Anionic Oligomerization as a Route to Chain Clusters

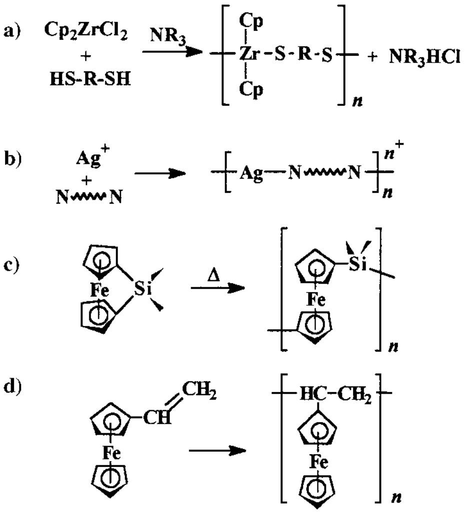
Giuseppe D'Alfonso*

Abstract: The combination of two old concepts (the "σ-donor" capability of M–H bonds and the propensity of unsaturated complexes for addition reactions) has led to the first example of *addition oligomerization* of an organometallic analogue of olefins: chains containing *cis*-[Re(CO)$_4$] units joined by Re-H-Re interactions have been obtained through the oligomerization of the unsaturated complex [Re$_2$(μ-H)$_2$(CO)$_8$] promoted by anionic "initiators". The limits of the method and the possible extension to other substrates are discussed.

Keywords: chain structures • cluster compounds • hydrides • isolobal relationship • oligomerizations

Introduction

Cluster chemistry has traditionally focused on two- or three-dimensional frameworks, leaving one-dimensional clusters in a marginal position.[1] Instead, in other fields of inorganic chemistry a great deal of attention has been paid to species containing chains of metal atoms. The peculiar electrical and magnetic properties of one-dimensional systems have led to many studies on solid phases formed by stacks of individual molecules (typically square-planar d^8 ML$_4$ complexes) with different degrees of metal–metal interactions.[2] Moreover, increasing interest in polymers containing skeletal metal atoms[3–6] has prompted speculation on the possible synthesis of polymers made of covalently bonded metal atoms.[7–9] However, very few results have so far been obtained along this line: most of the methods currently used to synthesize inorganic and organometallic polymers[4, 5, 10] (see Scheme 1 for transition metal containing polymers) give chains where organic ligands connect the metal atoms and no direct metal-metal bond is present. Notable exceptions are the *zigzag* infinite -Cu-Co- chain present in [CuCo(CO)$_4$]$_\infty$ (made of *cis*-[Co(CO)$_4$] units connected by digonal Cu atoms)[11] or the linear chains present in [Ru(CO)$_4$]$_\infty$[12] and in the "solvated molecular wire" {[Rh(CH$_3$CN)$_4$]$^{1.5+}$}$_\infty$[13] (both containing planar ML$_4$ moieties, linked by two *transoid* M–M bonds).



Scheme 1. The main routes to transition metals containing organometallic polymers: a) condensation, b) coordination, c) ring-opening, d) addition polymerization.

With regard to molecular (i. e. not polymeric) chain clusters, most contain bridging ligands that are essential to the stability of the metal chain. In fact, the *bridge-assisted* metal–metal bond formation method has found wide application in the synthesis of such clusters.[14] Another powerful approach, developed by Stone's group,[15] consists in alternating additions of electron-rich [Pt(cod)$_2$] (cod = cyclo-octadiene) and metal–carbyne complexes M≡CR (M = Mo or W), as shown in Scheme 2.

The molecular species of nuclearity higher than 3 in which the metal centers are connected only by unsupported M–M or M-H-M interactions are much rarer.[16] Several rational procedures have been applied for their synthesis, such as the reaction of a metal halide with a nucleophilic carbonylmetalate (Scheme 3a),[17] or the replacement of a labile ligand by suitable metal fragments (Scheme 3b).[18, 19] On the other hand, ring opening by the addition of electron donors[20] is penalized by the fact that the number of ring clusters of nuclearity higher than 3 is very limited.

