Synthesis and *X*-Ray Crystal Structure of the Novel Hydridocarbonyl Cluster $[NEt_4][Re_4(\mu\text{-}H)_5(CO)_{14}]$†

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The reaction between $[Re_3(\mu\text{-}H)_3(CO)_{10}(NCMe)_2]$ and $[ReH_2(CO)_4]^-$ affords the novel hydridocarbonyl cluster $[Re_4(\mu\text{-}H)_5(CO)_{14}]^-$. Its NEt_4^+ salt has been investigated by *X*-ray analysis; the crystals are monoclinic, space group $P2_1/n$, with $a = 14.038(6)$, $b = 15.152(5)$, $c = 15.501(6)$ Å, $\beta = 101.79(3)°$, and $Z = 4$. The structure was solved and refined on the basis of 3 169 significant counter data, to a final R value of 0.031. The anion contains a butterfly metallic skeleton [Re–Re bond lengths 3.206(1)—3.247(1) Å] with all the edges bridged by hydride ligands. The most unusual feature is the absence of ligands bridging the wing tips of the butterfly cluster.

The limited number of known tetranuclear carbonyl cluster compounds of rhenium exhibit a variety of structures and valence electron (v.e.) numbers. They include the unsaturated tetrahedral species $[Re_4(\mu\text{-}H)_4(CO)_{12}]$ (56 v.e.s),[1] the tetrahedral (60 v.e.s) anions $[Re_4(\mu\text{-}H)_6(CO)_{12}]^{2-}$ [2] and $[Re_4(\mu\text{-}H)_4(CO)_{13}]^{2-}$,[3] the rhombic anion $[Re_4(CO)_{16}]^{2-}$ (62 v.e.s),[4] the open 'triangle-plus-apical' (64 v.e.s) species $[Re_4H(\mu\text{-}H)_3(CO)_{15}]^{2-}$,[5] and $[Re_4(\mu\text{-}H)_4I(CO)_{15}]^-$,[6] and the distorted square anion $[Re_4(\mu_4\text{-}C)I(CO)_{15}]^-$ (64 v.e.s).[7] We report here the synthesis and *X*-ray characterization of a novel 62-electron hydridocarbonyl cluster of rhenium, namely the anion $[Re_4(\mu\text{-}H)_5(CO)_{14}]^-$, which contains an unusual 'unsupported-butterfly' metal atom geometry, *i.e.* without bridging ligands between the wing tips.

Results and Discussion

The recently reported compound $[Re_3(\mu\text{-}H)_3(CO)_{10}(NCMe)_2]$ (**1**) contains two nitrile molecules that can easily be substituted by neutral (L) or anionic (X^-) donor species, leading respectively to $[Re_3(\mu\text{-}H)_3(CO)_{10}L_2]$ or $[Re_3(\mu\text{-}H)_3(\mu\text{-}X)(CO)_{10}]^-$ derivatives.[8] This suggested that compound (**1**) could be a suitable starting point for reactions of cluster growth, as previously reported for analogous osmium cluster compounds.[9,10] We have therefore treated compound (**1**) with a slight excess of the $[NEt_4]^+$ salt of $[ReH_2(CO)_4]^-$.[11] Under reflux, in tetrahydrofuran solution, a mixture of products was formed in a few minutes, as revealed by the ^1H n.m.r. spectrum. On lowering the temperature to 45 °C or below, the reaction became slower, but without relevant modification of the product distribution. Crystallization from dichloromethane–di-isopropyl ether allowed, however, the isolation (yield *ca.* 30%) of a species that has been characterized on the basis of an *X*-ray investigation as the novel compound $[NEt_4][Re_4(\mu\text{-}H)_5(CO)_{14}]$. In spite of the low isolated yields, the reaction yields (estimated from the ^1H n.m.r. spectrum) are *ca.* 70% with respect to compound (**1**), thus showing that the main reaction process is the expected one, fully comparable with the reaction of compound (**1**) with anionic species X^- leading to $[Re_3(\mu\text{-}H)_3(\mu\text{-}X)(CO)_{10}]^-$ derivatives [here $X = ReH_2(CO)_4$].

