J. Am. Chem. Soc. **1998,** *120,* 2971−2972

Chain Clusters through the Anionic Oligomerization of [Re$_2$(μ-H)$_2$(CO)$_8$]

M. Bergamo, T. Beringhelli,* and G. D'Alfonso*

Dipartimento di Chimica Inorganica
Metallorganica e Analitica e Centro CNR CSSMTBO
Via Venezian 21, 20133 Milano, Italy

P. Mercandelli, M. Moret,* and A. Sironi

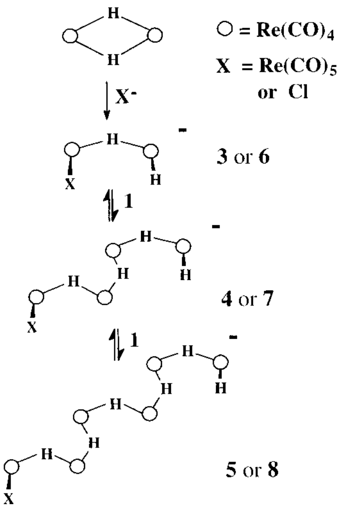
Dipartimento di Chimica Strutturale e Stereochimica
Inorganica e Centro CNR CSSMTBO
Via Venezian 21, 20133 Milano, Italy

Received December 2, 1997

The isolobal analogy relates the organometallic fragments d^7-ML$_5$ and d^8-ML$_4$ (M = transition metal) to the CH$_3$ and CH$_2$ groups.[1] Methyl and methylene groups are the building blocks of hydrocarbon chains, but until now in the field of transition-metal carbonyl clusters, the examples of isolobal analogues of linear hydrocarbons were very scant.[2] We show here that hydridocarbonyl clusters containing chains of up to 9 or 10 metal atoms can be obtained, through a synthetic route that strictly resembles the anionic polymerization of the olefins. The starting material is the "ethylene-like" molecule [Re$_2$(μ-H)$_2$(CO)$_8$] (**1**),[7] whose reactivity does agree with the formal electronic unsaturation.[8]

The addition of the carbonyl rhenate [Re(CO)$_5$]$^-$ (**2**) to **1** gives the L-shaped open cluster [Re(CO)$_5$Re(CO)$_4$(μ-H)ReH(CO)$_4$]$^-$ (**3**).[4] We have now found that this addition product is able to further react with the starting "alkene", giving rise to an unprecedented[11] oligomerization process. Thus, the treatment of a solution of **3** with increasing amounts of **1**, at 193 K, leads to the formation at first of the pentanuclear [Re$_5$H$_4$(CO)$_{21}$]$^-$ (**4**) and subsequently of the heptanuclear [Re$_7$H$_6$(CO)$_{29}$]$^-$ (**5**) chain anions (see Scheme 1).[14] Each [Re(CO)$_5${ReH(CO)$_4$}$_{2n}$]$^-$ oligomer (**3**, $n = 1$; **4**, $n = 2$; **5**, $n = 3$) contains $2n - 1$ Re−H−Re interactions and one terminal hydride, bound to the Re atom at the end of the chain opposite to the [Re(CO)$_5$] group. It is this terminal Re−H bond that allows the progress of the oligomerization, acting as a "ligand" toward the unsaturated complex **1**. The ^{13}C NMR data indicate a local C_{2v} symmetry of each H$_2$Re(CO)$_4$ fragment (cis oligomerization, at variance with respect to the trans arrangement found in the solid state for polymeric Ru(CO)$_4$)[15] and also suggest a high conformational freedom,[16] a feature common to their isolobal analogues, the linear hydrocarbons.

Scheme 1



The stepwise growth of the chains is nicely illustrated by the formation of samples of **4** or **5** selectively ^{13}CO enriched in different positions of the metallic skeleton, by alternating the use of natural abundance or ^{13}CO-enriched **1**. However, while the formation of **3** is quantitative, the subsequent steps give mixtures and require an excess of **1** to draw the equilibria toward the higher oligomers.