In principle, some of the above methods could be modified to give oligomerization rather than single-step syntheses. For

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[*] Prof. G. D'Alfonso
Dipartimento di Chimica Inorganica
Metallorganica e Analitica
Via Venezian 21, 20133 Milano, Italy
Fax: (+39) 02-2362748
E-mail: dalf@csmtbo.mi.cnr.it

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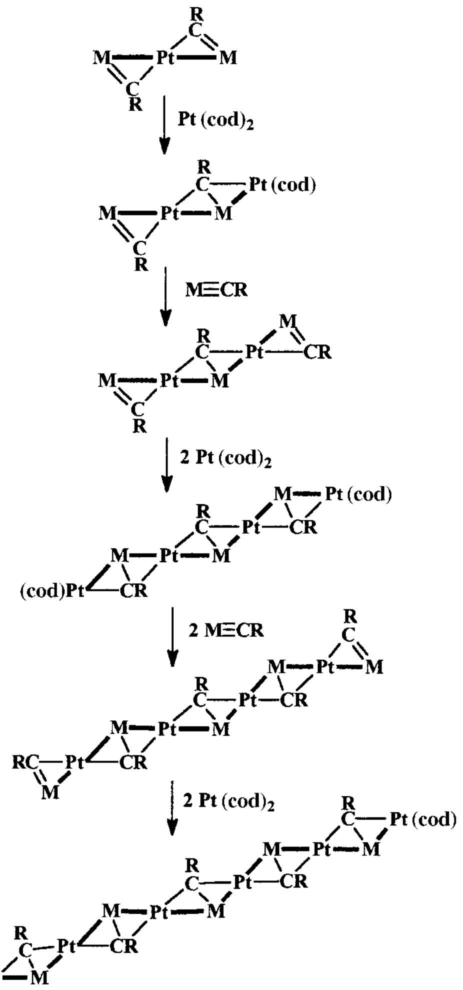
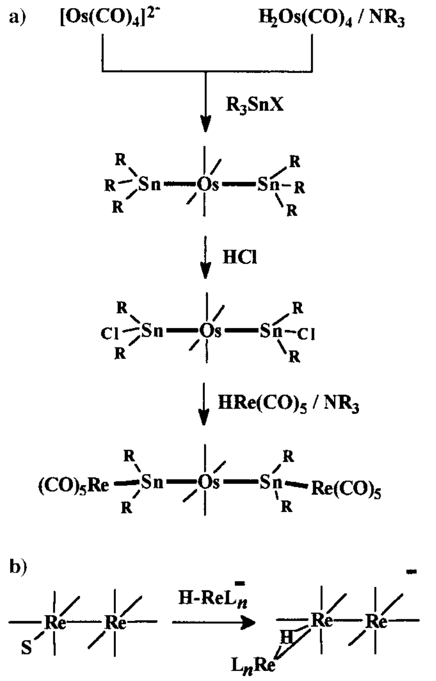
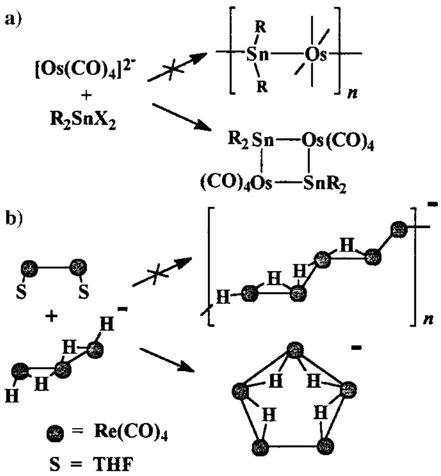


Scheme 2. Stepwise synthesis of metal chains from $Pt(cod)_2$ and M≡CR (M = Mo or W).