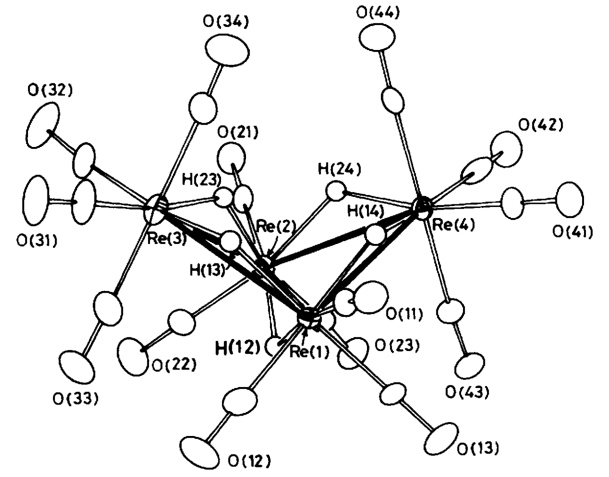

Figure. A view of the anion $[Re_4(\mu\text{-}H)_5(CO)_{14}]^-$. The carbonyls are indicated by the numbers of their oxygen atoms

Attempts to cause (**1**) to react with the neutral $[ReH(CO)_5]$, in order to obtain a pentanuclear rhenium species of the type $[Re_3(\mu\text{-}H)_3(CO)_{10}L_2]$ [L = $ReH(CO)_5$] were unsuccessful.

The structure of the anion $[Re_4(\mu\text{-}H)_5(CO)_{14}]^-$ is shown in the Figure and selected bond parameters are given in Table 1. The overall idealized symmetry is C_{2v}, but significant distortions are present due to packing effects. The metal atom cluster has a butterfly geometry, as expected from the number of valence electrons (62). The rhenium atoms at the hinge of the butterly [Re(1) and Re(2)] bear three terminal CO ligands, while the remaining two metals bear four such ligands. The geometry is such that the entering metal of the moiety $[ReH_2(CO)_4]^-$ becomes indistinguishable from the other wing-tip metal atom. The five hydride ligands have been located in bridging positions on all the Re–Re edges so that, neglecting the direct metal–metal bonds, each rhenium atom attains an almost octahedral co-ordination [Re(1) and Re(2) with three CO and

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† Tetraethylammonium tetradecacarbonylpenta-μ-hydrido-tetrarhenate (5*Re–Re*).

Supplementary data available (No. SUP 56474, 5 pp.): thermal parameters, 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 selected bond angles (°) within $[NEt_4][Re_4(\mu-H)_5(CO)_{14}]$

Re(1)–Re(2)	3.209(1)	Re(3)–C(33)	1.96(2)	Re(3)–H(23)	1.89(9)	C(41)–O(41)	1.17(1)
Re(1)–Re(3)	3.247(1)	Re(3)–C(34)	1.97(2)	Re(2)–H(24)	1.86(10)	C(42)–O(42)	1.13(2)
Re(1)–Re(4)	3.237(1)	Re(4)–C(41)	1.90(1)	Re(4)–H(24)	1.89(10)	C(43)–O(43)	1.11(1)
Re(2)–Re(3)	3.244(1)	Re(4)–C(42)	1.95(2)	C(11)–O(11)	1.16(1)	C(44)–O(44)	1.14(1)
Re(2)–Re(4)	3.206(1)	Re(4)–C(43)	1.99(1)	C(12)–O(12)	1.15(2)	N–CT(11)	1.52(2)
Re(1)–C(11)	1.92(1)	Re(4)–C(44)	2.00(1)	C(13)–O(13)	1.12(1)	N–CT(12)	1.52(2)
Re(1)–C(12)	1.92(2)	Re(1)–H(12)	1.87(10)	C(21)–O(21)	1.14(1)	N–CT(13)	1.51(2)
Re(1)–C(13)	1.93(1)	Re(2)–H(12)	1.92(10)	C(22)–O(22)	1.19(2)	N–CT(14)	1.52(2)
Re(2)–C(21)	1.92(1)	Re(1)–H(13)	1.95(10)	C(23)–O(23)	1.13(1)	CT(11)–CT(15)	1.51(2)
Re(2)–C(22)	1.87(2)	Re(3)–H(13)	1.80(10)	C(31)–O(31)	1.13(2)	CT(12)–CT(16)	1.48(2)
Re(2)–C(23)	1.90(1)	Re(1)–H(14)	1.82(10)	C(32)–O(32)	1.17(2)	CT(13)–CT(17)	1.53(2)
Re(3)–C(31)	1.92(1)	Re(4)–H(14)	1.85(10)	C(33)–O(33)	1.17(2)	CT(14)–CT(18)	1.48(2)
Re(3)–C(32)	1.89(1)	Re(2)–H(23)	1.72(10)	C(34)–O(34)	1.12(2)		

