Re(1)–C(12)	159.5(3)	Re(1)–Re(2)–C(23)	92.4(3)	Re(2)–Re(3)–C(31)	100.6(3)	O–Re(3)–C(32)	99.8(3)
Re(3)–Re(1)–C(13)	97.2(3)	Re(3)–Re(2)–C(21)	101.4(3)	Re(2)–Re(3)–C(32)	145.9(3)	O–Re(3)–C(33)	170.6(3)
Re(3)–Re(1)–C(14)	82.4(3)	Re(3)–Re(2)–C(22)	146.2(3)	Re(2)–Re(3)–C(33)	124.4(3)	Re(2)–O–Re(3)	86.2(2)
C(11)–Re(1)–C(12)	93.6(4)	Re(3)–Re(2)–C(23)	121.9(3)	C(31)–Re(3)–C(32)	89.9(4)	Re(2)–O–C(1)	131.7(5)
C(11)–Re(1)–C(13)	91.5(4)	C(21)–Re(2)–C(22)	89.4(4)	C(31)–Re(3)–C(33)	86.9(4)	Re(3)–O–C(1)	133.0(5)
C(11)–Re(1)–C(14)	89.1(4)	C(21)–Re(2)–C(23)	88.1(4)	C(32)–Re(3)–C(33)	88.2(4)	Re–C–O	175(1)—178(1)
C(12)–Re(1)–C(13)	88.5(5)						

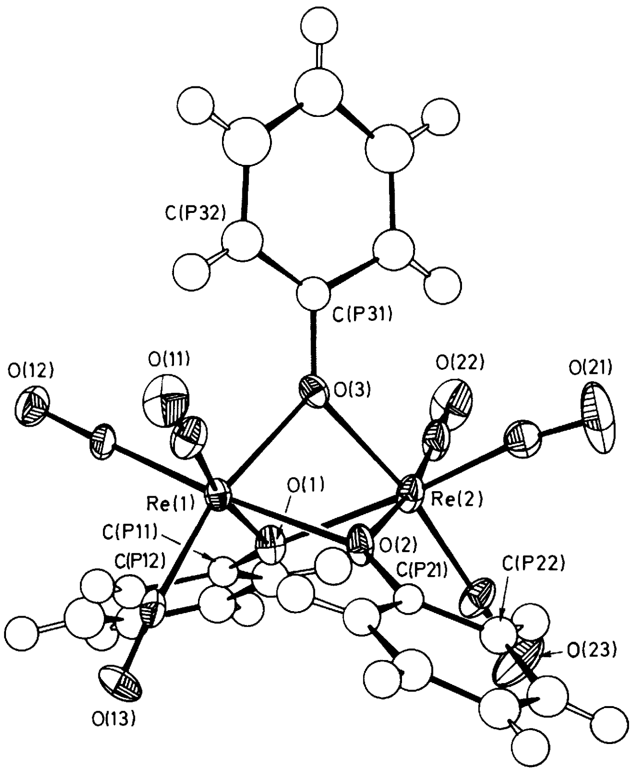

Figure 2. A view of the anion $[Re_2(\mu\text{-}OC_6H_5)_3(CO)_6]^-$ (**4**). The phenyl carbon atoms are labelled C(P*ij*), where *i* indicates the phenyl group and *j* the carbon atom

Re(3), exhibit bond lengths typical of Re–H–Re hydrogen-bridged bonds, 3.215(1) and 3.243(1) Å, respectively, comparable with the corresponding interactions in various species.[3,4] The third shorter edge, Re(2)–Re(3) [2.975(1) Å], doubly bridged by a hydride and the phenoxide ligand, compares well with the Re(μ-H)(μ-Cl)Re interaction in $[Re_3(\mu\text{-}H)_3(\mu\text{-}Cl)(CO)_{10}]^-$, 2.995(2) Å, the moderate shortening being in line with the suggestion[14] that this type of M(μ-H)(μ-X)M bond length decreases with decreasing size of the bridgehead X atom.

