DOI: 10.1002/ejic.201001364

Radical Coordination Chemistry and Its Relevance to Metal-Mediated Radical Polymerization

Rinaldo Poli*[a]

Keywords: Radicals / Electron transfer / Atom transfer / Radical reactions / Polymerization / Transition metals

The reactions engaged by organic radicals with transition-metal complexes are reviewed with a particular focus on how they can interplay with and affect the results of radical polymerization. Radicals can either add to a metal centre to establish metal–carbon bonds, abstract an atom or group, be abstracted by an atom or group, undergo associative exchange, transfer a β-H atom or add to existing ligands in the metal coordination sphere. Reversibility is key for certain controlled polymerization methods. The various ways in which metal complexes can play a role in radical polymerization lead to atom-transfer radical polymerization (ATRP), organometallic-mediated radical polymerization by either reversible termination (OMRP-RT) or degenerative transfer (OMRP-DT) and chain-transfer-catalysed radical polymerization (CTCRP).

Introduction

Organic radicals are implicated in a large range of chemical processes, from organic synthesis, through biological processes, to polymerization. In all these areas the intervention of metals can profoundly modify the reactivity and selectivity or control other specific parameters. In recent years, different types of metal-mediated radical polymerizations have attracted growing attention, particularly "atom-transfer radical polymerization" (ATRP), which has now surpassed metal-catalysed polymerization in terms of volume of yearly published research articles.

Organic radicals may interact with transition-metal complexes in many different ways, including by direct bond formation, atom abstraction, hydrogen atom transfer or by addition to ligands. Each of these phenomena may be reversible or irreversible and, when reversible, play an important role in combination with other radical reactions such as chain propagation in polymerization. New findings have revealed the possibility for organic radicals to exchange in the coordination sphere of organometallic complexes under mild conditions by either dissociative or associative processes, reviving interest in one-electron processes occurring in the coordination sphere of a transition-metal complex.

Several reviews have already been devoted to the chemistry of radicals with metal complexes and metal-induced radical reactions, especially with a focus on organic synthesis,[1] ligand radical reactivity[2] and biological phenomena.[3] This microreview focuses on the reactivity of radicals with transition-metal complexes of relevance to radical polymerization processes, attempting to identify trends and principles of general use.

Reaction Types and Their Relevance to Radical Polymerization

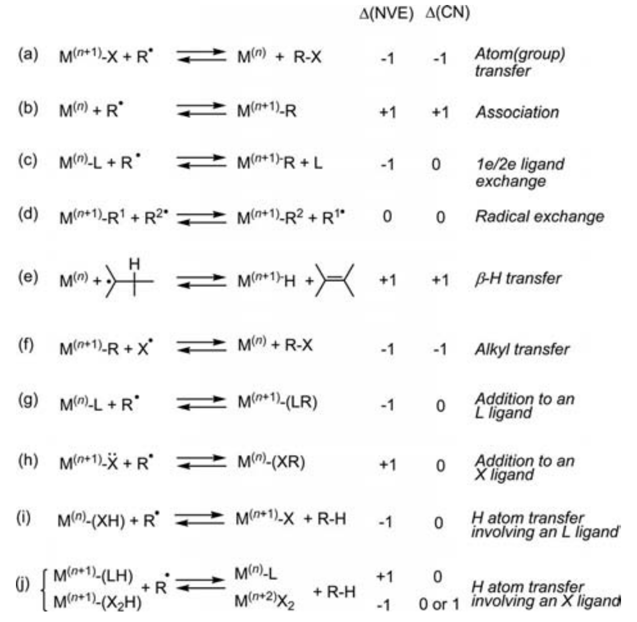
A classification of the possible reactions between an organic radical and a transition-metal complex is presented in Scheme 1. All reactions are shown with a double arrow because the process may occur, depending on the type of radical and metal complex and on conditions, either reversibly or irreversibly in either direction. For each process, the change in the number of valence electrons (NVE) and coordination number (CN) is also given. The Green "MLX"

---

[a] Laboratoire de Chimie de Coordination (LCC), CNRS,
Université de Toulouse; UPS, INPT,
205, route de Narbonne, 31077 Toulouse, France
Fax: +33-5-61553003
E-mail: rinaldo.poli@lcc-toulouse.fr
http://www.lcc-toulouse.fr/equipe_g/pages/poli/index.html

Rinaldo Poli obtained a Ph. D. degree in 1985 from Scuola Normale Superiore (Pisa, Italy) under Fausto Calderazzo, with one year also spent at Imperial College, London with Geoffrey Wilkinson. After a two-year post-doctoral fellowship with F. A. Cotton at Texas A&M University, he joined the faculty of the University of Maryland at College Park where he stayed until 1996. Then he moved to France, first to Dijon until 2003, and then to his current position in Toulouse where he teaches at ENSIACET and leads a research group at the Laboratoire de Chimie de Coordination of the CNRS. His research interests are in transition-metal chemistry, spanning structure–bonding–reactivity relationships, especially for open-shell organometallic compounds, to the application of metal complexes to catalysis and to controlled radical polymerization.

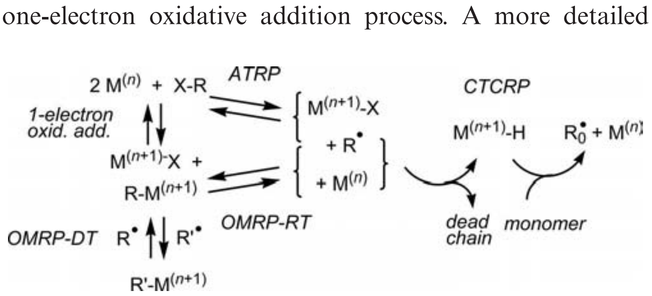
nomenclature (M = metal, L = generic two-electron ligand, X = generic one-electron ligand) will be used throughout this microreview.



Scheme 1. Possible reactions between a transition-metal complex and an organic radical.

One of the most important processes (a) is the transfer of an atom or a group. The most interesting case is when X is a halogen atom, but pseudo-halogen groups may also be involved. This is the ubiquitous deactivation–activation equilibrium in ATRP. The activation process (right to left) also corresponds to the initial step of the one-electron oxidative addition of alkyl halides. Direct bond formation (b) and its reverse, homolytic bond dissociation, are in principle the simplest processes. When there is reversibility with a suitable equilibrium position, they regulate the "organometallic-mediated radical polymerization" by reversible termination (OMRP-RT). Process (c) is a variant in which metal–carbon bond formation occurs only if a two-electron ligand leaves the coordination sphere. Process (d) is an associative exchange between a free radical and a latent radical, a process that has only become appreciated recently. It is of fundamental importance in a second type of OMRP, by degenerative transfer (OMRP-DT). Process (e) consists of the transfer of a β-H atom from the radical to the metal to yield a hydride complex. When occurring reversibly, this process is also of importance in radical polymerization because it is the basis of catalysed chain transfer to a monomer in "chain-transfer-catalysed radical polymerization (CTCRP). Process (f) consists of the transfer of an alkyl radical from an organometallic compound to an external acceptor reagent, which may also be a second metal complex or a second organic radical. In the latter case, it would correspond to a metal-mediated termination step in polymerization. Note that processes (a) and (f) are identical if X is an organic radical. Processes (g) and (h) correspond to radical addition to a ligand without its abstraction from the coordination sphere. When the ligand is of L type (including multidentate ligands, L_2, L_3 etc. such as a diene, arene, etc., but also L_nX such as allyl), one of the electrons involved in M–L bonding is sequestered to establish the L–R bond and the ligand becomes an X type. Conversely, when the ligand is of X type (including multidentate) but also contains a nonbonding pair of electrons, the latter will be used to keep the :XR product bonded to the metal. If such an additional electron pair is not available, the reaction becomes of type (a). Finally, processes (i) and (j) are analogous to process (a) (X = H), except that the hydrogen atom is abstracted from a ligand and not from the metal first coordination sphere. Abstraction from an X-type ligand, shown in (j), may either convert this to an L ligand with metal reduction and ligand oxidation or to a formally X_2 ligand with metal oxidation. The ubiquitous example of the last situation is the transformation of OH^- into O^{2-} with Δ(CN) = 0, but cases in which a monodentate X ligand is transformed into a bidentate X_2, Δ(CN) = +1, may also occur. We can also envisage hydrogen atom transfer from a radical to a ligand, namely a process equivalent to (e) but with a ligand as the hydrogen acceptor. These radical addition and hydrogen atom transfer processes involving a ligand are not per se implicated in radical polymerization processes to the extent that they are usually irreversible. However, they must be known and understood, because engineering a metal complex for use in metal-mediated radical polymerization requires their absence, or reversibility, or a low impact relative to the processes of interest.

Given the multitude of reaction types, it is no surprise that two or more of these may compete, interfere or synergistically interplay in radical polymerization processes. These intricate relations are summarized in Scheme 2. Thus, when a radical reacts with a complex, $M^{(n)}$ can expand its coordination number and electron count by one unit and both process (b) and (e) may take place resulting in OMRP-RT/CTCRP competition. In the presence of excess radicals and for suitable coordination spheres, process (d) may also take place resulting in OMRP-RT/OMRP-DT/CTCRP interplay, as highlighted for the Co^{II}/Co^{III}-mediated polymerization of vinyl acetate (VAc).[4] In the presence of halogen atoms, process (a) may also come into play together with processes (b) and (e), resulting in ATRP/OMRP-RT/CTCRP interplay, as highlighted for a Mo^{III}/Mo^{IV}-mediated polymerization of styrene.[5] The combination of ATRP activation and OMRP-RT trapping gives rise to a one-electron oxidative addition process. A more detailed



Scheme 2. Relation between different radical–metal reaction modes in radical polymerization processes.

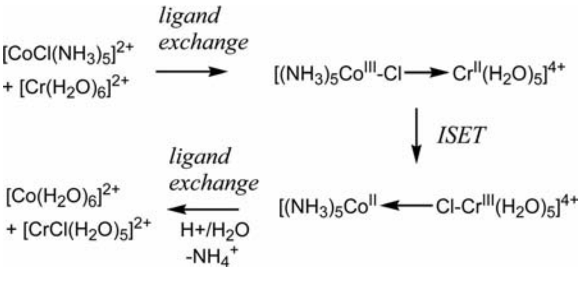
analysis of metal-mediated radical polymerizations with the simultaneous intervention of various one-electron processes is available elsewhere.[6]

Note that one-electron ligands such as organic radicals can be treated, in terms of addition to, departure from and exchange in the coordination sphere of a metal complex, like the more ubiquitous two-electron ligands. The systematic classification of ligand-exchange processes from the limiting associative and dissociative variants, through the different degrees of intermediate interchange type, is the most important cornerstone of coordination chemistry.[7] It is shown here that this classification can be extended to the exchange of one-electron ligands as well as to the exchange of a one-electron ligand with a two-electron ligand, or vice versa [process (c) in Scheme 1].

Atom Transfer, OSET and ISET

Process (a) of Scheme 1 is possible in principle for any one-electron donor X atom or group. For instance, when X = H this reaction plays a fundamental role in a large number of catalysed olefin hydrogenation reactions that occur by a radical mechanism.[3a] We shall focus here only on processes in which X = halogen because these are of relevance in controlled radical polymerizations that take place by the ATRP mechanism. We do not intend to provide a comprehensive review of ATRP, which is extensively covered in other excellent reviews.[8]

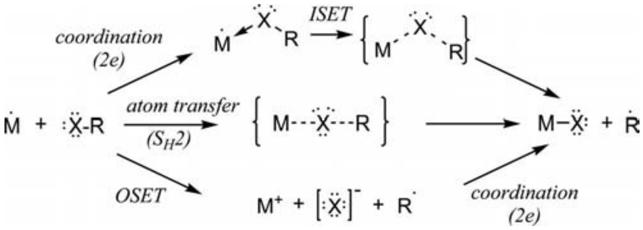
There tends to be confusion between the terminologies "atom transfer" and "inner-sphere electron transfer" (ISET). The latter term is used for an elementary process (i.e., a single step, without intermediates) in which an electron is transferred between two redox reagents linked together by a bridging atom or group that belongs to the coordination sphere of both centres. The seminal study of Taube et al., illustrated in Scheme 3,[9] represents the best example of an ISET process. Mechanistically, this may be imagined as involving three independent steps: two two-electron ligand-exchange processes and one ISET, even though no intermediate has been detected for this reaction.



