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[13] In **3**, each cavity **A** accommodates two hydrogen-bonded ether molecules, and each cavity **B** accommodates one non-hydrogen-bonded ether molecule.

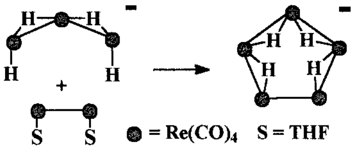
[14] In **4**, each cavity in a sheet is filled with two molecules of DMF (O7, O8) that are hydrogen-bonded in the same sheet and two molecules of DMF (O9, O10) which are hydrogen-bonded to each of the adjacent sheets.

[15] Single crystals of **3** quickly become opaque, probably due to loss of non-hydrogen-bonded diethyl ether.

$[Re_6(\mu\text{-H})_5(CO)_{24}]^-$: The First Carbonyl Cluster with a Cyclohexane-Like Structure[**]

Mirka Bergamo, Tiziana Beringhelli, Giuseppe D'Alfonso,[*] Pierluigi Mercandelli, Massimo Moret,[*] and Angelo Sironi

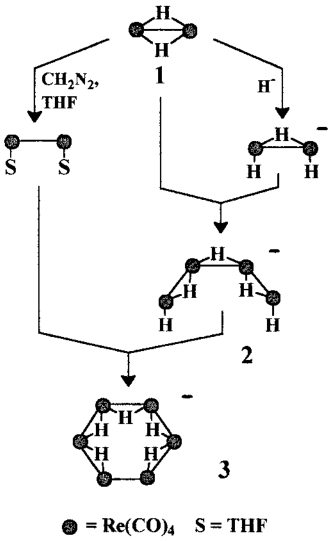
We have recently reported[1] the synthesis of the pentametallic ring cluster $[Re_5(\mu\text{-H})_4(CO)_{20}]^-$ through the cycloaddition of the $[Re_3H_2(\mu\text{-H})_2(CO)_{12}]^-$ anion and the $Re_2(CO)_8$ fragment originated from the labile complex $[Re_2(CO)_8(thf)_2]$[2] (Scheme 1). The reaction exploits the well-known σ-donor capability of M–H bonds toward coordinatively unsaturated metal centers[3] and shows that polyhydridic complexes can behave as multidentate "ligands". The Re_5 cluster anion—or, better, its neutral $[Re_5(\mu\text{-H})_5(CO)_{20}]$ protonation derivative[1]—were the highest members of a series of cyclic $[ReH(CO)_4]_n$ oligomers ($n = 3-5$),[4] which are isolobal analogues of the corresponding $(CH_2)_n$ cycloalkanes owing to the isolobal relationship[5] between (singlet) methylene and the $ReH(CO)_4$ moiety.



Scheme 1. Synthesis of the pentametallic ring cluster $[Re_5(\mu\text{-H})_4(CO)_{20}]^-$.

If this approach would be used to obtain a six-membered ring cluster, a tetranuclear chain complex would be required containing two terminal hydrides, which should thus act as a bidentate bridging "ligand" toward the $Re_2(CO)_8$ fragment. The unsaturated complex $[Re_2(\mu\text{-H})_2(CO)_8]$ (**1**) is known to easily add M–H⁻ anions, giving L-shaped $[M(\mu\text{-H})Re(CO)_4(\mu\text{-H})ReH(CO)_4]^-$ derivatives.[1, 6, 7] We therefore treated **1** with one equivalent of the $[NEt_4]^+$ salt of the dinuclear anion $[Re_2H_2(\mu\text{-H})(CO)_8]^-$ [4, 8] and obtained rapidly and with satisfactory selectivity the addition derivative $[Re_4H_2(\mu\text{-H})_3(CO)_{16}]^-$ (**2**).

In Scheme 2 we have depicted one of the possible rotational conformers of **2**, whose fast dynamics accounts for the 2:2:1 pattern of the hydride resonances in the ¹H NMR spectrum. High conformational lability around the Re-H-Re linkages has been observed in all the other Re_4 chain clusters characterized so far.[6, 7]



Scheme 2. Synthesis of the hexametallic ring cluster $[Re_6(\mu\text{-H})_5(CO)_{24}]^-$.