The pentafluorophenoxide ligand forms a symmetric bridge on the Re(2)–Re(3) edge. The two Re–O bond distances are identical, 2.176(5) Å, and are very similar to other Re–O bonds, *e.g.* in $[Re_3(\mu\text{-}H)_3(\mu_3\text{-}OEt)(CO)_9]^-$ (mean 2.17 Å)[5] and in $[Re_3(\mu\text{-}H)_3(\mu\text{-}O_2CH)(CO)_{10}]^-$ (mean 2.17 Å)[4] [see also the mean value of 2.14 Å in compound (**4**)]. The dihedral angle between the Re_3 plane and the Re(2),Re(3),O plane is 100.4°. All the atoms of the OC_6F_5 ligand are coplanar (maximum out-of-plane displacement of *ca.* 0.04 Å) and the dihedral angle between their 'best plane' and the Re(2),Re(3),O plane is 91.2°. This orientation of the phenyl ring is very probably due to the necessity of minimizing intramolecular non-bonding repulsion.

The carbonyl groups can be assigned to three classes: (*i*) *trans* to CO (two groups), mean Re–C and C–O 1.99 and 1.13 Å; (*ii*) *trans* to hydrides (six groups), mean Re–C and C–O 1.92 and 1.15 Å; (*iii*) *trans* to the phenoxide (two groups), mean Re–C and C–O 1.88 and 1.16 Å.

The bond parameters for the three hydrides are affected by too high uncertainties to be discussed in detail. They are comparable to similar parameters determined in other rhenium compounds[15] and the main features are as follows: H(1) and H(2) show shorter bonds with Re(1) (mean 1.72 Å) than with Re(2) or Re(3) (mean 1.95 Å); the Re–H(1,2)–Re angles (mean 123°) are larger than Re–H(3)–Re (109°); the dihedral angle between the Re_3 plane and the Re(2),Re(3),H(3) plane is 102.5°.

The binuclear anion $[Re_2(\mu\text{-}OC_6H_5)_3(CO)_6]^-$ is shown in Figure 2 and the bond distances and angles are given in Table 2. This anion belongs to a family of $[Re_2(\mu\text{-}X)_3(CO)_6]^-$ anions, where X is a three-electron donor group, *e.g.* an alkoxide[10,11] or a halide[12] ligand. Each metal atom in these species exhibits a slightly distorted octahedral geometry and attains a noble-gas configuration without the need of a direct metal–metal bond. The Re–Re distances are therefore related only to the nature of the bridging groups. The Re(1)–Re(2) distance in (**4**), 3.154(1) Å, is longer than the Re–Re contact in $[Re_2(\mu\text{-}OMe)_3(CO)_6]^-$ [3.086(3) Å],[16] because of both the lower donor power and higher steric hindrance of the phenoxides; it is shorter than the corresponding contacts in the halide-bridged species [X = Cl,[17] 3.375(1) Å; X = Br,[18] 3.46 Å].

Table 2. Selected bond distances (Å) and angles (°) within the anion $[Re_2(\mu\text{-}OC_6H_5)_3(CO)_6]^-$ (**4**)

Re(1)···Re(2)	3.154(1)	Re(2)–C(23)	1.87(2)	Re(2)–O(3)	2.15(1)	C(22)–O(22)	1.15(2)
Re(1)–C(11)	1.90(2)	Re(1)–O(1)	2.15(1)	C(11)–O(11)	1.15(2)	C(23)–O(23)	1.16(2)
Re(1)–C(12)	1.87(2)	Re(1)–O(2)	2.11(1)	C(12)–O(12)	1.18(2)	O(1)–C(P11)	1.40(2)
Re(1)–C(13)	1.89(2)	Re(1)–O(3)	2.13(1)	C(13)–O(13)	1.18(2)	O(2)–C(P21)	1.39(2)
Re(2)–C(21)	1.86(2)	Re(2)–O(1)	2.13(1)	C(21)–O(21)	1.15(2)	O(3)–C(P31)	1.38(2)
Re(2)–C(22)	1.89(2)	Re(2)–O(2)	2.15(1)				