Scheme 3. Inner-sphere electron transfer between $[CoCl(NH_3)_5]^{2+}$ and $[Cr(H_2O)_6]^{2+}$.[9]

When one of the two partners is an alkyl group, formally changing its redox state between carbocation and radical, the ISET process implies electron transfer within R–X→M$^{(n)}$, which must first be obtained by RX coordination to M$^{(n)}$, to yield formally R$^{\cdot}$←(X)$^{-}$–M$^{(n+1)}$ in an elementary step that is followed by R–X bond-breaking in a subsequent third step. The sum of the last two steps corresponds to the reverse of process (h) in Scheme 1. Studies of alkyl halide reductions suggest that these proceed as dissociative single-step processes rather than as two-step processes with radical-anion intermediates,[10] therefore the ISET and X–R bond-breaking appear to be concerted events. From the point of view of the metal centre, however, it is still justified to consider the overall process as an ISET. On the other hand, for the reverse of process (a), in which the electron is transferred through an M···X···R transition state concertedly with the establishment of the M–X bond and homolytic cleavage of the X–R bond, use of the term ISET is not fully justified because XR is not part of the coordination sphere on the reagent side. This process may also be termed "bimolecular heterolytic substitution" (S_H2), although this terminology is generally restricted by organic chemists to one-electron substitutions at carbon.[11] The best way to refer to this process is simply as "atom transfer".

The most important point is that there are two different kinds of atom-transfer processes, a direct one (reverse of process a) and a two-step one involving preliminary coordination of RX through one of the lone-pairs of the halogen atom followed by ISET (reverse of process h). In the first case, the transition state features a three-centre-three-electron interaction with a linear geometry, whereas in the second case it involves a three-centre-five-electron interaction and is expected to be bent (see Scheme 4).



Scheme 4. Different possible mechanisms for the halogen atom transfer reaction.

A third possibility that can also be imagined for this reaction involves an "outer-sphere electron transfer" (OSET) yielding R$^{\cdot}$ and X^{-} (the presence of a [RX]$^{\cdot-}$ radical-anion intermediate is in question as stated above) followed by two-electron halide addition. An OSET mechanism should be favoured when the R–X substrate is easily oxidizable and the metal complex is a strong reductant, and also when the reaction is carried out in highly dielectric solvents. Whereas OSET processes between two metal complexes or between a metal complex and a dihalogen (X_2) are well established, OSET for the reduction of alkyl halides by metal complexes as shown in Scheme 4 poses more interesting questions. In recent work using Cu^{I} complexes as reducing agents, estimates based on Marcus theory have shown much smaller predicted OSET rate constants relative to the experimentally measured rates, which implies that an atom-transfer process is preferred.[10b]

Whether an atom-transfer process occurs by direct S_H2 or preliminary RX coordination and ISET depends on the electronic configuration of the metal complex, as shown by a theoretical analysis of the atom-transfer step for the reaction between various combinations of ATRP catalysts (M) and initiators (R–X).[12] Complex $[RuCl_2(PPh_3)_3]$, a five-coordinate diamagnetic 16-electron complex of d^6 Ru^{II}, is a well-known ATRP catalyst.[13] It has a vacant orbital at low energy and can thus accept two electrons from an additional ligand (see Figure 1, a). Indeed, the interaction between the model $[RuCl_2(PH_3)_3]$ and CH_3Cl system was calculated as exoergic, albeit weakly so (–7.8 kcal mol^{-1}). The 18-electron $[RuCl_2(PH_3)_3(CH_3Cl)]$ adduct then leads to CH_3–Cl bond breaking to give $[RuCl_3(PH_3)_3]$ and $CH_3^{\cdot}$ by a high-energy transition state with a bent $[Cl_2(PH_3)_3Ru\cdots Cl\cdots CH_3]$ geometry.[12]

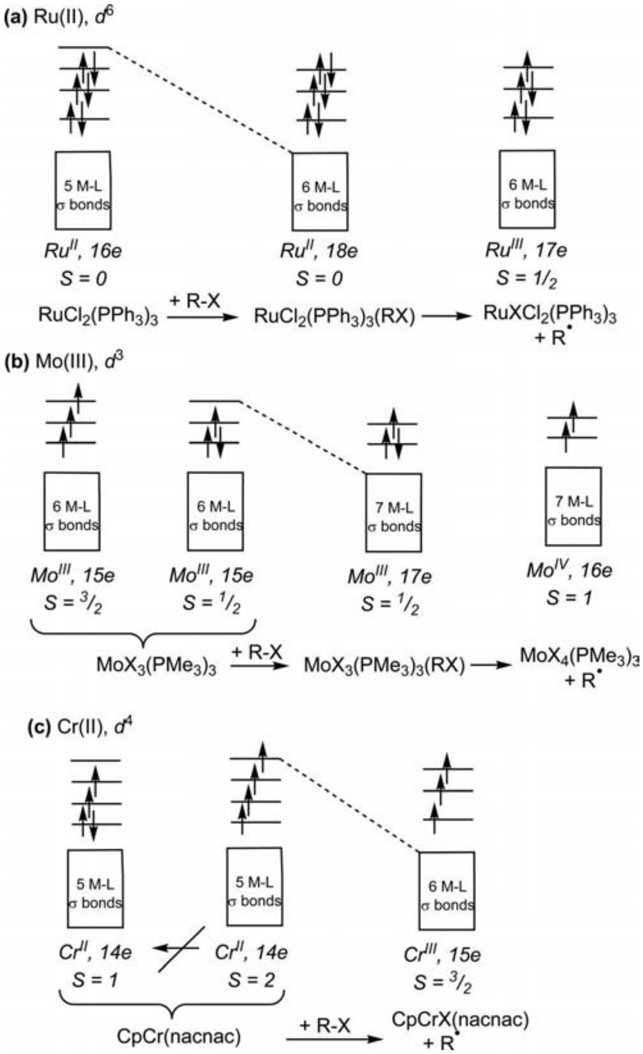


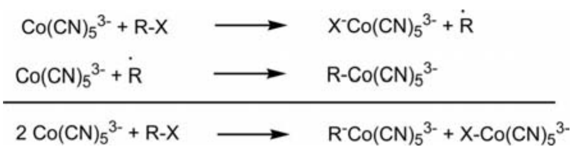
Figure 1. Schematic representation of the evolution of electronic structure during the process of RX coordination to a) $[RuCl_2(PPh_3)_3]$ and b) $[MoX_3(PMe_3)_3]$.

A slightly different situation is displayed by the $[MoX_3(PMe_3)_3]$ complexes (X = Cl, Br, I), six-coordinate 15-electron complexes of d^3 Mo^{III} with three unpaired electrons ($S = {}^3/_2$), that also function as ATRP catalysts.[14] A direct two-electron donation from RX is impossible in this case because all valence metal orbitals are occupied, but becomes possible after pairing two electrons, promoting the system to an excited $S = {}^1/_2$ state (see Figure 1, b). Because this electron pairing is not too costly for Mo^{III},[15] this is indeed what happens, as suggested by calculations on the model $[MoCl_3(PH_3)_3]$ + CH_3Cl system. The coordination process that yields the 17-electron spin doublet $[MoCl_3(PH_3)_3(CH_3Cl)]$ intermediate is endoergic by +18 kcal mol^{-1}, but still energetically more favourable than direct atom transfer without prior coordination. Again, the transition state of this process, $[Cl_3(PH_3)_3Mo\cdots Cl\cdots CH_3]$, has a bent geometry.[12] On the other hand, in the case of spin doublet $[CpMoCl_2(PH_3)_2]$, a model for the $[CpMoCl_2L_2]$ ATRP catalysts [L_2 = $(PMe_3)_2$, dppe, η^4-C_4H_6],[5] it is not possible to create an empty orbital to accept the R–X lone-pair and the calculations indicate a direct atom-transfer pathway through a linear $[CpCl_2(PH_3)_2Mo\cdots Cl\cdots CH_3]$ transition state.[12]

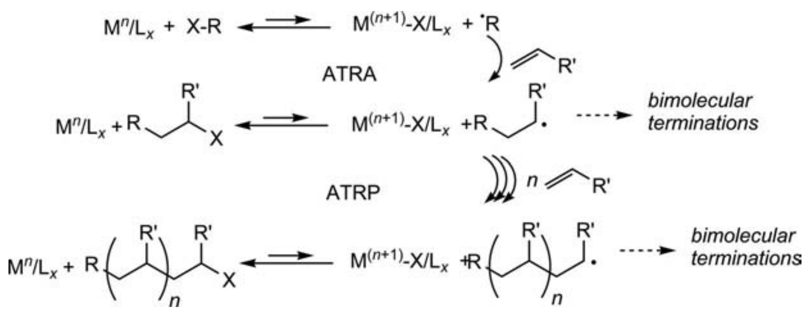
Another interesting situation is presented by the half-sandwich "nacnac" complexes of Cr^{II} [nacnac = ArN(Me)-CHC(MeAr)], which are d^4 pseudo-five-coordinate complexes with an $S = 2$ ground state. For this system, the electron pairing needed to liberate an orbital costs too much energy, thus RX coordination to Cr^{II} cannot occur (Figure 1, c). The atom transfer is direct, with an almost linear transition state featuring a three-electron $Cr\cdots Cl\cdots C$ interaction.[16]

Outside the realm of organic radicals, but also well known to chemists handling organic radicals, the Fenton reaction is another example of a three-centre-five-electron interaction that may play a role in the ISET pathway. The detailed mechanism of this reaction, in spite of very intense studies, is still debated, but it seems that the first step is H_2O_2 coordination to form a $Fe^{II}(H_2O_2)$ [or $Fe^{II}(O_2H)$ + H^+] intermediate, which then releases the hydroxy radical.[17]

A halogen atom transfer is the first rate-determining step of the one-electron version of the oxidative addition reaction of alkyl halides, a well-known process in organometallic chemistry.[18] This is followed by association of the leftover radical with a second $M^{(n)}$ complex to produce the organometallic product $M^{(n+1)}$–R (see example in Scheme 5).[19] Note that in these processes the halogen atom does not enter or leave the coordination sphere as a free radical. Instead, it is delivered by a suitable "atom donor" or captured by a suitable "atom acceptor". Free halogen atoms do not appear to be frequently involved in the chemistry of coordination compounds. Contrary to the chlorina-



Scheme 5. Mechanism of the one-electron oxidative addition of alkyl halides to $[Co(CN)_5]^{3-}$.[19]



Scheme 6. Mechanism of the ATRA and ATRP processes.

tion of inert C–H bonds, which requires photolytic activation with Cl$^\cdot$ formation, simple metal aqua ions react with dihalogens by OSET to generate $X_2^{\cdot-}$ as an intermediate[20] and low-valent complexes (including those containing metal–metal bonds) in organic solvents react with dihalogens by non-radical mechanisms.[21]

As already stated, a reversible halogen atom transfer process is key for ATRP. It is also key to metal-catalysed atom-transfer radical addition (ATRA), also known as Kharasch addition.[22] The two processes are exemplified by the common general pathway shown in Scheme 6. ATRA is currently enjoying renewed attention, mainly because tricks have been found to reduce the amount of catalyst to extremely low levels,[8d,23] greatly widening the reaction scope for organic synthesis.[24]

Association of Organic Radicals with a Transition-Metal Centre

Alkyl groups are most typically incorporated into a transition-metal coordination sphere by two-electron processes. However, the one-electron addition of radicals is also well documented. The one-electron oxidative addition reaction of alkyl halide substrates, already highlighted in Scheme 5, is one of the earliest described phenomena in which carbyl radicals are involved in transition-metal chemistry. Perhaps the oldest report is the generation of $[PhCH_2–Cr(H_2O)_5]^{2+}$ and $[CrCl(H_2O)_5]^{2+}$ from $[Cr(H_2O)_6]^{2+}$ and $PhCH_2Cl$ by Anet and Leblanc,[25] although the implication of free radicals was not immediately appreciated.[26]

Meyerstein and co-workers pioneered the investigation of direct metal–carbon bond formation by the addition of radicals to metal centres, the radicals being generated by pulse radiolytic techniques in aqueous solution. It has thus been shown that $CH_3^\cdot$ and a few related radicals $R^\cdot$ add to many metal ions M^n, including Cr^{II},[27] Mn^{II},[28] Fe^{II},[28,29] Ni^{II},[30,31] Cu^{I}[32] and Cu^{II},[33] to generate labile $M^{(n+1)}$–R adducts. Unfortunately, this technique cannot be easily extended to a wide range of radicals. Metal–carbon bond-forming reactions involving other radicals have been studied, however, by the use of flash photolysis techniques with radicals generated from photolytically labile organocobalt(III) derivatives[34] or by the thermal decomposition of diazo compounds.[34b,35] A more elegant way to selectively produce $M^{(n+1)}$–R from $M^{(n)}$ is to carry out the one-electron oxidative addition of RX in the presence of a reducing agent capable of converting the $M^{(n+1)}$–X co-product back to $M^{(n)}$, as recently demonstrated for the synthesis of $[CpCr^{III}(nacnac)–CH_2SiMe_3]$ [nacnac = $(ArNCMe)_2CH$] from $[CpCr^{II}(nacnac)]$ and Me_3SiCH_2I in the presence of Mn.[36]