Re(2)–Re(1)–C(11)	155.9(4)	C(13)–Re(1)–H(12)	89(3)	C(31)–Re(3)–C(32)	91.9(6)	C(42)–Re(4)–C(43)	86.6(5)
Re(2)–Re(1)–C(12)	110.2(4)	C(13)–Re(1)–H(13)	165(3)	C(31)–Re(3)–C(33)	86.8(7)	C(42)–Re(4)–C(44)	89.7(5)
Re(2)–Re(1)–C(13)	107.7(3)	C(13)–Re(1)–H(14)	94(3)	C(31)–Re(3)–C(34)	87.6(7)	C(43)–Re(4)–C(44)	175.1(5)
Re(1)–Re(2)–C(21)	155.2(5)	H(12)–Re(1)–H(13)	106(4)	C(32)–Re(3)–C(33)	89.7(7)	C(41)–Re(4)–H(14)	81(3)
Re(1)–Re(2)–C(22)	108.0(4)	H(12)–Re(1)–H(14)	110(4)	C(32)–Re(3)–C(34)	93.9(7)	C(41)–Re(4)–H(24)	168(3)
Re(1)–Re(2)–C(23)	109.7(4)	H(13)–Re(1)–H(14)	86(4)	C(33)–Re(3)–C(34)	173.5(6)	C(42)–Re(4)–H(14)	172(3)
C(11)–Re(1)–C(12)	89.4(5)	C(21)–Re(2)–H(12)	172(3)	C(31)–Re(3)–H(13)	86(3)	C(42)–Re(4)–H(24)	84(3)
C(11)–Re(1)–C(13)	86.0(5)	C(21)–Re(2)–H(23)	82(3)	C(31)–Re(3)–H(23)	171(3)	C(43)–Re(4)–H(14)	99(3)
C(12)–Re(1)–C(13)	88.3(6)	C(21)–Re(2)–H(24)	74(3)	C(32)–Re(3)–H(13)	171(3)	C(43)–Re(4)–H(24)	100(3)
C(21)–Re(2)–C(22)	88.7(6)	C(22)–Re(2)–H(12)	83(3)	C(32)–Re(3)–H(23)	84(3)	C(44)–Re(4)–H(14)	85(3)
C(21)–Re(2)–C(23)	88.5(6)	C(22)–Re(2)–H(23)	103(3)	C(33)–Re(3)–H(13)	99(3)	C(44)–Re(4)–H(24)	77(3)
C(22)–Re(2)–C(23)	88.2(6)	C(22)–Re(2)–H(24)	163(3)	C(33)–Re(3)–H(23)	102(3)	H(14)–Re(4)–H(24)	101(4)
C(11)–Re(1)–H(12)	172(3)	C(23)–Re(2)–H(12)	90(3)	C(34)–Re(3)–H(13)	78(3)	Re(1)–H(12)–Re(2)	116(5)
C(11)–Re(1)–H(13)	79(3)	C(23)–Re(2)–H(23)	166(3)	C(34)–Re(3)–H(23)	84(3)	Re(1)–H(13)–Re(3)	120(5)
C(11)–Re(1)–H(14)	77(3)	C(23)–Re(2)–H(24)	93(3)	H(13)–Re(3)–H(23)	96(4)	Re(1)–H(14)–Re(4)	124(5)
C(12)–Re(1)–H(12)	84(3)	H(12)–Re(2)–H(23)	100(4)	C(41)–Re(4)–C(42)	93.6(6)	Re(2)–H(23)–Re(3)	128(5)
C(12)–Re(1)–H(13)	89(3)	H(12)–Re(2)–H(24)	114(4)	C(41)–Re(4)–C(43)	91.9(6)	Re(2)–H(24)–Re(4)	117(5)
C(12)–Re(1)–H(14)	166(3)	H(23)–Re(2)–H(24)	74(4)	C(41)–Re(4)–C(44)	91.5(5)	Re–C–O	174(1)—179(1)