The reaction of **2** with an equimolar amount of $[Re_2(CO)_8(thf)_2]$ afforded a complex mixture containing several unidentified species. Monitoring by ¹H NMR spectroscopy showed that the resonance of the expected $[Re_6(\mu\text{-H})_5(CO)_{24}]^-$ anion (**3**, Scheme 2) never exceeded 40% of the total integrated intensity of the hydride region. Crystallization of this mixture led to the isolation of orange crystals of the $[NEt_4]^+$ salt of **3**.

An X-ray diffraction analysis[9] confirmed the nature of anion **3**. Indeed, the metal centers in $[Re_6(\mu\text{-H})_5(CO)_{24}]^-$ (96 valence electrons) exhibit a cyclohexane-like geometry (Figure 1), which is unprecedented among clusters containing only carbonyl ligands. Some metal complexes containing Ag, Ni, or Pd have metallic cores with hexagonal geometries, but the metals centers are held together by bridging sulfur ligands.[12] The closest structural analogue of **3** is the irregular hexagon made of alternating $Fe(CO)_4$ and Cd(2,2′-bipyridyl) groups, which is present in $[Fe(CO)_4\{\mu\text{-Cd(bipy)}\}]_3$.[13] Therefore anion **3** represents to our knowledge the first example of a hexagonal frame of metal centers built of three-center, two-

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[**] This work was supported by Italian CNR (CSMTBO) and by MURST (Project Metal Clusters: Basic and Functional Aspects).

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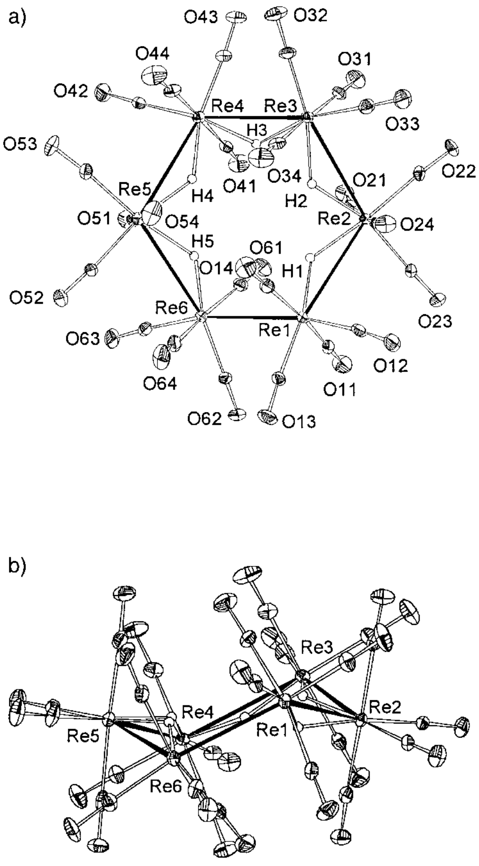

Figure 1. X-ray crystal structure of anion **3**. a) Top view and b) side view showing the cyclohexane-like geometry in a chair conformation (thermal ellipsoids with 30 % probability; hydrogen atoms were given arbitrary radii). Selected bond lengths [Å]: Re1–Re2 3.3100(8), Re2–Re3 3.3148(8), Re3–Re4 3.3582(8), Re4–Re5 3.3342(8), Re5–Re6 3.2972(8), Re1–Re6 3.1109(7).

electron M-H-M bonds and two-center, two-electron M–M bonds.

Compound **3**, in fact, comprises six octahedral $Re(CO)_4$ units, with local idealized C_{2v} symmetry, connected through one direct and five μ-H-bridged Re–Re interactions. In contrast to the pentanuclear analogue, which displayed an *e/s/s/s/e* (*s* = staggered, *e* = eclipsed) relative conformation of the $Re(CO)_4$ units,[1] **3** exhibits an all-staggered (*s/s/s/s/s/s*) concatenation of these moieties. The only Re–Re bond length that is significantly different is that of the unbridged Re1–Re6 edge, which is considerably shorter (3.1109(7) Å) than the bridged ones (3.2972(8)–3.3582(8) Å), even if longer than normal unbridged Re–Re interactions.