Radicals may occasionally be implicated in the alkylation of transition-metal halides by carbanions when a single-electron transfer (SET) takes place rather than the expected nucleophilic ligand substitution. This phenomenon is related to the classical Wurtz coupling in organic chemistry, in which R^- from a Grignard or lithium reagent and an alkyl halide R'–X may also undergo SET to produce $R^\cdot$ and $R'^\cdot$ rather than the expected S_N2 exchange. However, subsequent recombination of the two radicals leads again to the expected R–R′ product.[37] Transition-metal halide complexes are often easily reducible and their interaction with relatively strongly reducing Grignard or lithium reagents is well known to suffer from metal reduction, which is one of the greatest plagues of synthetic organometallic chemistry. The radicals resulting from this reaction are typically lost and the reaction leads to the isolation of the reduced metal complex. However, it is possible to envisage recombination between the radical and the reduced metal complex, as in the above-mentioned SET mechanism for Wurtz coupling, to generate the anticipated alkylation product. The first suggestion of this possibility seems to be by Legzdins and co-workers for the alkylation of $[Cp^*Mo(NO)X_2]$ by Me_3SiCH_2MgCl, based on the EPR observation of $[Cp^*Mo^I(NO)X_2]^-$ when X = Br. Also, the reaction leads to $[Cp^*MoX(NO)]_2$ when X = I and to $[Cp^*Mo(NO)(CH_2SiMe_3)_2]$ when X = Cl.[38] Another example was discovered in our own laboratory for the reaction of $[CpMoCl_2(PMe_3)_2]$ with MeLi, leading to the stable 17-electron dimethyl complex $[CpMo(CH_3)_2(PMe_3)_2]$. Evidence based on redox potentials, kinetics and the chemical behaviour of related complexes led to the mechanistic proposal of initial PMe_3 dissociation and reduction leading to a $\{[CpMoCl_2(PMe_3)]^-Li^+\cdot CH_3^\cdot\}$ cage pair, which favours the radical addition process because of the diradical (*S* = 1) nature of the metal complex.[39] It is quite possible that other alkylation reactions occur by the same unsuspected SET/recombination pathway.

Homolytic Metal–Carbon Bond Scission

This is the reverse of the association process discussed in the previous section. Three different ways to activate this process can be distinguished: thermal, photochemical and electrochemical.

The thermal treatment of organometallic compounds eventually leads to decomposition according to a variety of mechanisms, most of them involving two-electron processes, depending on the metal electronic structure, the nature of the ancillary ligands and the presence or absence of other suitable reagents. Typical decomposition pathways, which require, however, the presence of a vacant coordination site *cis* to the alkyl group or a suitable *cis*-accepting group, involve β-H or α-H elimination.[40] For suitable alkyl groups and coordination spheres, these decomposition pathways may be blocked or disfavoured and the homolytic bond cleavage with the production of radicals may then become preferred if the homolytic bond dissociation energy is sufficiently small.

The homolytic metal–carbon bond dissociation energies for "thermally stable" compounds (i.e., isolatable and storable under standard laboratory conditions) cover a relatively wide range, although they have been measured with sufficient accuracy only in a limited number of cases.[41] They have rarely been obtained by direct measurement of the bond-breaking process and the indirect methods used suffer from many approximations. Values as high as $375 \pm 9\ \mathrm{kJ\,mol^{-1}}$ ($90 \pm 2\ \mathrm{kcal\,mol^{-1}}$) for $Cp_3Th–Me$[42] or $350 \pm 10\ \mathrm{kJ\,mol^{-1}}$ ($84 \pm 2\ \mathrm{kcal\,mol^{-1}}$) for $Cp_2Ti(p\text{-}C_6H_4OMe)_2$[43] and as low as $70–100\ \mathrm{kJ\,mol^{-1}}$ ($17–24\ \mathrm{kcal\,mol^{-1}}$) for a range of $(dmg)_2(L)Co–CH(Me)Ph$, depending on the nature of L,[44] have been reported. Computational methods have been of invaluable assistance in this area.[45]

For any given radical, the metal–carbon bond strength is expected to grow upon descending down a group of transition metals (3d < 4d < 5d). On the other hand, for a given metal complex, the bond strength should be, roughly speaking, inversely proportional to the radical stabilization: a very reactive radical such as $CH_3^{\cdot}$ should give stronger bonds whereas one that enjoys greater stabilization by hyperconjugation or mesomeric effects should give weaker bonds. The same is expected for any other R–X bond, but some care should be exercised because bond strengths are also affected by polar effects (when the electronegativity difference between R and X is significant) and steric effects (when X contains bulky substituents that do not allow the adoption of the most favourable geometry of the R–X adduct).[46] Hence, correlation of R–M bond strengths with the strength of other R–X bonds, for example, R–H,[45b] are dangerous. It has been shown, for instance, that polar effects are more important in the relative strengths of R–Cl and R–Br compounds (initiators for ATRP), whereas steric effects play a greater role in ZC(S)S–R (Z = Me, Ph; transfer agents for "reversible addition/fragmentation chain-transfer polymerization").[47] For organometallic complexes (X = metal complex), the R–X bond is relatively apolar whereas the metal coordination sphere may be rather encumbering, thus the bond is more likely affected by steric effects than by polar effects.

The most interesting thermolytic processes are those of relatively labile bonds, which lead to the rapid production of radicals under mild conditions. The ubiquitous example is that of vitamin B12 (5′-deoxyadenosylcobalamin) and numerous related organocobalt(III) complexes.[48] Systems with such weak metal–carbon bonds are important not only in Nature but also in OMRP-RT (see the next section).

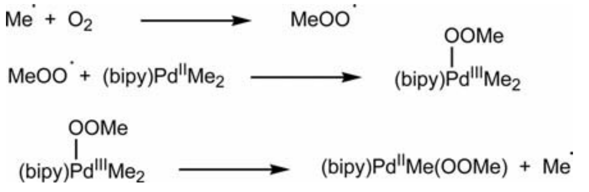
Photochemistry is another commonly used method for radical release from organometallic compounds. Although the most common phenomenon for coordination compounds is the photolabilization of L-type ligands (particularly CO) and metal–metal bonds (when such bonds are present), the homolytic rupture of a metal–carbon bond may also occur.[49] The nature and reactivity of the excited state is of primary importance for the outcome of the process. One well-studied example is the tricarbonyl diimine rhenium(I) complexes $[Re(R)(CO)_3(dmb)]$ (R = Me, Et, *i*Pr, Bz; dmb = 4,4′-Me_2-2,2′-bipyridyl). The primary excited state has mixed ^{1}MLCT and $^1\sigma\pi^*$ character (charge transfer from a metal d orbital and from the Re–R σ bond to a ligand π* orbital). It evolves either to a dissociative $^3\sigma\pi^*$ state or to a non-dissociative ^{3}MLCT state.[50] Although the latter has a lower energy and decays back to the ground state for Me, it is higher in energy and decays to the dissociative $^3\sigma\pi^*$ state for Et. As a consequence, the quantum yield for photodissociation is about 0.4 for the Me derivative and unity for the Et derivative.[51]

Organocobalt(III) complexes are a well-known family of compounds for which radical dissociation may be photochemically induced. When the alkyl group generates stabilized radicals such as allyl and benzyl, radical dissociation easily occurs under thermal conditions, but more reactive radicals associated with simpler alkyl groups such as Me are formed only upon irradiation. For instance, photolysis of methylcobaloxime derivatives $[(dmg)_2(L)Co–Me]$ (L = H_2O, pyridine) in air produces $[(dmg)_2(L)Co–OOCH_3]$.[52] Photolytic Co–R splitting occurs more readily for alkylcobalamins[53] than for cobaloximes, whereas secondary alkylcobalt(III) compounds are photolysed more readily than primary alkylcobalt(III) analogues.[54] Alkylcobalt(III)–porphyrins have also been shown to undergo photolytically activated homolytic Co–R cleavage.[55] The Cp(nacnac)-Cr^{III}–R family of compounds has recently been shown to undergo room-temperature homolysis for R = CH_2*t*Bu, CH_2Ph and CH_2*i*Pr, whereas primary alkyl, phenyl and alkenyl derivatives, which do not undergo appreciable homolysis under these conditions, can be activated photolytically.[36]

Concerning electrochemical activation, it is generally well appreciated that the covalent component of metal–ligand bonds weakens upon metal oxidation and metal–alkyl bonds are no exception. This proposition has been corroborated by a few theoretical studies, for instance, we reported that the Mo–X bond dissociation energy in a series of half-sandwich complexes decreases progressively on going from

Mo^{II} through Mo^{III} to Mo^{IV}, be X a halide or a methyl group.[5] Analogously, the Cu–CH_3 BDE in $[LCu–CH_3]^{n+}$ (L = *N*-heterocyclic carbene ligand) decreases dramatically from 80 kcal mol^{-1} for Cu^I ($n = 0$) to 38 kcal mol^{-1} for Cu^{II} ($n = 1$).[56] Experimentally, oxidation reactions of compounds containing metal–alkyl bonds have provided evidence for the generation of radicals. Kochi and co-workers made a seminal contribution by comparing the thermal decomposition pathways of $[FeEt_2(bipy)_2]^{n+}$ (n = 0, 1, 2). Although the Fe^{II} complex decomposes upon heating to 50 °C exclusively by the β-H elimination pathway to yield ethane and ethylene (no butane), the Fe^{III} species yields a mixture of ethane, ethylene and butane as a result of the homolytic fragmentation of the Fe^{III}–Et bonds, and the transient Fe^{IV} species yields exclusively butane by reductive elimination.[57] Further studies have confirmed the activating effect of oxidation on both reductive elimination[58] and homolytic cleavage processes.[59]

A recent study of the autoxidation of $[(bipy)PdMe_2]$ to yield [(bipy)PdMe(OOMe)] suggests a radical chain mechanism consisting, after initiation, of the steps shown in Scheme 7.[60] Addition of a methylperoxy radical generates a five-coordinate Pd^{III} intermediate, which results in Pd–Me bond labilization. Although not a metal oxidation in an electrochemical sense, the $MeOO^{\cdot}$ addition indeed corresponds to a formal one-electron oxidation of the metal centre and a labilizing effect on the Pd–Me bond appears plausible.



Scheme 7. Proposed chain mechanism for the autoxidation of $[(bipy)PdMe_2]$.

Besides oxidation, reduction processes have also been shown to result in the activation of M–R homolytic splitting. For instance, whereas [phenylCo(salen)] can be easily reduced by two subsequent reversible one-electron steps to the observable $[PhCo(salen)]^{2-}$ product, [MeCo(salen)] leads to an unstable Co^{II} monoanion, which decomposes by releasing a methyl radical to generate $[Co^I(salen)]^-$.[61]

Reversible Dissociation of Alkyl Radicals – Basis for Organometallic-Mediated Radical Polymerization by Reversible Termination (OMRP-RT)

A reversible metal–carbon bond dissociation process is the basis of OMRP-RT. Because this is a less popular controlled polymerization method than ATRP, we will briefly recall here the thermodynamic/kinetic principles that regulate controlled polymer growth, although these are essentially the same as for ATRP. The reversible termination strategy consists of a temporary deactivation of the growing radical chain by a trapping agent, which transforms it into a dormant species that cannot undergo any chemical transformation other than reactivation. The dormant species is in this case an organometallic $M^{(n+1)}$–R complex in which the polymer chain acts as a σ-bonded one-electron ligand (see Figure 2). The polymerization process can be initiated either from a stable (but labile) organometallic species $M^{(n+1)}$–R or more conveniently from a classical source of radicals in the presence of the reduced complex $M^{(n)}$.

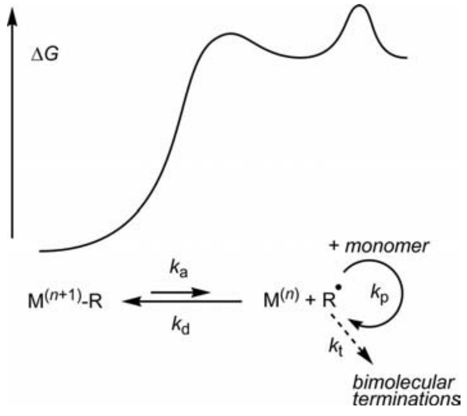
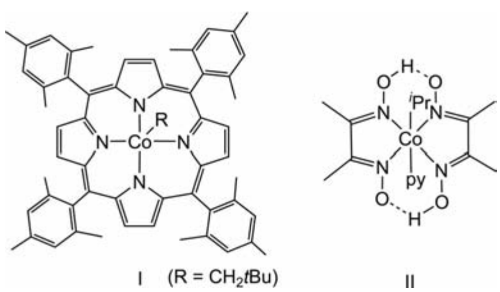


Figure 2. Reversible deactivation of growing radical chains in organometallic-mediated radical polymerization.