three hydrides, Re(3) and Re(4) with four CO and two hydrides].

The five metal–metal bond distances, in the range 3.206(1)—3.247(1) Å, have values typical for hydrogen-bridged Re–Re interactions. Their distribution shows some deviation with respect to the idealized symmetry.

The rhenium–carbonyl interactions are all linear [Re–C–O 174(1)—179(1)°]. We can distinguish three types of CO: (*i*) those of the $ReH_3(CO)_3$ moieties, mean Re–C and C–O 1.91 and 1.15 Å; (*ii*) those of the $ReH_2(CO)_4$ moieties lying *trans* to hydrides, mean Re–C and C–O 1.92 and 1.15 Å; (*iii*) those of the latter moieties *trans* to CO, mean Re–C and C–O 1.98 and 1.14 Å, showing the expected Re–C bond lengthening because of competition for the π-back donation.

The bonding parameters for the hydrides are affected by too high uncertainties to be discussed in detail. However both the Re–H bonds [range 1.72(10)—1.95(10) Å, mean 1.86 Å] and the Re–H–Re angles [range 116(5)—128(5)°, mean 121°] are normal.

The most unusual feature of the anion is the butterfly geometry of the metal core in the absence of ligands bridging the wing tips. This is, to our knowledge, the only example of such a situation for a 62-valence-electron species. Two related species, however, are known which exhibit a similar metallic geometry but possess only 60 valence electrons, namely $[Os_3Pt(\mu-H)_2(CO)_{10}(PPh_3)_2]$[12] and $[Os_3Pt(\mu-H)_2(CO)_{11}\{P(C_6H_{11})_3\}]$.[13] The electron deficit of these two species has been ascribed to the fact that the Pt atoms attain a 16-electron shell.

The dihedral angle between the two triangular planes in $[Re_4(\mu-H)_5(CO)_{14}]^-$ is 115.5°. For comparison, in $[Re_3(\mu-H)_3(\mu-Cl)(CO)_{10}]^-$ the dihedral angle between the Re_3 plane and the Re(μ-Cl)Re plane is 102.1°.[14] This angle seems therefore to be dictated by intramolecular repulsions, due to the steric hindrance of the ligands. It is rather variable and in $[Os_3Pt(\mu-H)_2(CO)_{10}(PPh_3)_2]$ it is only 88.4°.[12] When the two central metals bear four ligands, all terminally bound, steric requirements induce the attainment of a rhombic flattened cluster geometry, as in the $[Re_4(CO)_{16}]^{2-}$ anion or in the $[Os_3ReH(CO)_{15}]$ species.[15]

Experimental

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. Bonfa' on a Bruker WP 80 spectrometer. Elemental analyses were performed by the Microanalytical Laboratory of Milan University. Published methods were used for the synthesis of $[NEt_4][ReH_2(CO)_4]$,[11] $[NEt_4][Re_3(\mu-H)_4(CO)_{10}]$,[16] and $[ReH(CO)_5]$.[17] We report here also the detailed synthesis of compound (**1**), previously described only in brief.

Synthesis of $[Re_3(\mu-H)_3(CO)_{10}(NCMe)_2]$.—A sample (100 mg, 0.102 mmol) of $[NEt_4][Re_3(\mu-H)_4(CO)_{10}]$, dissolved in MeCN (3 cm^3) was treated at room temperature with 15 μl (0.17 mmol) of CF_3SO_3H and stirred for 2 h. The solution was then concentrated under reduced pressure and water was slowly added, causing the precipitation of pure $[Re_3(\mu-H)_3(CO)_{10}(NCMe)_2]$ (84 mg, 0.091 mmol, yield 89%, after drying under vacuum).