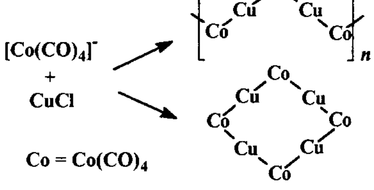
Scheme 3. Routes to chain clusters containing only M–M or M-H-M interactions.

instance, the transformation of the triangular cluster $[Ru_3(CO)_{12}]$ into the polymeric $[Ru(CO)_4]_\infty$ phase by sunlight irradiation, in the presence of carbon monoxide, is an example of *ring-opening polymerization*.[12] However, several factors hinder the development of oligomerization procedures, even when difunctional reactants are available. For instance, in Scheme 2 the reactions proceed in a stepwise manner, with the selective formation of the $n+1$ oligomer rather than a mixture of higher oligomers, probably because the reactivity of the parent $Pt(cod)_2$ and M≡CR reactants is higher than that of the moieties at the chain ends. Another major problem, frustrating attempts to realize *polycondensations* analogous to those of Scheme 1 a, is the easy formation of cyclic oligomers: Schemes 4 a[21] and 4 b[22] show the results using difunctional species in reactions similar to those of Scheme 3.



Scheme 4. The formation of cyclic rather than chain oligomers by using difunctional reactants in reactions similar to those of Scheme 3.

In the first of these reactions, the failure of the oligomerization was attributed to the stereochemical nonrigidity of the Sn-Os-Sn systems (dynamic mixtures of *cis* and *trans* isomers),[17b] suggesting the need for a rigid *trans* arrangement around the metal centers before attempting polymerization. On the other hand, the somewhat related reaction of $[Co(CO)_4]^-$ with CuCl afforded, besides a tetrameric cyclic $[CuCo(CO)_4]_4$ molecule, also the above-mentioned polymeric phase made of *zigzag* -Cu-Co- infinite chains (Scheme 5).[11] This shows that a C_{2v} (*cis*) arrangement of a $M(CO)_4$ group is not incompatible with the formation of a chain, provided a suitable "spacer" is present. This was further confirmed by obtaining chains containing *cis*-$[Re(CO)_4]$ units through

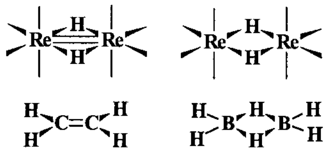


Scheme 5. The formation of both cyclic and chain $[CuCo(CO)_4]_n$ oligomers.

therecently reported anionic oligomerization of $[Re_2(\mu\text{-}H)_2(CO)_8]$.[23] This process provides an example of *addition oligomerization*, a method that has found little application in inorganic chemistry, but is the main route to organic polymers. Indeed, as shown in Scheme 1 d, the addition organometallic polymers described in the literature are not obtained by the polymerization of monomers containing multiple bonds between inorganic elements (organometallic analogues of olefins), but rather by the polymerization of vinyl groups attached to organic functions bound to a metal.[3, 5] Therefore, the metal centers are not involved in the polymerization process, whereas in the oligomerization of the "olefin-like" molecule $[Re_2(\mu\text{-}H)_2(CO)_8]$ they are the sites of addition.

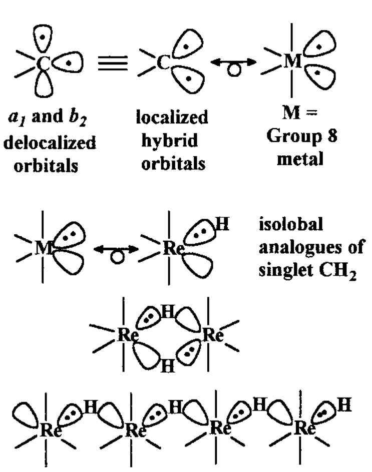
The unsaturated $[Re_2(\mu\text{-}H)_2(CO)_8]$ complex and its reactivity

The starting material of the title process is the dimeric complex $[Re_2(\mu\text{-}H)_2(CO)_8]$ (**1**, D_{2h} symmetry, Scheme 6).[24] Its electronic unsaturation (two electrons short) would require a formal Re–Re double bond in order to satisfy the effective atomic number (EAN) rule.[25] Alternatively, the $[Re(\mu\text{-}H)_2Re]$ system can be described as involving a pair of three-center, two-electron (3c-2e) bonds,[24a] and MO calculations[26] have found no direct metal–metal bond in this system, leading to the suggestion that the metal atoms are bonded exclusively through the hydrogen bridges. From this point of view $[Re_2(\mu\text{-}H)_2(CO)_8]$ is a close analogue of electron-deficient diborane, B_2H_6.[27]