Another striking feature of anion **3** is the conformation of the six-membered metal ring. Analyzing the ring conformation with Cremer and Pople's puckering coordinates,[14] we found a slightly distorted chair conformation (Figure 1 b; $q_2 = 0.052$ Å and $q_3 = 1.253$ Å, or, using the equivalent spherical coordinates,[14] $Q = 1.254$ Å and $\theta = 2.4°$, where $Q = (q_2^2 + q_3^2)^{1/2}$ represents the total puckering amplitude and θ is equal to 0° or 180° for a chair conformation). A comparative puckering analysis of **3**, cyclohexane,[15] and S_6[16] can be performed alternatively with Haasnoot's endocyclic torsion angles,[17] which allows a direct comparison of molecules with different average bond lengths (3.288, 1.52, and 2.067 Å in **3**, cyclohexane, and S_6, respectively). Applied to the three compounds Haasnoot's formalism yields total puckering amplitudes of 56.70°, 55.07°, and 73.77°, respectively. Thus, in spite of the octahedral coordination at the Re centers, the total puckering amplitude of **3** is close to that of its hydrocarbon analogue (which is composed of tetrahedral carbon atoms), analogous to what was observed for the $[Re_5(\mu\text{-}H)_4(CO)_{20}]^-$ ring. It is worth noting that the Re-Re-Re endocyclic angles average to 110.8° compared to 111.4° for cyclohexane, while in S_6, which has a significantly larger puckering amplitude, the S-S-S angles greatly deviate from the ideal tetrahedral angle (102.61°). The chair conformation adopted by **3** guarantees a good intramolecular packing of the carbonyl and hydride ligands, even if, compared to Re_3–Re_5 cycles, there are shorter intramolecular O···O contacts between axial carbonyl groups (average 3.09 Å for **3**, which is 0.2–0.4 Å shorter than those in the Re_3–Re_5 cycles).

The positions of the hydride ligands, which were located on the basis of a difference Fourier map, are in agreement with the Re–Re distances (five long H-bridged Re–Re interactions and one shorter and unbridged Re–Re interaction), the carbonyl ligands' local stereogeometry, and atom pair potential energy calculations.[18] All these approaches strongly indicate that all the Re–H vectors are pointing inside the metal ring. Previously we reported a similar situation for the pentametallic clusters $[Re_5(\mu\text{-}H)_{5-n}(CO)_{20}]^{n-}$ ($n = 0, 1$)[1] and for two of the Re(μ-H)Re interactions of $[Re_4(\mu\text{-}H)_4(CO)_{16}]$.[4] This feature, which seemed extravagant the first time it appeared,[4] has now been observed in four different cyclic rhenium clusters with different nuclearities and conformations; it probably arises from the steric demands that force the less bulky ligands, in other words, the hydrides, to lie inside the "empty" metal ring.

Protonation of **3** to obtain the still-elusive neutral $[\{ReH(CO)_4\}_6]$ derivative resulted in the formation of a white precipitate, whose very low solubility has so far prevented analysis by single-crystal X-ray diffraction.

In principle, the interaction of two difunctional reactants such as **1** and **2** could result not only in cyclization, but also in polycondensation, thus providing a novel route to chain clusters. This would be an alternative to the recently reported anionic oligomerization of **1**.[7] The probability of this second reaction path should increase with the length of the chain of the hydridic anionic reactant, making ring closure progressively more difficult. This could be the reason for the lower selectivity of the cycloaddition leading to **3**, with respect to the reaction affording the Re_5 ring.[19]

Experimental Section

A sample of $[Re_2(\mu\text{-}H)_2(CO)_8]$ (60 mg, 0.10 mmol) was added to a solution of $[NEt_4][Re_2H_2(\mu\text{-}H)(CO)_8]$ (73 mg, 0.10 mmol) in THF at 273 K. The temperature was increased to room temperature, then the solution was concentrated to dryness. NMR analysis showed that the residue consisted of almost pure (ca. 90 %) $[NEt_4]$**2**. Extraction with diethyl ether and concentration afforded a yellow precipitate, which was crystallized from CH_2Cl_2/*n*-hexane at 253 K. IR (THF): $\tilde{\nu} = 2092$w, 2070w, 2016s, 2001sh, 1970ms, 1932m cm^{-1} (C=O); ^1H NMR (300 MHz, $[D_8]THF$, 183 K): $\delta = 3.29$ (q, 8H, CH_2), 1.71 (t, 12H, CH_3), −5.79 (s, 2H), −15.89 (s, 2H), −17.56 (s, 1H).