Activation yields the reduced metal complex $M^{(n)}$ and the free radical chain, which can add to a monomer and extend the chain according to the propagation rate constant (k_p) or be deactivated by recombining with the reduced metal complex according to the deactivation rate constant (k_d). The reversible deactivation equilibrium ($K_{OMRP-RT} = k_a/k_d$) greatly reduces the concentration of free radicals in solution disfavouring the irreversible bimolecular terminations ($v_t = k_t[R^{\cdot}]^2$) to a greater extent than the chain propagation ($v_p = k_p[R^{\cdot}][monomer]$). For the best results (low polydispersity), however, the system must also rapidly deactivate ($k_d > k_p$) leading to the insertion of ideally no more than one monomer between subsequent activation/deactivation steps. Note that every irreversible termination event removes two dormant macromolecules converting them into two reduced complexes $M^{(n)}$. The resulting $[M^{(n)}]$ increase favours deactivation ($v_d = k_d[R^{\cdot}][M^{(n)}]$). This self-regulation mechanism, valid for all controlled polymerizations operating by reversible deactivation, is well known under the terminology of "persistent radical effect".[62]

The process illustrated in Figure 2 corresponds to the dissociation of an X-type (one-electron) ligand. A dissociation/association cycle, in which a given radical is not necessarily trapped by the same metal complex and a metal complex does not necessarily trap again the same radical, can be thought of as a dissociative one-electron ligand-exchange process (or "monomolecular homolytic substitution", S_H1) and parallels the more common S_N1 process for the exchange of two-electron ligands. The mechanistic study of S_N reactions has the advantage that both free and bonded forms of the exchanged reagent are generally stable species that do not undergo side-reactions. Comparative studies of one-electron ligand-exchange processes are hampered by the instability of the free radical. However, the existence of the persistent radical effect, effectively removing or at least dramatically reducing the importance of bimolecular termination processes under suitable conditions, allows the investigation of thermodynamic and kinetic parameters for equilibria involving radical species. This principle has been applied to the investigation of the ATRP activation/deactivation equilibrium,[63] but can equally be applied to other equilibria involving radicals.

Wayland et al. pioneered the field OMRP-RT and showed that (tetramesitylporphyrin)neopentylcobalt(III) (**I** in Scheme 8) is a thermal initiator for the well-controlled polymerization of methyl acrylate[64] and followed up with a series of related studies.[65] Harwood and co-workers also showed similar results using a cobaloxime system (**II** in Scheme 8), although continuous photochemical activation was necessary in that case to maintain the dynamic equilibrium between the active and dormant radical.[66] The first suggestion of a metal···radical interaction, however, was made by Minoura and co-workers in the polymerization of vinyl monomers carried out in the presence of Cr^{2+}.[67] The best control is generally found for systems that are initiated by a preformed organometallic initiator, $R–M^{(n+1)}$, because the active radical is generated at the same time, in the same place and in equivalent amounts as its own trapping species. Therefore a suitable OMRP-RT equilibrium is established at the very beginning of the process. Initiation by a classical radical source in the presence of the trapping species $M^{(n)}$ takes a longer time (depending on the half-life of the radical source and the temperature) to arrive at the same equilibrium with an initial imbalance of dormant, trapping and free radical species. When the trapping process is not very efficient, greater polydispersities are observed for the resulting polymer. Sufficiently stable and yet thermally labile $R–M^{(n+1)}$ initiators, however, are rare. Examples are **I** in Scheme 8[64] and [CpCr(nacnac)(CH$_2t$Bu)].[68]



I (R = CH$_2t$Bu) II

Scheme 8. Cobalt complexes used in the first reports of OMRP-RT.

Because other commonly used trapping agents are stable free radicals (for example, nitroxides), the name "stable free-radical polymerization" (SFRP) is sometimes used to describe this general family of controlled polymerizations. However, this acronym is not suitable in general for OMRP-RT because the radical trapping ability with the formation of a $M^{(n+1)}–R$ dormant species is not limited to a $S = {}^1/_2$ metal complex (with free-radical character). OMRP-RT trapping has been shown, for example, for diamagnetic Os^{II} complexes (yielding a dormant Os^{III} $S = {}^1/_2$ species),[69] Cr^{II} $S = 2$ complexes (yielding a dormant Cr^{III} $S = {}^3/_2$ species)[16,68,70] and Co^{II} $S = {}^3/_2$ complexes (yielding a dormant diamagnetic Co^{III} species).[4,71]

With respect to other reversible deactivation methods, OMRP-RT has the obvious disadvantage of generating macromolecules that contain a stoichiometric amount of metal as a chain end and then needing metal removal for most applications. Other controlled polymerization techniques yield macromolecules with less harmful (or more useful for post-functionalization) chain ends such as halogens, alkoxylamines and dithioesters. The main problems of cost and toxicity associated with the use of metal complexes are less critical in ATRP in which the metal complex functions as a catalyst. However, a strategy for the recovery and reuse of metal complexes also exists for the OMRP-RT approach, which is based on exchange with a stronger radical-trapping species, such as TEMPO, in a post-functionalization step [Equation (1)].[72]

$$\text{Polymer–M}^{(n+1)} + \text{TEMPO} \rightarrow \text{Polymer–TEMPO} + \text{M}^{(n)} \qquad (1)$$

An advantage of OMRP-RT, on the other hand, is the fine-tuning of the thermally labile bond by the appropriate choice of metal and coordination sphere. The validity of the steric activation concept for the metal–carbon bond in the dormant species has been shown for the polymerization of vinyl acetate by Cr^{II}/Cr^{III}–PVAc[70] and Co^{II}/Co^{III}–PVAc systems [PVAc = poly(vinyl acetate)].[4] Indeed, the PVAc active radical is quite reactive and other controlled polymerization techniques based on the reversible deactivation strategy, including ATRP, have only had limited success. OMRP-RT, on the other hand, has provided the best control reported so far for this monomer (e.g., $M_n > 20000$, $M_w/M_n = 1.05$).[73] In principle, any polymer chain, including those associated with the most reactive radicals, can be imagined to undergo an OMRP-RT process given a suitable metal and coordination sphere that efficiently prevent side-reactions.

Associative Radical Exchange Processes − Basis of Organometallic-Mediated Radical Polymerization by Degenerative Transfer (OMRP-DT)

In the previous section we analysed the dissociative radical exchange (S_H1) process (Figure 2). The same exchange process may also occur by an associative pathway (S_H2). This is possible, however, at two conditions. The first one is that a substantial amount of free radicals is present because the exchange rate is first-order in radical. Contrary to the exchange of stable L ligands, stable high concentrations of reactive radicals are not possible because of bimolecular terminations. Experimental fulfilment of this first condition requires continuous radical injection by activation of a stable radical source, which will clearly be compensated by continuous bimolecular termination events. The second condition, common to associative two-electron processes, is that the coordination sphere must allow the incorporation of an additional one-electron ligand from the electronic and steric points of view.

The S_H2 process is the basis of the so-called "degenerative transfer radical polymerization" (DTRP; see Figure 3). In DTRP there must be continuous injection of new radicals from a stable source, for example, by thermal decomposition of AIBN. The process stops when the radical initiator is completely consumed. The associative exchange swaps active and dormant radicals so that the active one becomes dormant and the dormant one becomes active. The dormant species in this process is also called the "transfer agent" and the exchange is degenerate, hence the name of the process. It is a well-known procedure in controlled radical polymerization with a number of stable organic molecules such as dithioesters, xanthates, alkyl iodides, dialkyltellurium and trialkylbismuth compounds being used as transfer agents.[74]

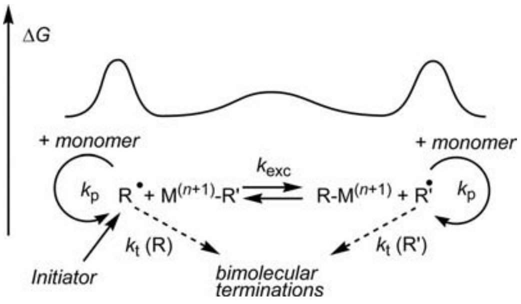
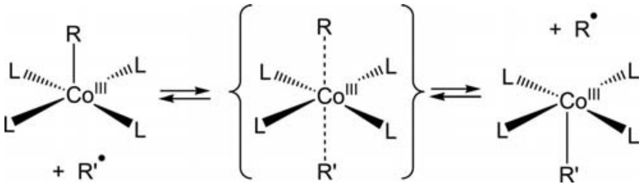


Figure 3. Degenerate transfer polymerization with an organometallic transfer agent.

The technique is effective at controlling the polymer chain growth because the termination rate constant is markedly chain-length dependent. Shorter chains terminate faster than longer ones and the viscosity of the medium (which depends on the degree of conversion) also has an effect on k_t.[75] Thus, whereas the radicals $R^{\cdot}$ (Figure 3) are continuously generated from an initiator and rapidly terminate because their amount is large (like in free-radical polymerization), the associative radical exchange allows the continuous and reversible release of longer radical chains $R'^{\cdot}$, which terminate at a much lower rate $[k_t(R') << k_t(R)]$ and therefore continue to propagate in a pseudo-living manner. Good control, however, is only insured if the rate of exchange ($v_{exc} = k_{exc}[R^{\cdot}][R\text{–}M^{(n+1)}]$) is greater than the rate of propagation ($v_p = k_p[R^{\cdot}][\text{monomer}]$).[76]

Organometallic-mediated radical polymerization by degenerate transfer (OMRP-DT) was first proposed as a controlled radical polymerization mechanism by Wayland and co-workers for methyl acrylate polymerization mediated by the same alkylcobalt(III)–porphyrin systems previously used in OMRP-RT (**I** in Scheme 8) in the presence of excess radicals.[77] This compound has a square-pyramidal arrangement with an apical R ligand and a vacant coordination site. Therefore an associative radical exchange is quite possible, which illustrates the second principle alluded to above. DFT calculations support the occurrence of a three-centre-three-electron transition state (S_H2 mechanism) for the exchange without any local minimum for a putative dialkylcobalt(IV) intermediate (see Scheme 9) and with a low activation free energy.[78]



Scheme 9. Associative radical exchange for a square-pyramidal 16-electron d^6 alkylcobalt(III) complex.

The above studies were preceded by a report by Jérôme and co-workers on controlled VAc polymerization using $[Co(acac)_2]$ as controlling agent and V-70 (a thermally labile diazo compound with $t_{1/2}$ = 10 h at 30 °C) as initiator.[79] This process was initially interpreted on the basis of a dissociative mechanism but later proven to follow an OMRP-DT pathway.[71a] More interestingly, it was shown that either OMRP-DT or OMRP-RT occurs with this system depending on the presence of neutral ligands. This conclusion was based on the results shown in Figure 4 and interpreted on the basis of Scheme 10 as follows.[71a]

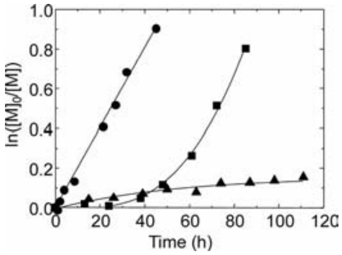
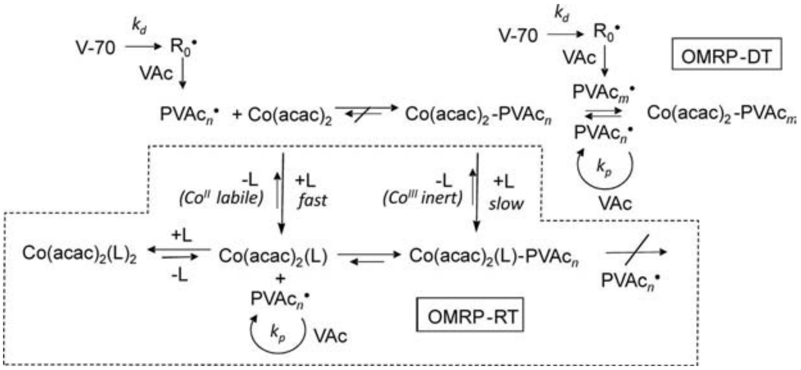
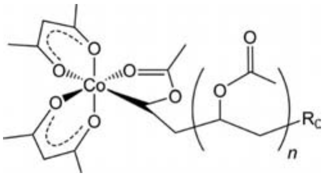


Figure 4. Kinetics of the $[Co(acac)_2]$-mediated radical polymerization of VAc in the absence (■) or presence of Lewis bases L (30 equiv.): L = py (●), NEt_3 (▲). Conditions: $[VAc]_0/[Co(acac)_2]_0/[V\text{-}70]_0/[L]_0$ = 500:1:1:30; bulk polymerization, 30 °C. Reproduced from ref.[71a] with permission.