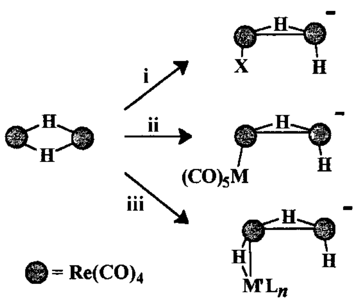
Scheme 6. Two different views of the unsaturated $[Re_2(\mu\text{-}H)_2(CO)_8]$ complex (**1**), as ethylene-like or borane analogue.

From a different point of view, the well known isolobal relationship between CH_2 and d^8 $M(CO)_4$ fragments[28] (Scheme 7) could be extended to the isoelectronic $HRe(CO)_4$ fragment, since its frontier orbitals allow interaction with two metal centers, through 3c-2e bonds, that arise from the empty orbital acting as an electron acceptor and the Re–H bond as an electron donor (due to the well known σ-donor capability of M–H bonds toward coordinatively unsaturated centers).[29] This can give rise to a "double-bonded" dimer (the "ethylene-like" **1**) or to $[HRe(CO)_4]_n$ cyclic oligomers (analogues of cycloalkanes, with n up to 5)[22, 24] or even to the chains described in this paper, which are reminiscent of the $[CH_2]_n$ chains of linear hydrocarbons.



Scheme 7. The isolobal relationship between CH_2, d^8 $M(CO)_4$ and $HRe(CO)_4$ fragments.

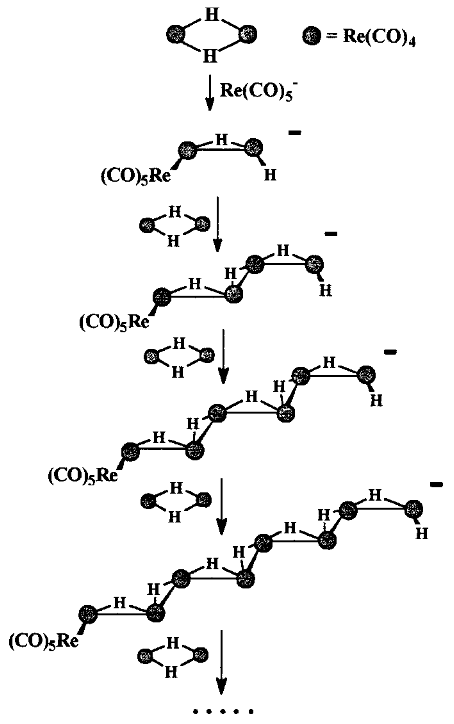
As expected from its unsaturation, the chemistry of **1** is characterized by easy addition reactions. Nucleophiles, not electrophiles, are added: therefore the behavior of **1** should be considered closer to electron-poor diborane than to olefins. In spite of this, its analogy with olefins is more fruitful in describing several aspects of its reactivity, including the title oligomerization, which has no analogue in borane chemistry. Neutral Lewis bases usually react with **1** to give unstable addition derivatives,[30] as observed for diborane.[31] Anionic X^- reactants give more stable $[Re_2HX(\mu\text{-}H)(CO)_8]^-$ anions,[23, 32] in which one of the bridging hydrides of **1** has moved to a terminal location (Scheme 8). It was subsequently shown that replacement of X^- with isolobal carbonylmetalates affords trinuclear L-shaped cluster anions,[19, 33] due to the formation of M–Re bonds (Scheme 8). More recently we proved that also carbonylates containing terminal hydrido ligands can add to **1**,[22, 18] through M-H-Re interactions (Scheme 8).[34] This last achievement has been decisive in discovering the anionic oligomerization of **1**. Indeed, all the addition products shown in Scheme 8 contain terminal hydrides: we therefore argued that such hydrides could be capable of further addition to **1**, leading to clusters containing longer metal chains. This expectation was proved correct.