C(11)–Re(1)–C(12)	85.2(7)	C(13)–Re(1)–O(2)	97.3(6)	C(21)–Re(2)–O(3)	98.4(9)	Re(1)–O(1)–Re(2)	94.8(4)
C(11)–Re(1)–C(13)	88.3(8)	C(13)–Re(1)–O(3)	167.2(6)	C(22)–Re(2)–O(1)	103.2(6)	Re(1)–O(2)–Re(2)	95.6(4)
C(12)–Re(1)–C(13)	90.3(7)	O(1)–Re(1)–O(2)	71.5(4)	C(22)–Re(2)–O(2)	171.3(7)	Re(1)–O(3)–Re(2)	95.0(5)
C(11)–Re(1)–O(1)	170.9(6)	O(1)–Re(1)–O(3)	71.7(4)	C(22)–Re(2)–O(3)	101.2(7)	Re(1)–O(1)–C(P11)	130.1(9)
C(11)–Re(1)–O(2)	102.1(6)	O(2)–Re(1)–O(3)	71.9(4)	C(23)–Re(2)–O(1)	99.8(8)	Re(2)–O(1)–C(P11)	132.0(8)
C(11)–Re(1)–O(3)	100.3(7)	C(21)–Re(2)–C(22)	85.8(8)	C(23)–Re(2)–O(2)	100.7(6)	Re(1)–O(2)–C(P21)	134.7(9)
C(12)–Re(1)–O(1)	100.4(6)	C(21)–Re(2)–C(23)	89.0(11)	C(23)–Re(2)–O(3)	169.5(7)	Re(2)–O(2)–C(P21)	129.6(9)
C(12)–Re(1)–O(2)	169.6(6)	C(22)–Re(2)–C(23)	86.8(9)	O(1)–Re(2)–O(2)	71.3(4)	Re(1)–O(3)–C(P31)	131.4(10)
C(12)–Re(1)–O(3)	99.7(6)	C(21)–Re(2)–O(1)	167.6(8)	O(1)–Re(2)–O(3)	71.8(5)	Re(2)–O(3)–C(P31)	133.5(10)
C(13)–Re(1)–O(1)	98.9(6)	C(21)–Re(2)–O(2)	98.7(6)	O(2)–Re(2)–O(3)	70.9(4)	Re–C–O	170(3)—179(1)

The Re–O bond lengths, range 2.11(1)—2.15(1) Å, have a mean value of 2.14 Å, somewhat higher than that of the corresponding interactions in the analogous methoxo-bridged compound, 2.08 Å,[16] in full agreement with the above mentioned effect on the metal–metal distances.

Each of the three phenyl rings is essentially coplanar with the corresponding Re, O, Re plane (dihedral angles of 15.1, 10.2, and 2.0°); this situation differs from that observed in compound (**3**), in which the phenyl ring is nearly perpendicular to the Re(2), Re(3),O plane.

The mean values of the Re–C and C–O bond lengths are 1.88 and 1.16 Å, respectively.

Experimental

Compound (**1**) was prepared as described previously.[1] Phenol of high purity was provided by Montedison. Pentafluorophenol was purchased from Fluka and used as received. The reactions were performed under nitrogen, using the Schlenk technique, and 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 by M. Bonfà on a Bruker WP 80 spectrometer. Mass spectra were obtained by P. Russo on a Varian MAT 112 instrument, with a direct-inlet probe. Gas chromatographic analyses were performed on a Dani 3200 instrument, fitted with HWD and a 1-m column of molecular sieves, using Ar or He as carrier. Elemental analyses were performed by the Microanalytical Laboratory of Milan University.