Homolytic cleavage of the Co–C bond in the dormant species requires too much energy; radical trapping is irreversible. Therefore in the absence of Lewis bases, the short PVAc chains generated from the primary radicals are immediately quenched and no polymerization occurs, which explains the induction period (see Figure 4). After complete conversion of $[Co(acac)_2]$ to dormant $[(acac)_2Co\text{–}PVAc]$ with short oligomer chains, additional radicals trigger the rapid consumption of monomer by OMRP-DT with $[(acac)_2Co\text{–}PVAc]$ now playing the role of transfer agent. When a Lewis base is present, on the other hand, this adds to the dormant Co^{III} species and to $[Co(acac)_2]$ to generate a six-coordinate $[(acac)_2(L)Co\text{–}PVAc]$ chain end and a six-coordinate $[Co(acac)_2(L)_2]$. Because the Co^{II} state is stabilized to a greater extent than the Co^{III} state, homolytic Co–PVAc cleavage from $[(acac)_2(L)Co\text{–}PVAc]$ is activated, favouring OMRP-RT. This is in agreement with the absence of



Scheme 10. Mechanism for the [$Co(acac)_2$]-mediated OMRP of VAc.



Scheme 11. Nature of the chain end in the [$Co(acac)_2$]-mediated OMRP of VAc. R_0 is the primary radical originating from the initiator.

an induction period in this case (see Figure 4). Furthermore, whereas d^7 Co^{II} is kinetically labile, low-spin d^6 Co^{III} is inert. Therefore the new dormant [$(acac)_2(L)Co$–PVAc] can no longer operate as transfer agent and any radical associative exchange is shut down; OMRP-DT can no longer take place.[71a] The polymerization is equally well controlled under both OMRP-DT and OMRP-RT conditions. This example clearly illustrates the importance of coordination chemistry in metal-mediated controlled radical polymerization.

As can be appreciated from Figure 4, the rate of polymerization depends on the nature of L (faster with pyridine than with NEt_3). This is because ligand binding changes the relative energy of the Co^{II} and Co^{III} species and therefore the position of the OMRP-RT equilibrium. The relative polymerization rates for the VAc/[$Co(acac)_2$] systems in the presence of a variety of ligands (DMF, DMSO, water) were studied and the results rationalized on the basis of Scheme 10, with validation by DFT calculations.[73] Ligand coordination was also critical for the successful switch from a PVAc chain to a PAN chain, allowing growth of well-controlled diblock PVAc-*b*-PAN copolymers using [$(acac)_2$-Co–PVAc] as a macroinitiator.[71c]

Attempts to generate a suitable organometallic initiator/transfer agent of type [$(acac)_2(L)Co$–R] or [$(acac)_2Co$–R] have not met with success.[80] In contrast to complexes with N-based coordination spheres, no examples of alkylcobalt(III) complexes with a fully oxygen-based coordination sphere have been described so far. However, a mixture of [$Co(acac)_2$]-capped short oligomers with the structure shown in Scheme 11 (average $n \approx 4$) could be generated, isolated and characterized, by carrying out the OMRP-RT with a small amount of monomer and a large amount of [$Co(acac)_2$].[71b] This material is an excellent OMRP-RT initiator for the generation of a number of polymers.[71c,73,81]

Given the chelated structure of [$(acac)_2Co$–PVAc] and the known inertness of six-coordinate Co^{III}, an associative exchange should also be blocked for this compound. The fact that, contrary to this expectation, an associative exchange occurs may be related to the weakness of the chelation mode (the DFT calculations indicate an enthalpic stabilization by only 3 kcal mol^{-1}), perhaps with distortion of the structure away from octahedral and towards square pyramidal, and a consequent facile attack by the radical at the position *trans* to the alkyl group.

Analysis of the electronic structure of the square-pyramidal arrangement of **I** in Scheme 8 helps to explain why the S_H2 reaction is facile. The d_{z^2} orbital is empty for low-spin d^6 Co^{III}, which facilitates radical attack and electron redistribution from one Co–R bond to the other through the metal $sp_zd_{z^2}$ orbital mixing in the transition state. An analogous associative exchange can be predicted for other electronic configurations within this particular coordination geometry. Indeed, we have recently discovered that an OMRP-DT of VAc may also be mediated by [$Fe(acac)_2$], although with a poorer control, which indicates a lower exchange rate.[82] This appears to be the first example of associative radical exchange for a metal other than cobalt, but others will undoubtedly be discovered in the future.

Exchange between Two-Electron and One-Electron Ligands

We address in this section the direct exchange between one- and two-electron ligands [process (c) in Scheme 1]. This process can also be imagined to proceed by the two limiting mechanisms, associative or dissociative. It is possible to imagine a system in which the R–$M^{(n+1)}$ bond is weak (facile dissociation) and the resulting $M^{(n)}$ also forms a weak bond with L. If, in addition, $M^{(n)}$ has small barriers for both $R^{\cdot}$ and L additions (bond lability), as shown in the free-energy diagram of Figure 5 (left), then an associative exchange will hardly provide a kinetic advantage to the system. Conversely, for the opposite extreme case of strong R–$M^{(n+1)}$ and $M^{(n)}$–L bonds, it is possible to predict that a direct associative exchange through a three-centre-four-electron R···M···L transition state may be favoured, as shown in Figure 5 (right). To the best of our knowledge, the second situation has not so far been described for experimentally investigated systems and therefore remains only hypothetical.

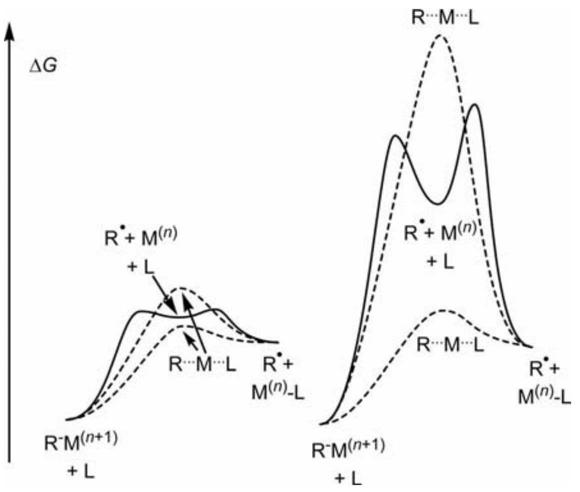


Figure 5. Ideal pathways for the replacement of a one-electron ligand with a two-electron ligand. The plain curves describe the ideal dissociative pathway and the dashed curves associative pathways. Left: the case of a weak R–$M^{(n+1)}$ bond and labile $M^{(n)}$–L bond. Right: the case of a strong R–$M^{(n+1)}$ bond and inert $M^{(n)}$–L bond.

The system presented in the previous section, in which a Lewis base affects the [Co(acac)$_2$]-mediated OMRP-RT or VAc, is an example of the first type because the PVAc–Co^{III} bonds in the dormant [(acac)$_2$(L)Co–PVAc] species are easily thermally activated and the Co^{II}–L bonds are weak and labile.[71d] ^{1}H NMR analysis shows very rapid exchange of the free and coordinated L by paramagnetic line-broadening methods, which confirms the labile character of d^7 Co^{II} in an octahedral geometry. For the reaction in the opposite direction, the starting [(acac)$_2$(L)Co–PVAc] compound is coordinatively saturated and substitutionally inert. Hence, it is unlikely that the PVAc dissociation is pushed by the entering ligand L. A certain degree of dissociative interchange character (I_d), however, seems possible.

The above example illustrates a reversible one-electron/two-electron ligand exchange. There is also at least one example of an irreversible one-electron/two-electron ligand exchange. Compound [Cp*Cr(L)(CH$_2$Ph)$_2$] (L = THF or py) is thermally stable. Whether it reversibly dissociates a benzyl radical to sustain an OMRP-RT process has apparently not been investigated. However, treatment with bipyridine promotes homolytic scission of one Cr–CH$_2$Ph bond and the formation of [Cp*Cr(bipy)(CH$_2$Ph)] with the presumed release of one benzyl radical.[83] The mechanism for this process has not been scrutinized, but it seems likely that it is initiated by the substitution of L to yield a 15-electron [Cp*Cr(κ^1-bipy)(CH$_2$Ph)$_2$] complex in which the bipy ligand is bonded in a monodentate fashion. Rearrangement to a bidentate coordination mode to yield a 17-electron intermediate requires a spin-pairing process that is known to be rather costly for Cr^{III}.[15,84] Hence, it is more likely that the second step entails dissociation of one benzyl radical followed by coordination of the second bipy nitrogen donor atom.

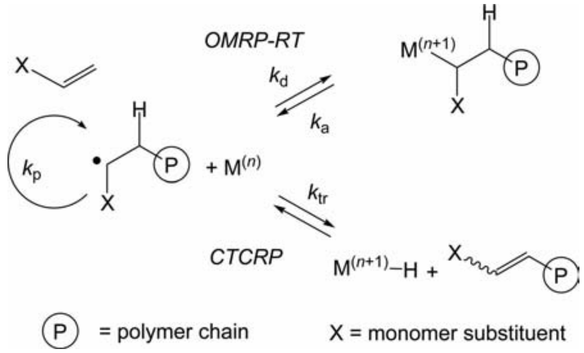
The numerous radical additions to aqua ions mentioned in a previous section are examples of processes in which a two-electron ligand is replaced by a one-electron ligand because the coordination sphere of the metal ions in aqueous solution is certainly saturated by aqua ligands. Again, these probably occur by addition to the unsaturated $[M(H_2O)_5]^{n+}$ species in rapid equilibrium with $[M(H_2O)_6]^{n+}$. A kinetic study of the reverse homolysis process for a series of $[(H_2O)_5Cr–R]^{2+}$ shows activation enthalpies and entropies consistent with a pure S_H1 mechanism.[85]

β-H Transfer Processes

The ability of transition-metal compounds, mostly having radical character, to abstract hydrogen atoms from organic radicals has been appreciated since the 1970s. For instance, [Pt^{II}(H)I(PEt$_3$)$_2$] is a byproduct of the oxidative addition of *i*PrI to Pt(PEt$_3$)$_3$, which takes place by a radical pathway by I$^·$ transfer with the generation of the (PEt$_3$)$_3$Pt^{I}I and *i*Pr$^·$ radicals.[86] Several Co^{II} complexes, of the same type as those discussed in previous sections as OMRP-RT trapping species, are efficient catalysts in CTCRP.[87] This process occurs by transfer of a hydrogen atom from the growing radical chain to $M^{(n)}$ to form a hydride complex $M^{(n+1)}$–H and a dead polymer chain with an unsaturated chain end. Reversal of this step with a new monomer yields back to $M^{(n)}$ and a new radical, which starts a new chain. The catalytic efficiency is measured by the k_{tr}/k_p ratio, also known as transfer constant.

The presence of CTCRP can be experimentally assessed rather easily from the polymer average molecular weight. For a pure OMRP-RT process (absence of chain transfer) only one macromolecule is generated by each initiator, therefore the average molecular weight can be predicted exactly from the molar monomer/initiator ratio and from the conversion. In the presence of chain transfer to monomer, more chains are produced and the average molecular weight therefore decreases. Metal-mediated radical polymerizations in which the molecular weight indicates the presence of CTCRP, for example, are those of acrylonitrile initiated by [Co(NN)$_2$(CH$_2$Ph)$_2$]$^+$ (NN = bipy, phen, Me$_2$phen)[88] and the isoelectronic [Fe(bipy)$_2$Et$_2$].[89]

As discussed in a previous section, the β-H transfer and OMRP-RT trapping processes [processes (e) and (b) in Scheme 1] have the same molecularity and hence the same first-order dependence on the metal complex and on the radical chain (see Scheme 12). Thus, their competition is not affected by concentration. It is affected, on the other hand, by the relative barriers of the two processes, k_d and k_{tr}, which depend on the nature of the metal, on its coordination sphere and on the nature of the radical chain. For the Co^{II} catalysts, both steps have been shown to occur at or close to diffusion-controlled rates, which indicates that the activation energies are extremely low.[90] When OMRP-RT is sought, the intervention of any amount of CTCRP is unwanted, whereas when CTCRP is the desired process, the intervention of reversible OMRP-RT trapping only has the effect of slowing down the polymerization but does not affect the catalyst ability to moderate the polymer molecular weight. For less active catalysts such as porphyrin derivatives, a significant isotope effect k_H/k_D of 3.5 for the $H^{\cdot}$ transfer process was observed, which suggests a direct hydrogen atom transfer.[91] This conclusion may not be general for all chain transfer catalysts, however, because a process involving direct β-H elimination from an OMRP-RT dormant species (giving the same hydride complex and dead polymer chain as products) has been suggested instead for a $FeCl_2$(diimine)-mediated polymerization.[92]



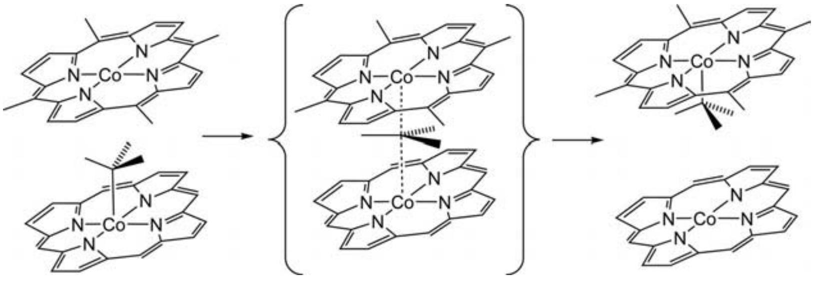
Scheme 12. Competitive OMRP-RT trapping and β-H atom transfer for a $M^{(n)}/L_x$ chain-carrying radical pair.