A solution of [NEt$_4$]**2** (40 mg, 0.030 mmol) in THF was treated at 273 K with one equivalent of [Re$_2$(CO)$_8$(thf)$_2$]. The temperature was increased to room temperature, then the solution was concentrated to dryness and the residue dissolved in CH$_2$Cl$_2$. IR and NMR spectra showed the formation of a complex mixture containing, besides anion **3**, several unidentified species. Crystals of [NEt$_4$]**3** were obtained by slow diffusion of *n*-hexane into a solution in CH$_2$Cl$_2$. Spectroscopic data of the anion **3** (from isolated crystals): IR (CH$_2$Cl$_2$): $\tilde{\nu} = 2119$vw, 2100mw, 2089w, 2053w, 2031s, 2002ms, 1952ms, 1889mw cm^{-1} (C=O); ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 193 K): $\delta = -15.42$. The reaction has been repeated several times directly in CD$_2$Cl$_2$ in an NMR tube at 193 K. In all cases the resonance of **3** was the most intense, but many other unattributed resonances were also present.

Received: July 20, 1999 [Z 13753 IE]
German version: *Angew. Chem.* **1999**, *111*, 3695–3697

Keywords: carbonyl complexes · cluster compounds · hydrides · isolobal relationship · rhenium

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[1] M. Bergamo, T. Beringhelli, G. D'Alfonso, P. Mercandelli, M. Moret, A. Sironi, *Angew. Chem.* **1998**, *110*, 2201; *Angew. Chem. Int. Ed.* **1998**, *37*, 2128.

[2] L. Carlucci, G. D'Alfonso, D. M. Proserpio, *Organometallics* **1999**, *18*, 2091.

[3] a) R. H. Crabtree, *Angew. Chem.* **1993**, *105*, 828; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 789; b) L. M. Venanzi, *Coord. Chem. Rev.* **1982**, *43*, 251; c) see also M. Bergamo, T. Beringhelli, G. D'Alfonso, G. Ciani, M. Moret, A. Sironi, *Inorg. Chim. Acta* **1997**, *259*, 291, and references therein.

[4] N. Masciocchi, A. Sironi, G. D'Alfonso, *J. Am. Chem. Soc.* **1990**, *112*, 9395.

[5] R. Hoffmann, *Angew. Chem.* **1982**, *94*, 725; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 711.

[6] M. Bergamo, T. Beringhelli, G. D'Alfonso, P. Mercandelli, M. Moret, A. Sironi, *Organometallics* **1997**, *16*, 4129.

[7] M. Bergamo, T. Beringhelli, G. D'Alfonso, P. Mercandelli, M. Moret, A. Sironi, *J. Am. Chem. Soc.* **1998**, *120*, 2971.

[8] T. Beringhelli, G. D'Alfonso, L. Ghidorsi, G. Ciani, A. Sironi, H. Molinari, *Organometallics* **1987**, *6*, 1365.

[9] Crystal data for **3**: C$_{32}$H$_{25}$NO$_{24}$Re$_6$, $M_r = 1924.73$, triclinic, space group $P\bar{1}$ (no. 2), $a = 12.962(3)$, $b = 13.003(3)$, $c = 14.044(3)$ Å, $\alpha = 86.12(1)$, $\beta = 78.81(1)$, $\gamma = 84.08(1)^\circ$, $V = 2306.9(9)$ Å^3 (by least-squares refinement on diffractometer angles of centered reflections with $5 < \theta < 20^\circ$), $Z = 2$, $T = 298$ K, graphite-monochromated Mo$_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $\rho_{calcd} = 2.771$ g cm^{-3}, $F(000) = 1732$, orange crystal with the dimensions $0.26 \times 0.24 \times 0.14$ mm, μ(Mo$_{K\alpha}$) = 15.760 mm^{-1}, absorption correction with SADABS, relative transmission 0.39–1.00, SMART diffractometer, ω-scan, frame width 0.3°, maximum time per frame 15 s, θ range 2.1–28.3°, $-17 \leq h \leq 16$, $-16 \leq k \leq 16$, $-18 \leq l \leq 18$, 26009 reflections collected, 10293 independent reflections ($R_{int} = 0.0448$), no crystal decay, solution by direct methods (SIR96)[10] and subsequent Fourier syntheses, full-matrix least-squares on F_o^2 (SHELX97),[11] hydrogen atoms refined with a riding model, data/parameters = 10293/569, GOF(F_o^2) = 0.807, $R1 = 0.0485$ and $wR2 = 0.0603$ on all data, $R1 = 0.0304$ and $wR2 = 0.0587$ for reflections with $I > 2\sigma(I)$, weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0189P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$, largest peak and hole 1.62 and -1.67 e Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-131475. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[10] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *J. Appl. Crystallogr.* **1994**, *27*, 435.