Synthesis of $[NEt_4][Re_3(\mu\text{-}H)_3(\mu\text{-}OC_6H_5)(CO)_{10}]$.—A 100-mg sample (0.103 mmol) of the NEt_4^+ salt of complex (**1**) was suspended in molten phenol (1 cm^3) at 50 °C, for 1 week. At different times, samples of the gas in the reaction vessel were withdrawn by a syringe; g.c. analysis showed slow H_2 evolution. The excess of phenol was removed by sublimation under vacuum on a cold-finger. The residual pale yellow solid was washed several times with n-heptane, then treated five times with diethyl ether (5 cm^3) to extract the NEt_4^+ salt of unreacted (**1**). The remaining white powder was carefully dried under vacuum, resulting in 76 mg (0.071 mmol, 69.5%) of $[NEt_4][Re_3(\mu\text{-}H)_3(\mu\text{-}OC_6H_5)(CO)_{10}]$ (Found: C, 27.0; H, 2.8; N, 1.4. $C_{24}H_{28}NO_{11}Re_3$ requires C, 27.1; H, 2.6; N, 1.3%); $\nu_{max.}$(CO) 2 100w, 2 025m, 2 002s, 1 990(sh), 1 945m, 1 920ms, and 1 902s cm^{-1} (acetone); δ_H $[(CD_3)_2CO$, $SiMe_4$ standard] 7.0 (5 H, m, C_6H_5), 3.5 (8 H, q, 4 CH_2), 1.4 (12 H, tt, 4 CH_3), −8.9 (1 H, s, ReH), and −13.3 (2 H, s, 2 ReH). Upon heating, decomposition begins at about 100 °C.

Synthesis of $[NEt_4][Re_3(\mu\text{-}H)_3(\mu\text{-}OC_6F_5)(CO)_{10}]$.—A 50-mg sample (0.051 mmol) of the NEt_4^+ salt of (**1**), dissolved in dichloromethane–pentafluorophenol (1 : 1, 2 cm^3) was stirred at room temperature, in the dark, for 2 weeks. The cream solid obtained by addition of n-heptane (10 cm^3) was washed several times with n-heptane and dried under vacuum (45 mg). The ^1H n.m.r. spectrum indicated that the solid was constituted mainly by $[NEt_4][Re_3(\mu\text{-}H)_3(\mu\text{-}OC_6F_5)(CO)_{10}]$ (*ca.* 75%), together with the unreacted compound (**1**) (*ca.* 10%) and unidentified non-hydridic species. Crystallization from CH_2Cl_2–Et_2O afforded large crystals of the NEt_4^+ salt of (**3**) (32 mg, 0.028 mmol, isolated yield 54%) (Found: C, 25.2; H, 1.9; N, 1.4. $C_{24}H_{23}F_5NO_{11}Re_3$ requires C, 24.9; H, 2.0; N, 1.2%); $\nu_{max.}$(CO) 2 100w, 2 035m, 2 018s, 2 000s, 1 990(sh), 1 948m, 1 927ms, and 1 905s cm^{-1} (acetone); δ_H $[(CD_3)_2CO$, $SiMe_4$ standard)] 3.5 (8 H, q, 4 CH_2), 1.4 (12 H, tt, 4 CH_3), −8.5 (1 H, s, ReH), and −12.4 (2 H, s, ReH). Upon heating the compound decomposes at 138 °C.

Reaction with Phenol in Excess at High Temperature.—A 50-mg sample (0.051 mmol) of the NEt_4^+ salt of (**1**), dissolved in acetone–phenol (1 : 1), was refluxed for 3 h. The solution became colourless and i.r. spectra showed in the ν(CO) region two dominant bands at 2 015 and 1 900 cm^{-1} and three much less intense absorptions at 2 095, 2 035, and 1 975 cm^{-1}. Gas chromatographic analysis of the gas revealed H_2 (dominant) and CO. The acetone was removed under high vacuum and the excess of phenol sublimed on a cold-finger. The residual solid was treated several times with n-heptane–diethyl ether (1 : 1), resulting in the isolation of pure $[NEt_4][Re_2(\mu\text{-}OC_6H_5)_3(CO)_6]$ (38 mg, 0.040 mmol, 78%), which was crystallized from CH_2Cl_2–Et_2O (Found: C, 39.5; H, 3.8; N, 1.7. $C_{32}H_{35}NO_9Re_2$ requires C, 40.4; H, 3.7; N, 1.5%), m.p. 213 °C; $\nu_{max.}$(CO) 2 015s and 1 897vs cm^{-1} (acetone).