Co^{II} complexes with macrocyclic ligands are arguably the most developed family of chain-transfer catalysts. Empirical rules for the catalytic activity of this family have been offered, such as the crucial importance of a core of four nitrogen atoms, macrocycle planarity, π conjugation in the macrocyclic ligand and steric effects, and the moderate electronic effect of equatorial ligand substituents.[90] However, how the CTCRP/OMRP-RT interplay depends on molecular parameters is far from being clear in a general case. Most investigations related to $H^{\cdot}$ abstractions from growing polymer chains have been carried out on Co^{II} systems, particularly porphyrin complexes[78,93] and cobaloximes.[90,94] Studies of the reverse $H^{\cdot}$ atom transfer to olefins have also been carried out, particularly with $[(C_5R_5)Cr(CO)_3H]$ (R = H, Me, Ph) complexes that have weak Cr–H bonds.[95] This step is also involved in the catalysed hydrogenation of olefin substrates by certain monohydride complexes such as $[HCo(CO)_4]$,[96] $[HMn(CO)_5]$[97] and $[CpMH(CO)_3]$ (M = Mo or W),[98] which take place by a radical mechanism.[3a]

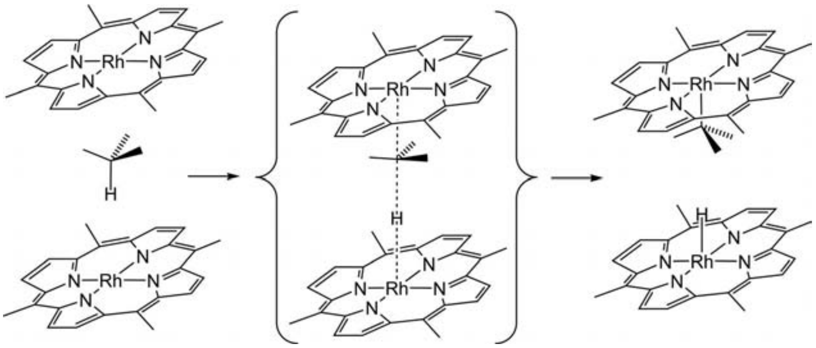
Alkyl Group Transfer Processes

We address here process (f) in Scheme 1, namely the transfer of an alkyl group from an organometallic compound to a radical acceptor. A number of alkylcobalt(III) complexes supported by macrocyclic ligands have been shown to directly transfer the alkyl group to aqueous Cr^{2+}[99] or to a cobalt(II) complex of a distinguishable macrocycle as an acceptor.[100] An S_H2 mechanism without the involvement of free radicals, as shown in Scheme 13, is suggested by a number of observations, such as a rate higher than predicted on the basis of the known Co–C bond dissociation energies, equal efficiency when the process is conducted in the absence of light or in the presence of radical traps, and by the fact that the absolute configuration at the carbon is inverted. The porphyrin systems are axial base-free, therefore no coordination/decoordination interferes with the process. Methyl, benzyl, primary and secondary alkyl, and acyl groups exchange, but phenyl groups do not. In agreement with this mechanism, the use of sterically encumbered cobalt–porphyrins with groups large enough to prevent the formation of a bridged Co–C–Co structure resulted in a dramatic decrease in the exchange rate.[100e] This mechanism is related, by swapping the position of the metal and radical partners, to the associative radical exchange shown in Scheme 9. It may also be related to Taube's X-bridged ISET process[9] involving two metal complexes (Scheme 3), but in this case it is a carbon-bridged group transfer process and does not involve preliminary coordination (three-centre-three-electron rather than three-centre-five-electron).

Alkyl group transfers between two metals that follow an S_H2 mechanism are less frequent than the corresponding two-electron version (S_N2). There are also examples of dissociative radical transfers, sometimes associated with electron transfer. For example, methyl transfer from $[MeCo^{III}(dmgBF_2)py]$ to $Ni^I(tmc)^+$ occurs by an initial outer-sphere electron transfer from Ni^I to Co^{III}, Co–C bond homolysis of the resulting anionic methylcobalt(II) complex and



Scheme 13. S_H2 mechanism for alkyl transfer between Co–porphyrin derivatives.



Scheme 14. Termolecular one-electron C–H oxidative addition to a Rh^{II}–porphyrin complex.

methyl radical addition to a second $Ni^{I}(tmc)^{+}$ molecule.[101] Transfer from an alkyliron(III)–porphyrin to an iron(II)–porphyrin, on the other hand, has been reported to occur by an S_H1 mechanism via the free radical.[102]

Processes involving an alkyl transfer from a metal to another accepting group, or vice versa, can also occur. Certain R–Co^{III} complexes have been shown to undergo highly specific carbon–carbon bond formation upon addition of radicals $R'^{\cdot}$.[103] The mechanism of this reaction was suggested to involve radical addition (either to the metal or to the ligand) followed by elimination of the R–R′ product rather than direct S_H2, on the basis of the similar rates observed for sterically very different R groups, Me and *i*Pr.[104] However, the S_H2 transition state in the porphyrin system of Scheme 13 was shown to be rather insensitive to the steric bulk of the R group and it was therefore suggested that the S_H2 pathway for this carbon–carbon bond formation should be reconsidered.[100e] A better understanding of this process in relationship with cobalt-mediated radical polymerizations is desirable. Indeed, cobalt complexes have been shown to support controlled polymerizations by the associative exchange (OMRP-DT) process, which has the same molecularity as the present transfer of an alkyl group [$M^{(n+1)}$–R + $R^{\cdot}$]. An alkyl transfer from an alkylcobalt(III) to an external radical represents a metal-mediated termination reaction. Therefore it is important to understand what factors facilitate or disfavour this group transfer compared with the associative radical exchange of interest for controlled chain growth.

Finally, a remarkable reaction leading to the transfer of an alkyl group to a metal centre, namely the reverse of process (f) in Scheme 1, is the peculiar one-electron C–H oxidative addition reported by Wayland and co-workers for a variety of Rh^{II}–porphyrin systems. The process occurs by the concomitant action of two metal complexes in a four-centre-four-electron process with a linear transition state, as shown in Scheme 14. The reaction is selective for aliphatic C–H bonds and totally excludes aromatic C–H bond activation.[105] Methanol reacts more favourably by addition of the C–H bond than the O–H bond. Use of a "packman" system, in which two Rh^{II}–porphyrin complexes are tied together by a *m*-xylyldioxy tether, results in great rate enhancements relative to the termolecular system.[106]

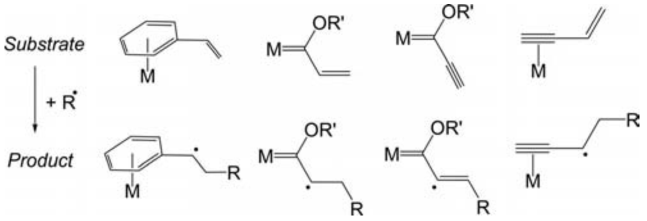
This process can be compared with the one-electron oxidative additions of other R–X substrates (X = halogen) discussed at the beginning of this microreview (e.g., Scheme 5), but unlike them it cannot take place in a stepwise manner. For X = halogen, the $M^{(n+1)}$–X bond alone is sufficient to nearly compensate the cost of breaking the R–X bond. In the present case, the R–H bond to be broken is much stronger and a single metal complex is not sufficient to make the stepwise process feasible. The synchronized action of two metal complexes for simultaneous formation of two bonds (the Rh^{III}–H and Rh^{III}–R bonds) is necessary to provide a low-energy pathway.

Radical Addition to Ligands

A radical may also lead to a bond being established with an existing ligand and to being incorporated into it without dissociation of the newly formed ligand rather than abstracting the ligand or binding to the metal, that is, processes (g) and (h) of Scheme 1. The addition to a halide ligand resulting in a coordinated alkyl halide has already been addressed in a previous section and will not be further commented upon.

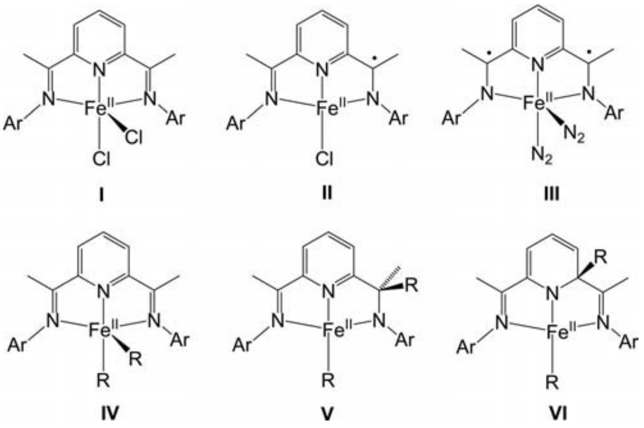
Most studies have involved the addition of radicals to unsaturated ligands. Coordination of an unsaturated substrate to a metal is expected to modify its reactivity towards free radicals as much as it does towards nucleophilic and electrophilic reagents, but there is still a much more limited understanding of how coordination affects the activation and thermodynamic parameters for the reaction with radicals relative to other types of reagents. When the added radical has nucleophilic character, as for an unstabilized alkyl radical, the reaction is usually promoted because coordination exalts the electrophilic character of the unsaturated substrate. For example, the ketyl radical $I_2Sm–OCMe_2^{\cdot}$ generated from acetone has been shown to add to the benzene ligand of $[(C_6H_6)Cr(CO)_3]$ more than 10^5 times faster than to uncomplexed benzene.[107] Radical additions to π-bonded aromatic rings have mostly been studied for 18-electron complexes, to arene ligands as in $[(arene)Cr(CO)_3]$,[107,108] $[(arene)Mn(CO)_3]^{+}$[109] and $[(C_6H_6)_2Cr]$,[110] but also to the cyclopentadienyl ligand in ferrocene.[111] Addition to Cp in 19-electron [Cp_2Co] leads to stable 18-electron [$CpCo(C_5H_5R)$] products.[112] Radical addition to Cp_2Ti^{III}-coordinated η^3-allyl or η^3-propargyl groups occurs selectively at the 2-position, transforming the three-electron XL-type allyl into a four-electron X_2-type ligand in the titanacyclobutane or -cyclobutene products.[113] Radical addition to Pd^{II}–allyl complexes, on the other hand, appears to take place at the metal centre, although some of the final products result from allyl–alkyl coupling.[34b,34c,35]

Evidence for radical addition to coordinated CO was invoked by Boese and Goldman to account for the observed activity of some alkane photocatalytic carbonylation systems mediated by d^8 metal–carbonyl complexes.[114] A theoretical study of $Me^{\bullet}$ addition to [$RhCl(CO)(PMe_3)_2$] shows that the radical adds to the CO ligand more favourably than to the metal, both processes being essentially barrierless, but the addition is thermodynamically less favourable than to free CO.[115] For analogous additions to CO ligands in 18-electron complexes, on the other hand, the barrier is greater relative to the addition to free CO.[116] Radicals also appear to react selectively with unsaturations that are conjugated to coordinated ligands because of the additional stabilization enjoyed by the product radical. This is the case for styrene,[108b,117] α,β-unsaturated Fischer carbenes[118] and enynes[119] (see Scheme 15).



Scheme 15. Radical addition to unsaturations conjugated to metal-coordinated groups.