Scheme 8. The premises for the anionic oligomerization of **1**: addition of i) X^- ($X = H$, Cl), ii) $[M(CO)_n]^-$ ($M = Mn$, Re, Ir), or iii) $[HML_n]^-$ ions, $ML_n = HRe(CO)_4$, $Re_2(CO)_9$.

The oligomerization of $[Re_2(\mu\text{-}H)_2(CO)_8]$

Low-temperature NMR monitoring revealed that successive additions of one equivalent of **1** to a solution containing a nucleophile X^- cause the stepwise formation of monoanions containing progressively longer metal chains as shown in Scheme 9 for $X = Re(CO)_5$.[23] Usually only the first steps are quantitative, increasingly larger fractions of **1** remaining



Scheme 9. The anionic oligomerization of **1** promoted by $[Re(CO)_5]^-$.

unreacted as its amount increases. Throughout the addition, a significant amount of precipitate was formed in the NMR tube (dissolving upon dilution or increasing the temperature).

On the basis of these results, we devised a different approach to the synthesis of the oligomers, which consists in reacting **1** with an amount of $[Re(CO)_5]^-$ significantly lower than the stoichiometric amount (down to 0.1–0.2 equivalents). The results were very similar to those obtained by the stepwise addition of **1** to the nucleophiles. Product nuclearities increase as the amount of $[Re(CO)_5]^-$ decreases, as expected, but at the same time the amount of unreacted **1** and the precipitate in the NMR tubes also increase. The NMR data indicated the presence in solution of chains containing up to five units of the Re_2 "monomer". Higher oligomers might be present in the precipitate.

This second procedure can be defined as an oligomerization process promoted by an anionic nucleophile and is clearly reminiscent of olefin anionic polymerization. In line with this, every anion X^- able to add to **1** might act as "initiator" of the oligomerization process. We have already verified that a nucleophile as poor as Cl^- is able to promote the oligomerization process, with an efficiency not lower than that of the strong nucleophile $[Re(CO)_5]^-$. Other initiators are currently under investigation in our laboratory.[35]

So far we have succeeded in isolating as a single crystal suitable for X-ray analysis only one of these oligomers, namely the $Cl[Re_2H_2(CO)_8]_2^-$ ion, as an NEt_4^+ salt. The structural features revealed are in close agreement with the results obtained from ^{13}C NMR analysis. The chains are made of *cis*-$[Re(CO)_4]$ units joined by hydrogen bridges, with rather long Re-H-Re bonds (average value of 3.31 Å in the Re_4Cl^- ion structurally characterized).[23] The initiator X and one hydrido ligand are terminally bound to the opposite ends of the chains.

These $X[HRe(CO)_4]_n^-$ chains bear some resemblance to the previously mentioned $[CuCo(CO)_4]_n$ infinite chains (Scheme 5),[11] a proton replacing the Cu^+ ion. The structural interchangeability between H^+ and Group 11 cations is well known. However, in the present cases, due to the electron difference between Re and Co, no Co–Co bond is present in the Co-Cu-Co chains, while the Re atoms are connected through 3c-2e Re-H-Re bonds. This leads to distances between the $Re(CO)_4$ units that are much shorter than those between the corresponding $Co(CO)_4$ moieties, with possible 1,3- and 1,4-Re ⋯ Re interactions[18] that could destabilize the Re chains.

The thermodynamic limits of the oligomerization of 1

Several features make this oligomerization process quite different from alkene polymerization. First of all, for most of the addition steps the position of equilibrium (1) is not very favorable (usually only the addition of X^- to **1** is quantitative, as mentioned above).

$$[Re_2(\mu\text{-}H)_2(CO)_8] + X[Re_2H_2(CO)_8]_n^- \rightleftharpoons X[Re_2H_2(CO)_8]_{n+1}^- \qquad (1)$$

An excess of **1** is therefore required to draw the equilibria toward the higher oligomers, and this explains the presence, at equilibrium, of increasing amounts of unreacted **1** as the amount of the anionic "initiator" is lowered.