Mixtures of the same species can be obtained also through a different route, which more closely mimics the polymerization of olefins, i.e., by treating directly **1** with less than 1 equiv of the anion **2**.[17] The NMR spectra show that the length of the chains increases as the amount of the initiator of the oligomerization (i.e., **2**) decreases (Figure 1). At high [**1**]/[**2**] ratios, novel resonances appear in the NMR spectra (Figure 1b), suggesting the formation, in addition to **4** and **5**, of a nonanuclear oligomer [Re(CO)$_5${ReH(CO)$_4$}$_8$]$^-$ (as also supported by the relative integrated intensities of the hydridic signals). Attempts to increase the relative fraction of this species by further increasing the [**1**]/[**2**] ratio caused the formation of a high amount of precipitate.

In principle, not only carbonyl metallates such as **2**, but any anion able to add to **1** could act as initiator of polymerization. Indeed the reaction of **1** (ca. 0.02 mmol) with varying amounts

---

[1] Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711.

[2] Many of them pertain to rhenium chemistry: Re$_2$(CO)$_{10}$ is the obvious analogue of ethane, while the trinuclear open clusters [(CO)$_5$Re−HRe(CO)$_4$-Re(CO)$_5$] [3] and [(CO)$_5$Re−HRe(CO)$_4$−ReH(CO)$_4$]$^-$ [4] provide isolobal analogues of propane, and the tetranuclear chain cluster anion [(CO)$_5$Re−HRe(CO)$_4$−HRe(CO)$_4$−ReH(CO)$_4$]$^-$ [5] is an analogue of *n*-butane. As usual, Re(CO)$_4$L fragments (L = CO or H$^-$) are here considered isolobal with CH$_3$, while the 16 valence electron fragment ReH(CO)$_4$ is considered isolobal with (singlet) CH$_2$, since its frontier orbitals allow the interaction with two metal centers, given the σ-donor capability of M−H bonds.[6]

[3] (a) Fellmann, W.; Kaesz, H. D. *Inorg. Nucl. Chem. Lett.* **1966**, *2*, 63. (b) Yang, C. S.; Cheng, C. P.; Guo, L. W.; Wuang, J. *J. Chin. Chem. Soc. (Taipei)* **1985**, *32*, 17.

[4] Bergamo, M.; Beringhelli, T.; D'Alfonso, G.; Ciani, G.; Moret, M.; Sironi, A. *Organometallics* **1996**, *15*, 3876.

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

[6] Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 789.

[7] Bennet, M. J.; Graham, W. A. G.; Hoyano, J. K.; Hutcheon, W. L. *J. Am. Chem. Soc.* **1972**, *94*, 6232.

[8] See for instance, its easy reactions of addition of phosphines,[9a] hydrides,[9b] or carbonylmetalates[4,5,9c] and the insertion of carbenoid fragments into the Re−Re bond.[10]

[9] (a) Andrews, M. A.; Kirtley, S. W.; Kaesz, H. D. *Inorg. Chem.* **1977**, *16*, 1556. (b) Beringhelli, T.; D'Alfonso, G.; Ghidorsi, L.; Ciani, G.; Sironi, A.; Molinari, H. *Organometallics* **1987**, *6*, 1365. (c) Beringhelli, T.; Ciani, G.; D'Alfonso, G.; Garlaschelli, L.; Moret, M.; Sironi, A. *J. Chem. Soc., Dalton Trans.* **1992**, 1865.

[10] See: Bergamo, M.; Beringhelli, T.; D'Alfonso, G.; Ciani, G.; Moret, M.; Sironi, A. *Organometallics* **1996**, *15*, 1637 and references therein.

[11] The potential macromolecular chemistry of compounds containing metal−metal multiple bond has been little explored.[12] It has also been observed that synthetic techniques involving a chain-growth mechanism, such as the addition polymerization useful for organic polymers, are very difficult to apply to the synthesis of inorganic polymers.[13]

[12] Cayton, R. H.; Chisholm, M. H.; Huffman, J. C.; Lobkovsky, E. B. *J. Am. Chem. Soc.* **1991**, *113*, 8709.

[13] Manners, I. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1602.