Another ligand system that merits discussion is diiminopyridine (dip), made popular by the discovery of the catalytic activity of its iron and cobalt complexes in ethylene polymerization and by its "non-innocent" behaviour.[120] Although the direct addition of radicals to dip complexes of Fe and Co does not appear to have been described, such a reactivity mode is suggested by the demonstrated ligand spin density in complexes [(dip)FeCl] and [(dip)Fe(N_2)$_2$] (**II** and **III** in Scheme 16). These are best described as complexes of Fe^{II} with mono- and diradical ligands rather than as Fe^I and Fe^0 complexes with a neutral dip ligand (Ar = 2,6-$i$$Pr_2C_6H_3$).[120] Radical reactivity has indeed been proposed for reactions such as the one-electron oxidative addition of RX substrates to [(dip)Fe(N_2)$_2$], for which a putative [(dip)Fe(X)(R)] intermediate would undergo Fe–R bond homolysis and recapture by a second Fe complex to yield the observed [(dip)FeX] and [(dip)FeR] products.[121] The alkylation of **I** [or a mixture of $FeCl_2(thf)_2$ and dip] with $LiCH_2SiMe_3$ under a variety of conditions has led to the isolation and characterization of the expected **IV**, but also **V** and **VI**.[122] It appears possible that **V** and **VI** result from a SET process, which generates a free radical and [(dip)FeR] (which was independently obtained by alkylation of **II**[123]), followed by radical addition to the ligand. Interestingly, it was shown that **V** transforms into **IV**, whereas **VI** does not, but a mechanism for this rearrangement was not proposed. An intriguing possibility is that the radical addition to the imine C atom is reversible, although kinetically preferred.

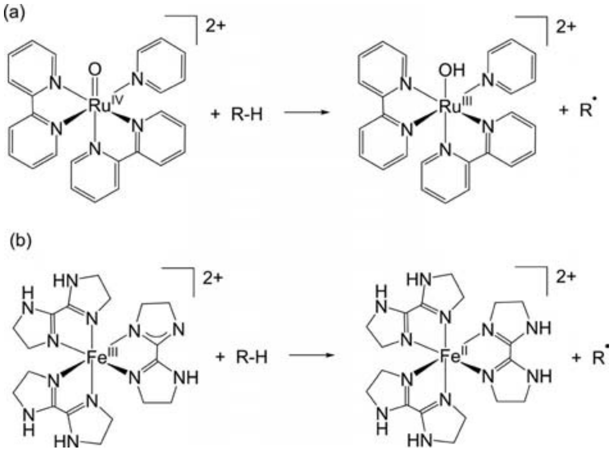


Scheme 16. Fe^{II} complexes with the "non-innocent" dip ligand (**I**–**IV**) and the products of ligand alkylation (**V** and **VI**).

Alkenes are ligands of particular interest because they are at the same time monomers for the radical polymerization process. Therefore, rather than harmful to the metal action as polymerization mediator, an enhanced reactivity towards radical addition for coordinated monomers could be exploited (especially for ethylene and higher olefins that have low propagation rate constants) if combined with weak $M^{(n+1)}$–R bonds in an OMRP-RT approach. Michl and co-workers reported a puzzling activity of naked Li^+ in the activation of olefins towards free-radical polymerization[124] that is consistent with olefin activation upon interaction with the strongly Lewis acidic Li^+.[125] No experimental studies appear to be available for the effect of coordination to a transition metal, but this process was analysed by using DFT calculations for the addition of $Me^{\bullet}$ to the two model propene complexes [(κ^3-pcp)Rh(C_3H_6)] of d^8 Rh^I [pcp = 1,3-$C_6H_3(CH_2PMe_2)_2$] and [$Cp_2Zr(OtBu)(C_3H_6)$]$^+$ of d^0 Zr^{IV}.[126] For the Rh system, the addition is thermodynamically favoured, but kinetically disfavoured relative to free propene, with a kinetic regioselectivity for the terminal C atom (as in free propene). For the Zr system, on the other hand, the addition is kinetically more facile and favours the substituted C atom leading to the primary isobutyl radical, which remains loosely bound to the Zr^{IV} [$Cp_2Zr(OtBu)$]$^+$ fragment. These effects were explained by the asymmetric coordination mode that places Zr closer to CH_2 than to CHMe and polarizes the coordinated olefin with a greater positive charge on CHMe and by an attractive ion-induced dipole force along the potential energy surface due to the positive charge of the metal ion. Therefore these studies seem to confirm alkene activation towards radical addition by highly Lewis acidic metals.

Hydrogen Atom Transfer Involving a Ligand

In this final section we briefly comment on hydrogen atom transfer to and from a ligand, transforming the nature of the latter. As mentioned in the general discussion on reaction types, this can involve L- or X-type ligands, processes (i) and (j) in Scheme 1. When a hydrogen atom is abstracted from an X-type ligand, it may become either L type, reducing the metal with formal ligand oxidation, or X_2 type, with metal oxidation. The latter situation (for the reverse process) occurs in the common one-electron C–H activation of saturated hydrocarbons by transition-metal oxido complexes, for example, $[(bipy)_2(py)Ru^{IV}O]^{2+}$ (Scheme 17, a).[127] Hydrocarbon oxidation by cytochrome P450 is another example of this situation. An example of process (i) is the C–H activation by $[Fe^{III}(H_2bim)_2(Hbim)]^{2+}$, which yields $[Fe^{II}(H_2bim)_3]^{2+}$ (H_2bim = bi-imidazoline; see Scheme 17, b).[128] Many of these reactions can be considered as standard hydrogen atom transfer reactions involving radicals, the only difference being that the hydrogen-atom donor (or the acceptor in the reverse process) is activated by metal coordination. Excellent coverage of these processes, which find most of their relevance in biotic alkane oxidation processes, may be found in recent reviews.[129] A situation in which a process of this type has the necessary level of reversibility to moderate a radical polymerization process has not yet been described to the best of our knowledge. Conversely, irreversible hydrogen atom transfer from ligands to growing radical chains has been invoked as a reason for the loss of control through unwanted termination processes, for example, in the ATRP of *n*-butyl acrylate catalysed by copper complexes with pentamethyldiethylenetriamine (PMDETA).[130]



Scheme 17. Hydrogen atom transfer (HAT) processes involving organic radicals and ligands.

Conclusions

The coordination chemistry of radicals is very rich. Radicals can react with transition-metal complexes in many different ways, as outlined in the various sections of this microreview, and the type of reaction has a profound influence on how the metal complex can mediate other radical processes, particularly alkene radical polymerization. This area has started to attract considerable attention, not only because of new reactivity patterns in organic syntheses and its relevance to biology, but also and especially because of the explosion of research in metal-mediated radical polymerizations. However, many questions still need to be answered. A deeper understanding of the parameters regulating the relative barriers of radical addition and β-H group transfer to a metal centre would be desirable. The competition between associative radical exchange and metal-mediated termination processes is currently not understood. Metal complexes that allow reversible metal–carbon bond formation with the most reactive radicals, controlling the polymerization of the associated monomers, still do not exist. Learning how to activate radical addition to a monomer in the presence of a reversible trapping mechanism would open the way to currently unachieved controlled polymerizations of unreactive monomers. Efficient ways to recover and recycle a metal complex from an OMRP dormant chain is a great practical challenge. Engineering a perfect coordination sphere, channelling the radical reactivity to the desired process (particularly for the more reactive radicals), requires a better understanding of ligand radical reactivity. All these questions and challenges, related to an area of booming research activity in the polymer community and of great academic and industrial interest, will certainly give rise to intense research work in the years to come.

Acknowledgments

The author is grateful to the Centre National de la Recherche Scientifique (CNRS), the Institut Universitaire de France, and the Agence National de la Recherche (ANR) (grant number 2010 BLANC 7101) for financial support.

---

[1] a) J. Iqbal, B. Bhatia, N. K. Nayyar, *Chem. Rev.* **1994**, *94*, 519–564; b) F. Csende, G. Stajer, *Curr. Org. Chem.* **2005**, *9*, 1737–1755; c) J. J. Eisch, A. A. Adeosun, S. Dutta, P. O. Fregene, *Eur. J. Org. Chem.* **2005**, 2657–2670; d) M. C. Juan, J. Justicia, J. L. Oller-Loopez, J. E. Oltra, *Top. Curr. Chem.* **2006**, *264*, 63–91.

[2] K. E. Torraca, L. McElwee-White, *Coord. Chem. Rev.* **2000**, *206*, 469–491.

[3] a) J. Halpern, *Pure Appl. Chem.* **1986**, *58*, 575–584; b) J. I. Toohey, *Biofactors* **2006**, *26*, 45–57; c) A. Levina, A. Mitra, P. A. Lay, *Metallomics* **2009**, *1*, 458–470; d) S. Y. Reece, D. G. Nocera, *Annu. Rev. Biochem.* **2009**, *78*, 673–699; e) U. Schatzschneider, *Eur. J. Inorg. Chem.* **2010**, 1451–1467.

[4] K. S. Santhosh Kumar, Y. Gnanou, Y. Champouret, J.-C. Daran, R. Poli, *Chem. Eur. J.* **2009**, *15*, 4874–4885.

[5] E. Le Grognec, J. Claverie, R. Poli, *J. Am. Chem. Soc.* **2001**, *123*, 9513–9524.

[6] a) R. Poli, *Angew. Chem.* **2006**, *118*, 5180; *Angew. Chem. Int. Ed.* **2006**, *45*, 5058–5070; b) R. Poli, in: *Comprehensive Polymer Science*, vol. 3 (Eds.: G. W. Coates, M. Sawamoto), Elsevier, Amsterdam, manuscript submitted; c) K. M. Smith, W. S. McNeil, A. S. Abd-El-Aziz, *Macromol. Chem. Phys.* **2010**, *211*, 10–16.

[7] F. Basolo in *Advances Chemistry Series*, vol. 49 (Ed.: R. F. Gould), American Chemical Society, Washington, DC, **1965**.

[8] a) M. Kamigaito, T. Ando, M. Sawamoto, *Chem. Rev.* **2001**, *101*, 3689–3745; b) K. Matyjaszewski, J. H. Xia, *Chem. Rev.* **2001**, *101*, 2921–2990; c) M. Ouchi, T. Terashima, M. Sawamoto, *Acc. Chem. Res.* **2008**, *41*, 1120–1132; d) T. Pintauer, K. Matyjaszewski, *Chem. Soc. Rev.* **2008**, *37*, 1087–1097; e) M. Ouchi, T. Terashima, M. Sawamoto, *Chem. Rev.* **2009**, *109*, 4963–5050; f) F. di Lena, K. Matyjaszewski, *Prog. Polym. Sci.* **2010**, *35*, 959–1021.

[9] H. Taube, H. Myers, R. L. Rich, *J. Am. Chem. Soc.* **1953**, *75*, 4118–4119.

[10] a) A. Cardinale, A. A. Isse, A. Gennaro, M. Robert, J. M. Savéant, *J. Am. Chem. Soc.* **2002**, *124*, 13533–13539; b) C. Y. Lin, M. L. Coote, A. Gennaro, K. Matyjaszewski, *J. Am. Chem. Soc.* **2008**, *130*, 12762–12774.

[11] J. C. Walton, *Acc. Chem. Res.* **1998**, *31*, 99–107.

[12] R. Poli, F. Stoffelbach, S. Maria, J. Mata, *Chem. Eur. J.* **2005**, *11*, 2537–2548.

[13] M. Kato, M. Kamigaito, M. Sawamoto, T. Higashimura, *Macromolecules* **1995**, *28*, 1721–1723.

[14] S. Maria, F. Stoffelbach, J. Mata, J.-C. Daran, P. Richard, R. Poli, *J. Am. Chem. Soc.* **2005**, *127*, 5946–5956.

[15] I. Cacelli, D. W. Keogh, R. Poli, A. Rizzo, *J. Phys. Chem. A* **1997**, *101*, 9801–9812.

[16] Y. Champouret, K. C. MacLeod, K. M. Smith, R. Poli, *Organometallics* **2010**, *29*, 3125–3132.

[17] A. Masarwa, S. Rachmilovich-Calis, N. Meyerstein, D. Meyerstein, *Coord. Chem. Rev.* **2005**, *249*, 1937–1943.

[18] J. Halpern, *Acc. Chem. Res.* **1970**, *3*, 386–392.

[19] P. B. Chock, J. Halpern, *J. Am. Chem. Soc.* **1969**, *91*, 582–588.

[20] P. R. Carter, N. Davidson, *J. Phys. Chem.* **1952**, *56*, 877–881.

[21] a) J. R. Chipperfield, J. Ford, A. C. Hayter, D. E. Webster, *J. Chem. Soc., Dalton Trans.* **1976**, 360–366; b) G. Kramer, J. Patterson, A. Poe, *J. Chem. Soc., Dalton Trans.* **1979**, 1165–1171; c) G. Kramer, J. Patterson, A. Poe, L. Ng, *Inorg. Chem.* **1980**, *19*, 1161–1169.

[22] M. S. Kharasch, E. V. Jensen, W. H. Urry, *Science* **1945**, *102*, 128–128.

[23] L. Quebatte, K. Thommes, K. Severin, *J. Am. Chem. Soc.* **2006**, *128*, 7440–7441.