Synthesis of $[NEt_4][Re_4(\mu-H)_5(CO)_{14}]$.—A sample (20 mg, 0.021 mmol) of $[Re_3(\mu-H)_3(CO)_{10}(NCMe)_2]$, dissolved in tetrahydrofuran (3 cm^3) was treated with 12 mg (0.027 mmol) of

Table 2. Final positional parameters within $[NEt_4][Re_4(\mu\text{-}H)_5(CO)_{14}]$

Atom	*x*	*y*	*z*
Re(1)	0.011 86(4)	0.288 61(4)	0.271 59(3)
Re(2)	−0.076 74(4)	0.177 73(4)	0.097 31(3)
Re(3)	−0.163 77(4)	0.149 67(4)	0.273 81(4)
Re(4)	−0.100 22(4)	0.388 21(4)	0.095 14(3)
C(11)	0.011(1)	0.374 1(9)	0.363 0(9)
O(11)	0.015 1(8)	0.427 1(7)	0.417 7(6)
C(12)	0.096(1)	0.215(1)	0.355(1)
O(12)	0.147 4(9)	0.174 9(8)	0.408 4(8)
C(13)	0.125 9(9)	0.349 8(9)	0.251 1(8)
O(13)	0.192 8(7)	0.387 4(8)	0.245 9(7)
C(21)	−0.178(1)	0.135 9(9)	0.004 0(9)
O(21)	−0.241 4(9)	0.112 6(8)	−0.050 1(7)
C(22)	−0.031(1)	0.062(1)	0.114(1)
O(22)	−0.003(1)	−0.012 4(8)	0.117 9(9)
C(23)	0.003(1)	0.192 0(8)	0.013 0(8)
O(23)	0.052 5(8)	0.195 9(8)	−0.036 7(7)
C(31)	−0.179(1)	0.125(1)	0.392(1)
O(31)	−0.187(1)	0.104 3(8)	0.460 2(7)
C(32)	−0.250(1)	0.058(1)	0.226 9(9)
O(32)	−0.310 4(9)	0.006 5(8)	0.197 1(8)
C(33)	−0.057(1)	0.065(1)	0.295(1)
O(33)	0.007(1)	0.014 9(9)	0.315 6(8)
C(34)	−0.268(1)	0.238(1)	0.267(1)
O(34)	−0.327 2(9)	0.288(1)	0.267 9(8)
C(41)	−0.076(1)	0.507 2(9)	0.131 5(8)
O(41)	−0.061 7(8)	0.580 5(7)	0.154 2(7)
C(42)	−0.141(1)	0.419(1)	−0.028 9(9)
O(42)	−0.166 3(9)	0.435 6(8)	−0.101 2(6)
C(43)	0.033(1)	0.374 8(9)	0.071 0(8)
O(43)	0.106 2(7)	0.370 8(7)	0.053 5(6)
C(44)	−0.238(1)	0.396 7(8)	0.109 5(9)
O(44)	−0.317 9(7)	0.402 7(8)	0.113 3(8)
N	0.361 5(9)	0.176 6(8)	0.127 6(7)
CT(11)	0.466(1)	0.159(1)	0.122(1)
CT(12)	0.296(1)	0.182(1)	0.037(1)
CT(13)	0.334(1)	0.099(1)	0.179(1)
CT(14)	0.352(1)	0.263(1)	0.174(1)
CT(15)	0.513(1)	0.230(1)	0.075(1)
CT(16)	0.286(1)	0.100(1)	−0.017(1)
CT(17)	0.228(1)	0.100(1)	0.190(1)
CT(18)	0.409(2)	0.272(1)	0.265(1)
H(12)	0.032(8)	0.203(7)	0.191(7)
H(13)	−0.098(8)	0.246(7)	0.320(7)
H(14)	−0.072(8)	0.372(7)	0.216(7)
H(23)	−0.170(7)	0.179(7)	0.154(6)
H(24)	−0.152(8)	0.276(7)	0.057(7)

* Atoms CT(11)–CT(18) are the $[NEt_4]^+$ carbons.