The n-heptane–diethyl ether solution was evaporated to dryness, washed several times with water to remove phenol, and dried under vacuum, giving pure $[Re_3(\mu\text{-}H)_3(CO)_{12}]$ (*ca.* 8 mg, 0.009 mmol, 17%); $\nu_{max.}$(CO) 2 095m, 2 035s, 2 008s, and 1 975 cm^{-1} (acetone); δ_H (CD_2Cl_2, $SiMe_4$ standard) −17.2; molecular ion multiplet centred at *m/z* 897 in mass spectrum.

Reaction with CO *in Molten Phenol.*—A 30-mg sample (0.031 mmol) of the NEt_4^+ salt of (**1**), suspended in molten phenol (1 cm^3), under a CO atmosphere, at 50 °C, was stirred for 3 d. The phenol was removed by sublimation under vacuum on a cold-finger and the residue washed with water and dried. Proton

Table 3. Final positional parameters within $[NEt_4][Re_3(\mu\text{-}H)_3(\mu\text{-}OC_6F_5)(CO)_{10}]$ (3)

Atom	*x*	*y*	*z*
Re(1)	0.200 37(4)	0.161 39(2)	0.068 41(2)
Re(2)	0.276 12(4)	0.278 92(2)	−0.048 00(2)
Re(3)	0.489 04(4)	0.255 98(2)	0.081 72(2)
C(11)	0.193(1)	0.117 1(5)	0.163 6(6)
O(11)	0.186 0(9)	0.092 2(4)	0.220 9(4)
C(12)	0.012(1)	0.127 2(6)	0.031 0(6)
O(12)	−0.096 2(9)	0.104 8(5)	0.009 8(5)
C(13)	0.288(1)	0.077 6(6)	0.026 1(6)
O(13)	0.331(1)	0.027 0(4)	0.005 4(5)
C(14)	0.114(1)	0.245 7(5)	0.109 8(5)
O(14)	0.058 4(9)	0.291 3(4)	0.133 7(4)
C(21)	0.348(1)	0.361 4(5)	−0.088 5(5)
O(21)	0.383 8(9)	0.413 0(4)	−0.114 3(4)
C(22)	0.208(1)	0.249 7(5)	−0.146 4(5)
O(22)	0.165 7(9)	0.235 0(4)	−0.205 7(4)
C(23)	0.100(1)	0.325 5(5)	−0.038 9(5)
O(23)	−0.005 1(8)	0.355 6(4)	−0.032 5(4)
C(31)	0.611(1)	0.334 4(6)	0.074 0(6)
O(31)	0.681 9(9)	0.383 3(4)	0.072 4(5)
C(32)	0.652(1)	0.203 0(6)	0.121 4(6)
O(32)	0.751 1(9)	0.171 1(5)	0.143 5(5)
C(33)	0.464(1)	0.285 4(6)	0.178 6(6)
O(33)	0.449 2(8)	0.305 3(5)	0.238 5(4)
O	0.479 6(6)	0.223 2(3)	−0.033 8(3)
C(1)	0.582 2(9)	0.210 7(4)	−0.081 1(5)
C(2)	0.668(1)	0.260 4(4)	−0.108 2(5)
C(3)	0.771(1)	0.246 3(5)	−0.157 5(6)
C(4)	0.789(1)	0.179 6(5)	−0.181 1(6)
C(5)	0.708(1)	0.129 3(5)	−0.152 1(6)
C(6)	0.607(1)	0.145 0(5)	−0.103 1(6)
F(1)	0.654 1(6)	0.327 4(3)	−0.087 1(4)
F(2)	0.850 8(6)	0.297 8(3)	−0.183 2(4)
F(3)	0.884 8(7)	0.165 4(4)	−0.229 2(4)
F(4)	0.724 3(8)	0.064 0(3)	−0.174 2(5)
F(5)	0.522 1(7)	0.093 8(3)	−0.082 2(4)
N	1.205 6(8)	0.010 7(4)	−0.301 0(4)
C(T1)	1.268(1)	0.048 6(5)	−0.364 2(6)
C(T2)	1.064(1)	−0.023 8(5)	−0.328 0(6)
C(T3)	1.306(1)	−0.047 0(6)	−0.273 1(6)
C(T4)	1.184(1)	0.063 1(5)	−0.241 6(6)
C(T5)	1.294(2)	0.006 6(6)	−0.432 9(6)
C(T6)	0.949(1)	0.023 4(8)	−0.360 0(8)
C(T7)	1.446(2)	−0.026(1)	−0.237 2(9)
C(T8)	1.125(1)	0.034 8(7)	−0.172 5(6)
H(1)	0.21(1)	0.188(5)	−0.026(6)
H(2)	0.37(1)	0.174(4)	0.100(5)
H(3)	0.35(1)	0.312(4)	0.043(5)
H(T11)	1.3578	0.0675	−0.3455
H(T12)	1.2032	0.0849	−0.3791
H(T21)	1.0288	−0.0471	−0.2870
H(T22)	1.0840	−0.0563	−0.3651
H(T31)	1.3236	−0.0753	−0.3143
H(T32)	1.2581	−0.0732	−0.2381
H(T41)	1.1192	0.0972	−0.2620
H(T42)	1.2748	0.0837	−0.2274
H(T51)	1.3327	0.0355	−0.4686
H(T52)	1.3595	−0.0297	−0.4197
H(T53)	1.2049	−0.0124	−0.4533
H(T61)	0.8651	−0.0028	−0.3751
H(T62)	0.9261	0.0561	−0.3235
H(T63)	0.9813	0.0468	−0.4016
H(T71)	1.4999	−0.0662	−0.2219
H(T72)	1.4974	−0.0005	−0.2712
H(T73)	1.4318	0.0014	−0.1950
H(T81)	1.1145	0.0713	−0.1381
H(T82)	1.0329	0.0144	−0.1852
H(T83)	1.1885	0.0009	−0.1506