The equilibrium is strongly affected by temperature. In fact, the lowest temperatures led to the formation of the longest chains, provided that the reaction time was long enough to satisfy the kinetic requirements (from minutes to a few hours). Increasing the temperature led to the reversal of the oligomerization process and increasing amounts of $[Re_2(\mu\text{-}H)_2(CO)_8]$ dissociate, resulting in progressively shorter chains.[23]

This is just what was expected on the basis of the thermodynamics of the reaction: polymerization processes are usually enthalpically driven because entropy decreases, due to the loss of the translational entropy of the monomer.[36] For instance, in the polymerization of alkenes the enthalpy released by the creation of two carbon–carbon single bonds always prevails over the enthalpy necessary to break the double bond of an alkene.

In the present case, not only can an unfavorable entropic term be expected, but also an enthalpic contribution that is less favorable than in typical addition polymerization. Indeed, in spite of the "olefin-like" nature of **1**, reaction (1) cannot be described as the formation of two Re–Re single bonds from a double bond, but rather as the replacement of a $Re(\mu\text{-}H)_2Re$ system by two $Re(\mu\text{-}H)Re$ interactions.[37] No literature data predict the sign of ΔH° for this process. However, if the strength of a metal–metal bond can be evaluated from the metal–metal distance (according to the relationship $E = Ad^{-k}$ used in recent work that analyzes the available thermodynamic data from transition metal carbonyl clusters, including hydrogen-bridged interactions),[27, 38] reaction (1) should be only *slightly* exothermic: on using the values of A and k given in ref.[27], the metal–metal bond enthalpy for **1** can be estimated as 103.6 kJ mol^{-1}, while that for one Re-H-Re interaction should amount to about 54 kJ mol^{-1} (assuming an average Re–Re bond length of 3.31 Å).[23] It is also likely that the absolute value of the (negative) entropic term is reduced by the higher conformational freedom enjoyed by the $Re(CO)_4$ units in the chains with respect to the rigid starting material **1**.[39] In agreement with these considerations, preliminary data concerning the $Re_4 \rightleftharpoons Re_6$ equilibrium for the Cl^--promoted oligomerization indicate that both the enthalpic and entropic terms are rather small (ΔH° ca. $-29(1)$ kJ mol^{-1}, ΔS° ca. $-64(5)$ J K^{-1} mol^{-1}).[35]

Another major problem hindering the formation of higher oligomers arises from the low solubility of **1**, particularly at low temperatures: it is known that the formation of long-chain polymers is favored by high monomer concentrations. The possible use of more effective solvents is under investigation at present.

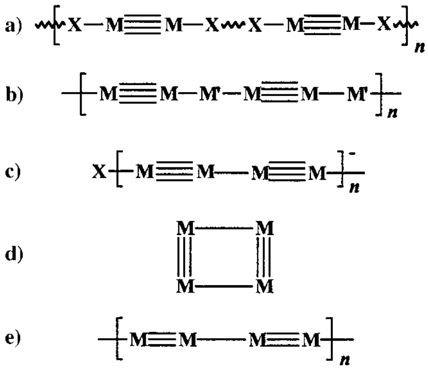
It is interesting to compare the title process with the anionic polymerization of disilenes (or, better, of "masked disilenes", due to the thermodynamic instability of true $R_2Si{=}SiR_2$ disilenes).[6] In the latter case, the reaction of the monomer with a suitable anionic initiator gives rise to a fast living polymerization.[40] Unlike our case, the reaction also occurs at room temperature and affords true polymers (up to about 20000 Da). However, under these conditions the polysilanyl anions are thermodynamically unstable with respect to cyclic oligomers. In the case of the Re chains there is no evidence of degradation processes leading to cyclic oligomers, even if $[ReH(CO)_4]_n$ cyclic oligomers (stable at room temperature) are known, with n up to 5.[22] Moreover, the stabilization of the polysilanyls requires a proton source (typically ethanol or water), to quench the reactive charged end of the chain,[40] whereas in the case of rhenium this termination step is not necessary, probably because polynuclear hydrido-carbonyl rhenates are less reactive than the corresponding silyl anions. On the contrary, some preliminary experiments suggest that for the Re chains the use of electrophiles as potential "terminators" results in destabilization of the oligomeric structure.[35]