[14] The reactions have been performed at 193 K, directly into NMR tubes, in THF-*d*$_8$, by successive additions of 1 equiv of **1** to a solution of (PPN)**2** (typically 10 mg, ca. 0.011 mmol). The products have been characterized through ^{1}H and ^{13}C NMR, as detailed in the Supporting Information. ^{1}H NMR data (THF-*d*$_8$, 193 K) for **4**: δ −5.61, −16.12, −16.99, −17.19 ppm. For **5**: δ −5.61, −15.99, −17.06, −17.08, −17.25, −17.29 ppm.

[15] Masciocchi, N.; Moret, M.; Cairati, P.; Ragaini, F.; Sironi, A. *J. Chem. Soc., Dalton Trans.* **1993**, 471.

[16] Apart from some accidental overlap in the higher oligomers, each ReH(CO)$_4$ fragment shows a 2:1:1 pattern of the carbonyl resonances, indicating the cis symmetry of the linkage and the averaging of the environment of the trans-diaxial carbonyls.

[17] Also these reactions have been studied directly into NMR tubes, by treating **1** (typically 12 mg, 0.02 mmol) with different amounts of (PPN)**2** (molar ratios from 3 to 9).

S0002-7863(97)04093-6 CCC: $15.00

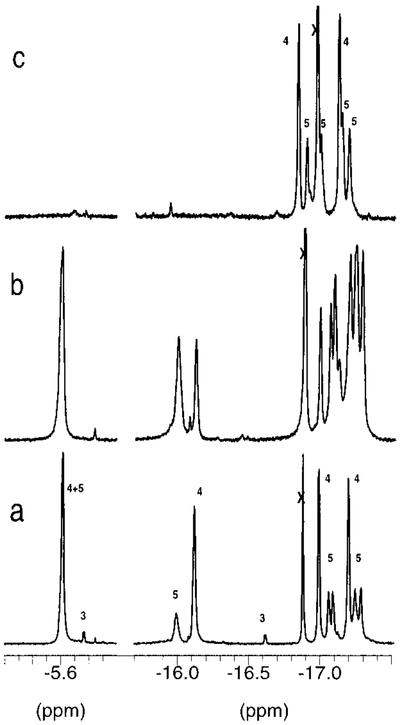


Figure 1. Relevant hydridic regions of the ^{1}H NMR spectra (THF-d_8, 11.7 T) of the mixtures formed in the reaction of **1** with $[Re(CO)_5]^-$ (**2**). (a) [**1**]/[**2**] = 3, 193 K; (b) [**1**]/[**2**] = 5, 193 K; (c) [**1**]/[**2**] = 5, 253 K. At this temperature, the signals of the geminal H ligands on the terminal Re atoms are collapsed, due to an intramolecular exchange. The × marks the signal of $[Re_3(\mu\text{-}H)_3(CO)_{12}]$, present as a byproduct in **1**.

of (PPN)Cl (PPN = bis(triphenylphosphine)iminium) (from 0.0017 to 0.01 mmol), in THF-d_8, gives mixtures containing a series of $[Cl\{ReH(CO)_4\}_{2n}]^-$ oligomers (at least up to Re_{10}).[18] We succeeded in isolating a single crystal of the NEt_4^+ salt of the tetranuclear species **7** ($n = 2$, Figure 2): the X-ray structure[19] clearly shows the presence of two Re_2 units linked by a hydrogen bridge, thus confirming the occurrence of the oligomerization. The anion **7** contains indeed four $Re(CO)_4$ units, with local C_{2v} symmetry, each of them bearing two cis ligands that complete a distorted octahedral coordination around the metals.