n.m.r. analysis gave the following approximate composition of the reaction mixture: unreacted (**1**), 30%; (**2**), 16%; and (**5**), 54%.

Synthesis of $[NEt_4][Re_3(\mu\text{-}H)_3(\mu_3\text{-}OC_6H_5)(CO)_9]$.—A 35-mg sample (0.033 mmol) of the NEt_4^+ salt of compound (**2**) was suspended in n-heptane (3 cm^3) and the mixture refluxed for 26 h. Gas chromatographic analysis showed CO evolution (only traces of H_2). After removal of the solvent, the product was analysed by n.m.r. spectroscopy, showing a multiplet at δ 7.2 and a singlet at −10.7 p.p.m., in the expected ratio with the cationic signals; $\nu_{max.}$(CO) 2 017s, 1 925vs, and 1 902(sh) cm^{-1} (acetone). The product, dissolved in acetone, was stirred under a CO atmosphere for 1 h, at room temperature. I.r. and n.m.r. spectra showed the disappearance of the bands of compound (**6**), and the appearance of those of compound (**2**).

X-Ray Analysis of Compounds (**3**) *and* (**4**).—*Crystal data.* Compound (**3**), $C_{24}H_{23}F_5NO_{11}Re_3$, M = 1 155.0, monoclinic, space group $P2_1/c$ (no. 14), a = 9.304(1), b = 19.357(3), c = 18.063(3) Å, β = 94.72(1)°, U = 3 242.1 Å^3, Z = 4, D_c = 2.37 g cm^{-3}, $F(000)$ = 2 128, Mo-K_α radiation (λ = 0.710 73 Å), μ(Mo-K_α) = 114.08 cm^{-1}.