Future developments

To the best of our knowledge, the oligomerization process described here is unprecedented in organometallic chemistry. It rests on two main concepts: i) complexes containing terminal M–H bonds can act as efficient "σ-donor" ligands;[29] ii) electron-short complexes like **1** (be they described as isolobal analogues of olefins or as borane-like molecules) can undergo addition of nucleophilic organometallic fragments, including M–H bonds. Neither of these concepts is novel, but in the case of **1** they combine to give a novel process, because the addition products maintain a terminal M–H bond with a nucleophilicity high enough to continue the addition process.

Is this chemistry destined to be restricted to $[Re_2(\mu\text{-}H)_2(CO)_8]$ only? The closest analogues of **1** are the isoelectronic $[M_2(\mu\text{-}H)_2(CO)_6(P{-}P)]$ complexes (M = Mn [41] or Re,[42] P–P = diphosphane): their expected lower propensity to undergo nucleophilic additions could be counterbalanced by higher nucleophilicity of the resulting anion. Several other neutral dimetal complexes containing hydrido-bridged short metal–metal interactions (and formal M–M multiple bonds, in order to adhere the EAN rule) are known.[43] Many of them, particularly those exhibiting the $M(\mu\text{-}H)_2M$ moiety present in **1**, could be good candidates for oligomerization studies.

As to the systems containing authentic metal–metal multiple bonds,[43] we are unaware of any addition reactions of the type depicted in Scheme 8, that should constitute the necessary premises for an oligomerization process. For instance, the reaction of the quadruply bonded complex $[Mo_2(DArF)_3Cl_2]$ (DArF = *N,N′*-diarylformamidinate) with $NaHBEt_3$ does not result in H^- *addition* but rather in reductive *substitution*, leading to the cyclic oligomer $[Mo_2(DArF)_3]_2(\mu\text{-}H)_2$, containing Mo_2 units that still retain the quadruple bond.[44] However, other types of addition reactions do occur: for instance the *addition* of bifunctional ligands in the axial positions of various multiply bonded M_2L_8 dimers (see Scheme 10a) leads to one-dimensional coordination polymers, without M–M bonds connecting M_2 units.[9, 45] If these bifunctional ligands could be replaced by some suitable organometallic fragment, copolymers made of -M_2-M′-M_2- chains would be obtained (Scheme 10b). To realize a true anionic oligomerization, the difunctional ligands ought to be first replaced by an "initiator" X^- and then by the $X\text{-}(M_2)_n^-$ addition products (Scheme 10c).



Scheme 10. Existing (a and d) and hypothesized (b, c, and e) oligomers from quadruply bonded dimers.

A different approach might involve the rearrangement of quadruple bonds to triple and single bonds, as occurs in the dimerization of some dinuclear compounds where rectangular metallocyclodiyne type complexes form (Scheme 10d).[46] If the loss of the δ component of the quadruple bonds could be used to provide electrons to axially bind other M_2 units, chains made of alternating M≡M and M–M bonds would be obtained (Scheme 10e). The stability of similar hypothetical chains of transition metal atoms has already been investigated theoretically,[8, 47] and the results did not condemn its thermodynamic possibility.

In conclusion: recent reviews discussing synthetic problems related to the preparation of inorganic and organometallic polymers[4, 10] have observed that "the most versatile method for the synthesis of organic polymer—the addition polymerization of unsaturated monomers—is currently not available for the preparation of inorganic backbone polymers".[10] This has been attributed to the small number of stable inorganic analogues of olefins and to the scarcity of studies concerning their behavior as polymerization monomers. Our work provides a first contribution in this direction. There is no doubt that much more still has to be done. The scope of the method and its possibility to produce true polymers, and not just unstable oligomers, has still to be investigated. In any case, what was until now only an appealing hypothesis, that is "que la caténation des ions métalliques pourrait être accessible au moyen d'un protocole de polymérisation inspiré de ceux utilisés en chimie organique",[8] has now been established.

Acknowledgment

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