Following the classification scheme introduced in ref 5, the anion **7** can be better described as having a *s*/*s*/*s* (*s* = staggered) conformation of the $Re(CO)_4$ moieties relative to each other, with a Re−Re−Re−Re torsion of 129.38(1)° (a type of anti conformation).[20]

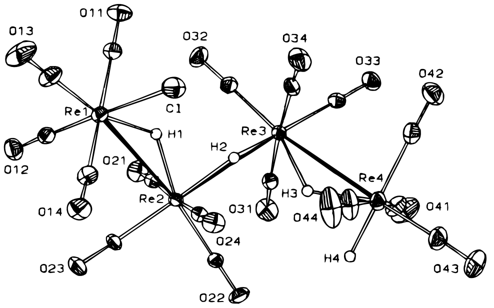


Figure 2. ORTEP view of $[Re_4H(\mu\text{-}H)_3Cl(CO)_{16}]^-$ (**7**) with partial labeling scheme. Relevant bond parameters: Re(1)−Re(2) 3.3243(5), Re(2)−Re(3) 3.3390(5), and Re(3)−Re(4) 3.2781(5) Å, Re(1)−Re(2)-Re(3) 105.87(1)°, Re(2)−Re(3)−Re(4) 102.42(1)°. Hydrides positions were calculated using the program HYDEX.[19]

The 16 valence electron fragment $HRe(CO)_4$ is therefore able to mimic the CH_2 fragment in the propensity to form long chains. To the best of our knowledge, these complexes are the first examples of molecular transition-metal complexes isolobal with linear hydrocarbons, made by the repetition of a same fragment.[21]

This analogy, however, must not be overemphasized: the stability of the Re chains is very different from that of the hydrocarbons, their aggregation being a reversible process. When the temperature is raised, dissociation of **1** is observed from the $[X\{ReH(CO)_4\}_{2n}]^-$ oligomers, the equilibria favoring the lighter oligomers (see Figure 1c). Also the addition of X^- causes the same results.

A major promising feature of the oligomerization here described is that the properties of the products appear tunable by varying the "initiator" or the "alkene-like" substrate or by adding suitable "terminators" of the chains. In particular, the obtainment of neutral chains (possibly up to a polymer) or of mixed-metal co-oligomers can be pursued.

Supporting Information Available: Experimental details, NMR spectra, and crystallographic data (21 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

JA9740935

---

[18] ^{1}H NMR data for the anions $[Cl\{ReH(CO)_4\}_{2n}]^-$ (THF-d_8, 193 K) δ: $n = 1$, **6**, −5.60, −12.94 ppm; $n = 2$, **7**, −5.78, −14.15, −15.88, −16.98; $n = 3$, **8**, −5.66 (1), −14.09 (1), −15.84 (1), −16.84 (1), −17.29 (2); $n = 4$, **9**, −5.63 (1), −14.09 (1), −15.90 (1), −16.84 (1), −17.29 (4). The mean length of the chains (2*n*, see the Supporting Information) varies from 4.8 to 7.4 up to ca. 9, as [**1**]/[Cl^-] varies from 3 to 6 to 12.

[19] Crystal data for (NEt_4)**7**: monoclinic, space group *C*2/*c*, almost colorless, $a = 26.920(3)$, $b = 9.595(1)$, and $c = 28.855(3)$ Å, $\beta = 91.26(1)°$, $V = 7451(1)$ Å^3, $Z = 4$, *R* indices $[F_o > 4\sigma(F_o)]$ R_1 0.0342, wR2 0.0660, GOF 0.908 ($T = 293$ K). Hydrides positions were calculated using the program HYDEX: Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1980**, 2509.

[20] Also the related anion $[Re_4(\mu H)(CO)_{18}]^-$ showed an *s*/*s*/*s* conformation, but with a torsion of the metallic skeleton of 47.47(3)° ("gauche"), responsible of significant 1,4 Re···Re interactions, as revealed by the Re−Re−Re angles (mean 111.2°).[5] In the present case, the Re−Re−Re angles (mean 104.1°) seem to indicate a minor steric crowding. Within the anion $[Re_4H(\mu H)_2(CO)_{17}]^-$,[5] the conformation sequence was *s*/*e*/*s* (with a torsion of 104.25(1)°).

[21] The previously known molecular chain clusters always contained main groups elements bridging between the metal atoms. See, for instance: (a) Davies, S. J.; Howard, J. A. K.; Musgrove, R. J.; Stone, F. G. A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 624. (b) Langebach, H. J.; Keller, E.; Vahrenkamp, H. *J. Organomet. Chem.* **1980**, *191*, 95. (c) Adams, C. J.; Bruce, M. I.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1992**, 26.