Compound (**4**), $C_{32}H_{35}NO_9Re_2$, M = 950.0, orthorhombic, space group $Pc2_1n$ [non-standard setting of $Pna2_1$ (no. 33)] from systematic absences and successful refinements, a = 9.568(1), b = 18.865(3), c = 18.948(3) Å, U = 3 420.1 Å^3, Z = 4, D_c = 1.85 g cm^{-3}, $F(000)$ = 1 824; Mo-K_α radiation (λ = 0.710 73 Å), μ(Mo-K_α) = 72.18 cm^{-1}.

Intensity measurements. An irregular crystal sample of compound (**3**) of dimensions 0.25 × 0.29 × 0.32 mm and a needle-shaped crystal of compound (**4**) of dimensions 0.06 × 0.11 × 0.43 mm, both mounted on glass fibres in the air, were transferred to an Enraf-Nonius CAD4 automated diffractometer. Graphite-monochromated Mo-K_α radiation was used. In both cases the setting angles of 25 random reflections ($16 < 2\theta < 22°$) were used to determine by least-squares fit accurate cell constants and orientation matrices. The two data collections were performed by the ω-scan method, within the limits $3 < \theta < 25°$, using a variable scan speed (from 3 to 20° min^{-1}) and a variable scan range of (α + 0.35tanθ)° [α = 1.2° (**3**) and 1.0° (**4**)], with a 25% extension at each end for background determination. Reflections corresponding to the $\pm h,k,l$ and $+h,k,l$ indices were collected for compounds (**3**) and (**4**), respectively. The total numbers of reflections measured were 5 662 (**3**) and 3 392 (**4**). Three standard reflections were measured every 3 h, in both cases; no significant crystal decay was observed during the collection for compound (**4**), while for (**3**) a moderate decay was detected and a correction applied (maximum correction *ca.* 8% on F_o). The intensities were corrected for Lorentz and polarization effects. An empirical absorption correction was applied in both cases based on ψ scans (ψ 0—360° every 10°) of suitable reflections with χ values close to 90°; the maximum, minimum, and average relative transmission values were 1.00, 0.55, and 0.84 for complex (**3**) and 1.00, 0.72, and 0.85 for (**4**), respectively. Two sets of 3 897 (**3**) and 2 168 (**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) and the physical

Table 4. Final positional parameters within $[NEt_4][Re_2(\mu\text{-}OC_6H_5)_3(CO)_6]$ (**4**)