[11] G. M. Sheldrick, SHELXL-97: Program for Structure Refinement, **1997**.

[12] a) R. Hesse, L. Nilson, *Acta Chem. Scand.* **1969**, *23*, 825; b) H. Dietrich, W. Storck, G. Manecke, *J. Chem. Soc. Chem. Commun.* **1982**, 1036; c) N. R. Kunchur, *Acta Crystallogr. Sect. B* **1968**, *24*, 1623; d) T. A. Wark, D. W. Stephan, *Organometallics* **1989**, *8*, 2836; e) K. Schulbert, R. Mattes, *Z. Naturforsch. B* **1994**, *49*, 770.

[13] R. D. Ernst, T. J. Marks, J. A. Ibers, *J. Am. Chem. Soc.* **1977**, *99*, 2098.

[14] D. Cremer, J. A. Pople, *J. Am. Chem. Soc.* **1975**, *97*, 1354.

[15] R. Kahn, R. Fourme, D. Andre, M. Renaud, *Acta Crystallogr. Sect. B* **1973**, *29*, 131.

[16] J. Steidel, J. Pickardt, R. Steudel, *Z. Naturforsch. B* **1978**, *33*, 1554.

[17] C. A. G. Haasnoot, *J. Am. Chem. Soc.* **1992**, *114*, 882.

[18] A. G. Orpen, *J. Chem. Soc. Dalton Trans.* **1980**, 2509.

[19] In agreement with this, the NMR data of the reaction mixtures provide evidence of the presence in solution of "linear" chains. Indeed two broad sets of signals are observed, at roughly $\delta = -6$ and -16, typical of terminal and bridging exchanging hydrides in all the X[HRe(CO)$_4$]$_n$$^-$ chain clusters so far characterized.

Interpenetrated and Noninterpenetrated Three-Dimensional Networks in the Polymeric Species Ag(tta) and 2 Ag(tta) · AgNO$_3$ (tta = tetrazolate): The First Examples of the μ_4-η^1:η^1:η^1:η^1 Bonding Mode for Tetrazolate

Lucia Carlucci, Gianfranco Ciani,* and
Davide M. Proserpio

The current interest in the self-assembly of polymeric coordination networks[1] has afforded many noteworthy two- and three-dimensional frameworks, which are of potential interest as novel materials.[2] Particular attention is now devoted to the use of new polyfunctional suitably tailored complex ligands that enable a certain control of the structural motifs and/or introduce peculiar features in the solid-state products. However, many interesting polymeric frameworks were also obtained in the past by using simple polydentate aromatic nitrogen heterocycles with five-membered (azoles) or six-membered (azines) rings.[3, 4] While the members of these families with two nitrogen atoms have been extensively used in the area of coordination polymers, and some examples of polymeric nets of triazoles[5] and triazines[6] are known, the networking ability and the full potential donor properties of species containing a higher number of nitrogen atoms, like tetrazoles and tetrazines, are almost completely unknown. Tetrazole (Htta) exists in two tautomeric forms (1*H* and 2*H*, see Scheme 1); it is an acidic species with a pK_a value of about 5, and the anion tetrazolate (tta) is a potentially tetradentate ligand, though in most of the reported adducts it functions as only a mono- or bidentate ligand.[3] Substituted tetrazole derivatives have also been studied for their potential properties as explosives or detonators.

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