$[NEt_4][ReH_2(CO)_4]$ and stirred for 15 min, in an oil-bath at 45 °C. The solvent was removed under reduced pressure and the reaction mixture, after i.r. and n.m.r. analyses, was dissolved in the minimum volume of dichloromethane; di-isopropyl ether was carefully stratified over this solution, leading after 2 d to the formation of cream crystals of $[NEt_4][Re_4(\mu\text{-}H)_5(CO)_{14}]$ [8 mg, 0.0063 mmol, isolated yields of 30% with respect to compound (**1**)] (Found: C, 21.05; H, 2.10; N, 1.30. $C_{22}H_{25}NO_{14}Re_4$ requires C, 20.75; H, 1.95; N, 1.10%); $\nu_{max.}$(CO) 2 100vw, 2 084mw, 2 025m, 2 012vs, 2 000s, 1 976m, 1 947m, and 1 915m cm^{-1} (tetrahydrofuran); δ [$(CD_3)_2CO$, $SiMe_4$ standard] 3.5 (8 H, q, 4 CH_2), 1.4 (12 H, tt, 4 CH_3), −15.02 (1 H, s, ReH), and −16.19 (4 H, s, ReH). Upon heating the solid compound decomposes at about 80 °C.

X-Ray Crystal Structure.—Crystal data. $C_{22}H_{25}NO_{14}Re_4$, M = 1 272.2, monoclinic, a = 14.038(6), b = 15.152(5), c = 15.501(6) Å, β = 101.79(3)°, U = 3 227.6 Å^3, D_c = 2.618 g cm^{-3}, Z = 4, $F(000)$ = 2 304, space group $P2_1/n$ [non-standard setting of $P2_1/c$, no. 14], λ(Mo-K_α) = 0.710 73 Å, μ(Mo-K_α) = 152.2 cm^{-1}.

Intensity measurements. The crystal sample, of dimensions 0.22 × 0.28 × 0.35 mm, was mounted on a glass fibre in the air. The intensity data were collected on a Enraf–Nonius CAD-4 automated diffractometer, using graphite-monochromatized Mo-K_α radiation. Intensities were measured, using the ω-scan technique, within the limits $3 < \theta < 25°$ (total number 5 867). No significant decay was observed during the collection. The intensities were corrected for Lorentz and polarization effects. An empirical absorption correction was applied, based on ψ scans (0—360° every 10°) of suitable reflections with χ values close to 90°. A set of 3 169 independent significant reflections, with $I > 3\sigma(I)$, was used in the structure solution and refinement.

Structure solution and refinements. All computations were performed on a PDP 11/34 computer using the Enraf–Nonius structure-determination package (SDP) and the physical constants tabulated therein. The structure was solved by conventional Patterson and Fourier methods and refined by full-matrix least squares. Anisotropic thermal parameters were assigned to all the non-hydrogen atoms. The cationic hydrogen atoms were located in their idealized positions (C–H 0.95 Å), with isotropic thermal parameters of 5.0 Å^2, after each cycle of refinement, but not refined. A Fourier-difference map obtained after refinement of the above model showed five peaks (range 0.9—0.6 e Å^{-3}) suggestive of hydridic hydrogens in bridging locations. They were therefore included in the refinements, with fixed thermal parameters of 2.5 Å^2, and gave convergence to reasonable locations. Weights were assigned according to the formula $w = 1/\sigma^2(F_o)$, with $\sigma(F_o) = \sigma(F_o^2)/2F_o$ and $\sigma(F_o^2) = [\sigma^2(I) + (AI)^2]^{\frac{1}{2}}/\text{Lp}$, A being assumed equal to 0.03. The final values of the conventional R and weighted R' agreement indices were 0.031 and 0.036 respectively.

The final positional parameters are reported in Table 2.

Acknowledgements

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