Atom	*x*	*y*	*z*
Re(1)	0.001 19(6)	0.000	−0.138 39(2)
Re(2)	−0.273 41(6)	−0.040 15(6)	−0.055 41(3)
C(11)	0.019(2)	0.042(1)	−0.228 9(8)
O(11)	0.035(2)	0.068 7(9)	−0.283 1(6)
C(12)	0.138(1)	0.065 4(9)	−0.110 9(8)
O(12)	0.221(1)	0.107 6(7)	−0.093 1(7)
C(13)	0.142(2)	−0.065 3(8)	−0.164 7(8)
O(13)	0.221(1)	−0.110 4(7)	−0.181 4(7)
C(21)	−0.454(2)	−0.028(1)	−0.089 8(9)
O(21)	−0.566(1)	−0.031(1)	−0.111 7(9)
C(22)	−0.344(2)	−0.004(1)	0.030 3(9)
O(22)	−0.388(1)	0.020 7(8)	0.081 5(6)
C(23)	−0.325(2)	−0.130(1)	−0.022 1(9)
O(23)	−0.356(2)	−0.184 9(8)	0.000 9(7)
O(1)	−0.054(1)	−0.044 5(8)	−0.037 5(4)
O(2)	−0.171(1)	−0.068 2(6)	−0.152 4(5)
O(3)	−0.181(1)	0.053 0(6)	−0.100 6(5)
C(P11)	0.025(1)	−0.050 4(9)	0.024 4(8)
C(P12)	0.168(2)	−0.043(1)	0.020 2(8)
C(P13)	0.248(2)	−0.049(1)	0.083(1)
C(P14)	0.179(2)	−0.061(1)	0.147 1(9)
C(P15)	0.046(2)	−0.069(1)	0.149(1)
C(P16)	−0.042(2)	−0.064 5(9)	0.088(1)
C(P21)	−0.211(2)	−0.117 2(8)	−0.203 5(7)
C(P22)	−0.320(2)	−0.163(1)	−0.193 9(8)
C(P23)	−0.352(2)	−0.215(1)	−0.247(1)
C(P24)	−0.276(2)	−0.213(1)	−0.307(1)
C(P25)	−0.175(2)	−0.168(1)	−0.319(1)
C(P26)	−0.135(2)	−0.120(1)	−0.267 2(9)
C(P31)	−0.224(2)	0.123(1)	−0.106 8(8)
C(P32)	−0.147(2)	0.173(1)	−0.142(1)
C(P33)	−0.197(3)	0.242(1)	−0.145(1)
C(P34)	−0.323(3)	0.263(2)	−0.117(1)
C(P35)	−0.401(3)	0.210(1)	−0.085(1)
C(P36)	−0.360(2)	0.137(1)	−0.076(1)
N	−0.024(2)	0.181(1)	0.125(1)
C(T1)	0.023(4)	0.183(2)	0.208(2)
C(T2)	0.082(3)	0.129(1)	0.090(1)
C(T3)	0.007(3)	0.259(1)	0.092(1)
C(T4)	−0.164(3)	0.149(1)	0.109(1)
C(T5)	−0.025(6)	0.102(3)	0.238(3)
C(T6)	0.237(3)	0.152(2)	0.095(1)
C(T7)	−0.020(3)	0.260(2)	0.015(2)
C(T8)	−0.286(4)	0.198(2)	0.135(2)
H(P12)	0.2122	−0.0328	−0.0236
H(P13)	0.3469	−0.0461	0.0821
H(P14)	0.2309	−0.0622	0.1897
H(P15)	0.0032	−0.0791	0.1931
H(P16)	−0.1400	−0.0705	0.0909
H(P22)	−0.3737	−0.1605	−0.1519
H(P23)	−0.4243	−0.2491	−0.2407
H(P24)	−0.2976	−0.2459	−0.3428
H(P25)	−0.1293	−0.1675	−0.3634
H(P26)	−0.0561	−0.0903	−0.2743
H(P32)	−0.0612	0.1608	−0.1642
H(P33)	−0.1413	0.2766	−0.1679
H(P34)	−0.3550	0.3109	−0.1194
H(P35)	−0.4896	0.2225	−0.0661
H(P36)	−0.4159	0.1026	−0.0532

constants tabulated therein. Both structures were solved by Patterson methods, which showed the positions of the Re atoms. After preliminary refinements of the parameters of these atoms, successive Fourier-difference maps revealed the location of all the non-hydrogen atoms.

The refinements were carried out by full-matrix least-squares methods. Anisotropic thermal parameters were assigned to all the non-hydrogen atoms of compound (**3**). In the case of compound (**4**) anisotropic thermal parameters were assigned only to the anionic non-phenyl atoms.

The cationic hydrogen atoms in compound (**3**) and the phenyl-hydrogen atoms in compound (**4**) 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 in (**4**), because of some disorder of the cation indicated by the rather high thermal parameters of some C atoms, were ignored.

The weights were computed 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 assumed equal to 0.03 (**3**) and 0.04 (**4**).

In the case of the non-centrosymmetric compound (**4**) the two structure enantiomorphs were tested and the case with the lower agreement indices was accepted.

Fourier difference maps obtained at this point showed residual peaks not exceeding *ca.* 0.8 e Å^{-3}. In the case of compound (**3**), three peaks of *ca.* 0.5 e Å^{-3} were found, appropriate to the three hydridic atoms bridging the Re–Re edges. They were refined isotropically to convergence, giving acceptable bond parameters, although affected by high uncertainties.

The final values of the conventional agreement indices R and R' were 0.028 and 0.033 for compound (**3**) and 0.031 and 0.037 for compound (**4**), respectively. The final positional parameters are listed in Tables 3 and 4.

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