[24] a) T. Pintauer, *Eur. J. Inorg. Chem.* **2010**, 2449–2460; b) W. T. Eckenhoff, T. Pintauer, *Catal. Rev. Sci. Eng.* **2010**, *52*, 1–59.

[25] F. A. L. Anet, E. Leblanc, *J. Am. Chem. Soc.* **1957**, *79*, 2649–2650.

[26] C. E. Castro, W. C. Kray, *J. Am. Chem. Soc.* **1963**, *85*, 2768–2773.

[27] A. Rotman, H. Cohen, D. Meyerstein, *Inorg. Chem.* **1985**, *24*, 4158–4164.

[28] H. Cohen, D. Meyerstein, *Inorg. Chem.* **1988**, *27*, 3429–3431.

[29] a) Y. Sorek, H. Cohen, D. Meyerstein, *J. Chem. Soc. Faraday Trans. 1* **1985**, *81*, 233–239; b) Y. Sorek, H. Cohen, D. Meyerstein, *J. Chem. Soc. Faraday Trans. 1* **1986**, *82*, 3431–3438.

[30] A. Sauer, H. Cohen, D. Meyerstein, *Inorg. Chem.* **1988**, *27*, 4578–4581.

[31] T. Kurzion-Zilbermann, A. Masarwa, E. Maimon, H. Cohen, D. Meyerstein, *Dalton Trans.* **2007**, 3959–3965.

[32] a) M. Freiberg, W. A. Mulac, K. H. Schmidt, D. Meyerstein, *J. Chem. Soc. Faraday Trans. 1* **1980**, *76*, 1838–1848; b) H. Cohen, D. Meyerstein, *Inorg. Chem.* **1986**, *25*, 1505–1506; c) N. Navon, G. Golub, H. Cohen, D. Meyerstein, *Organometallics* **1995**, *14*, 5670–5676.

[33] M. Masarwa, H. Cohen, D. Meyerstein, *Inorg. Chem.* **1986**, *25*, 4897–4900.

[34] a) D. G. Kelley, A. Marchaj, A. Bakac, J. H. Espenson, *J. Am. Chem. Soc.* **1991**, *113*, 7583–7587; b) S. J. Reid, N. T. Freeman, M. C. Baird, *Chem. Commun.* **2000**, 1777–1778; c) S. J. Reid, M. C. Baird, *J. Organomet. Chem.* **2004**, *689*, 1257–1264.

[35] S. J. Reid, M. C. Baird, *Dalton Trans.* **2003**, 3975–3980.

[36] K. C. MacLeod, J. L. Conway, B. O. Patrick, K. M. Smith, *J. Am. Chem. Soc.* **2010**, *132*, 17325–17334.

[37] J. March, *Advanced Organic Chemistry*, 4th ed., Wiley, New York, **1992**.

[38] F. G. Herring, P. Legzdins, G. B. Richter-Addo, *Organometallics* **1989**, *8*, 1485–1493.

[39] E. Le Grognec, R. Poli, P. Richard, *J. Chem. Soc., Dalton Trans.* **2001**, 2251–2257.

[40] J. P. Collman, L. S. Hegedus, J. R. Norton, R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, CA, **1987**.

[41] J. A. Martinho Simões, J. L. Beauchamp, *Chem. Rev.* **1990**, *90*, 629–688.

[42] D. C. Sonnenberger, L. R. Morss, T. J. Marks, *Organometallics* **1985**, *4*, 352–355.

[43] M. J. Calhorda, A. R. Dias, M. E. M. Dapiedade, M. S. Salema, J. A. M. Simoes, *Organometallics* **1987**, *6*, 734–738.

[44] a) F. T. T. Ng, G. L. Rempel, J. Halpern, *J. Am. Chem. Soc.* **1982**, *104*, 621–623; b) F. T. T. Ng, G. L. Rempel, J. Halpern, *Inorg. Chim. Acta* **1983**, *77*, L165–L166.

[45] a) T. Ziegler, V. Tschinke, A. Becke, *J. Am. Chem. Soc.* **1987**, *109*, 1351–1358; b) E. Clot, C. Megret, O. Eisenstein, R. N. Perutz, *J. Am. Chem. Soc.* **2006**, *128*, 8350–8357.

[46] J. L. Hodgson, C. Y. Lin, M. L. Coote, S. R. A. Marque, K. Matyjaszewski, *Macromolecules* **2010**, *43*, 3728–3743.

[47] K. Matyjaszewski, R. Poli, *Macromolecules* **2005**, *38*, 8093–8100.

[48] a) R. H. Abeles, D. Dolphin, *Acc. Chem. Res.* **1976**, *9*, 114–120; b) G. Li, F. F. Zhang, H. Chen, H. F. Yin, H. L. Chen, S. Y. Zhang, *J. Chem. Soc., Dalton Trans.* **2002**, 105–110.

[49] A. Vlcek, *Coord. Chem. Rev.* **2000**, *200*, 933–977.

[50] C. J. Kleverlaan, D. J. Stufkens, I. P. Clark, M. W. George, J. J. Turner, D. M. Martino, H. van Willigen, A. Vlcek, *J. Am. Chem. Soc.* **1998**, *120*, 10871–10879.

[51] I. R. Farrell, P. Matousek, C. J. Kleverlaan, A. Vlcek, *Chem. Eur. J.* **2000**, *6*, 1386–1394.

[52] C. Giannotti, B. Septe, D. Benlian, *J. Organomet. Chem.* **1972**, *39*, C5–C8.

[53] J. M. Pratt, B. R. D. Whitear, *J. Chem. Soc. A* **1971**, 252–255.

[54] D. Dodd, M. D. Johnson, *J. Organomet. Chem.* **1973**, *52*, 1–232.

[55] M. J. Kendrick, W. Alakhdar, *Inorg. Chem.* **1987**, *26*, 3971–3972.

[56] L. A. Goj, E. D. Blue, S. A. Delp, T. B. Gunnoe, T. R. Cundari, J. L. Petersen, *Organometallics* **2006**, *25*, 4097–4104.

[57] W. Lau, J. C. Huffman, J. K. Kochi, *Organometallics* **1982**, *1*, 155–169.

[58] a) A. Pedersen, M. Tilset, *Organometallics* **1993**, *12*, 56–64; b) E. Fooladi, M. Tilset, *Inorg. Chem.* **1997**, *36*, 6021–6027.

[59] B. J. Wik, M. Tilset, *J. Organomet. Chem.* **2007**, *692*, 3223–3230.

[60] L. Boisvert, M. C. Denney, S. K. Hanson, K. I. Goldberg, *J. Am. Chem. Soc.* **2009**, *131*, 15802–15814.

[61] D. J. Brockway, B. O. West, A. M. Bond, *J. Chem. Soc., Dalton Trans.* **1979**, 1891–1898.

[62] H. Fischer, *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 1885–1901.

[63] W. Tang, Y. Kwak, W. Braunecker, N. V. Tsarevsky, M. L. Coote, K. Matyjaszewski, *J. Am. Chem. Soc.* **2008**, *130*, 10702–10713.

[64] B. B. Wayland, G. Poszmik, S. Mukerjee, *J. Am. Chem. Soc.* **1994**, *116*, 7943–7944.

[65] a) B. B. Wayland, L. Basickes, S. Mukerjee, M. Wei, M. Fryd, *Macromolecules* **1997**, *30*, 8109–8112; b) B. B. Wayland, S. Mukerjee, G. Poszmik, D. C. Woska, L. Basickes, A. A. Gridnev, M. Fryd, S. D. Ittel, *ACS Symp. Ser.* **1998**, *685*, 305–315; c) Z. Lu, M. Fryd, B. B. Wayland, *Macromolecules* **2004**, *37*, 2686–2687; d) C.-H. Peng, M. Fryd, B. B. Wayland, *Macromolecules* **2007**, *40*, 6814–6819.

[66] L. D. Arvanatitopoulos, M. P. Greuel, H. J. Harwood, *Polym. Prep.* **1994**, *35*, 549–550.

[67] a) M. Lee, Y. Minoura, *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 1726–1737; b) M. Lee, T. Morigami, Y. Minoura, *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 1738–1749; c) Y. Minoura, M. Lee, *Polym. Prepr.* **1979**, *20*, 150–153; d) M. Lee, K. Utsumi, Y. Minoura, *J. Chem. Soc., Faraday Trans. 1* **1979**, *75*, 1821–1829; e) M. Lee, Y. Ishida, Y. Minoura, *J. Polym. Sci. Polym. Chem.* **1982**, *20*, 457–465.

[68] Y. Champouret, K. C. MacLeod, U. Baisch, B. O. Patrick, K. M. Smith, R. Poli, *Organometallics* **2010**, *29*, 167–176.

[69] W. A. Braunecker, W. C. Brown, B. Morelli, W. Tang, R. Poli, K. Matyjaszewski, *Macromolecules* **2007**, *40*, 8576–8585.

[70] Y. Champouret, U. Baisch, R. Poli, L. Tang, J. L. Conway, K. M. Smith, *Angew. Chem.* **2008**, *120*, 6158; *Angew. Chem. Int. Ed.* **2008**, *47*, 6069–6072.

[71] a) S. Maria, H. Kaneyoshi, K. Matyjaszewski, R. Poli, *Chem. Eur. J.* **2007**, *13*, 2480–2492; b) A. Debuigne, Y. Champouret, R. Jérôme, R. Poli, C. Detrembleur, *Chem. Eur. J.* **2008**, *14*, 4046–4059; c) A. Debuigne, C. Michaux, C. Jérôme, R. Jérôme, R. Poli, C. Detrembleur, *Chem. Eur. J.* **2008**, *14*, 7623–7637; d) A. Debuigne, R. Poli, C. Jérôme, R. Jérome, C. Detrembleur, *Prog. Polym. Sci.* **2009**, *34*, 211–239; e) K. S. Santhosh Kumar, Y. Li, Y. Gnanou, U. Baisch, Y. Champouret, R. Poli, K. C. D. Robson, W. S. McNeil, *Chem. Asian J.* **2009**, *4*, 1257–1265.

[72] V. Sciannamea, A. Debuigne, Y. Piette, R. Jerome, C. Detrembleur, *Chem. Commun.* **2006**, 4180–4182.

[73] A. Debuigne, R. Poli, R. Jérôme, C. Jérôme, C. Detrembleur, *ACS Symp. Ser.* **2009**, *1024*, 131–148.

[74] K. Matyjaszewski, Y. Gnanou, L. Leibler, *Macromolecular Engineering: Precise Synthesis Materials Properties, Applications*, Wiley-VCH, Weinheim, Germany, **2007**.

[75] A. Theis, T. P. Davis, M. H. Stenzel, C. Barner-Kowollik, *Macromolecules* **2005**, *38*, 10323–10327.

[76] A. H. E. Müller, R. G. Zhuang, D. Y. Yan, G. Litvinenko, *Macromolecules* **1995**, *28*, 4326–4333.

[77] a) B. B. Wayland, X.-F. Fu, Z. Lu, M. Fryd, Polymer Preprints, 230th ACS National Meeting, August 28–September 1, 2005, Washington, DC, **2005**; b) B. B. Wayland, C.-H. Peng, X. Fu, Z. Lu, M. Fryd, *Macromolecules* **2006**, *39*, 8219–8222; c) C. H. Peng, J. Scricco, S. Li, M. Fryd, B. B. Wayland, *Macromolecules* **2008**, *41*, 2368–2373.

[78] S. Li, B. de Bruin, C. H. Peng, M. Fryd, B. B. Wayland, *J. Am. Chem. Soc.* **2008**, *130*, 13373–13381.

[79] a) A. Debuigne, J. R. Caille, R. Jérôme, *Angew. Chem.* **2005**, *117*, 1125; *Angew. Chem. Int. Ed.* **2005**, *44*, 1101–1104; b) A. Debuigne, J.-R. Caille, R. Jérôme, *Macromolecules* **2005**, *38*, 5452–5458; c) A. Debuigne, J. R. Caille, N. Willet, R. Jerome, *Macromolecules* **2005**, *38*, 9488–9496; d) A. Debuigne, J. R. Caille, C. Detrembleur, R. Jerome, *Angew. Chem.* **2005**, *117*, 3505; *Angew. Chem. Int. Ed.* **2005**, *44*, 3439–3442; e) C. Detrembleur, A. Debuigne, R. Bryaskova, B. Charleux, R. Jerome, *Macromol. Rapid Commun.* **2006**, *27*, 37–41.

[80] U. Baisch, R. Poli, *Polyhedron* **2008**, *27*, 2175–2185.

[81] A. Debuigne, J. Warnant, R. Jerome, I. Voets, A. de Keizer, M. A. Stuart, C. Detrembleur, *Macromolecules* **2008**, *41*, 2353–2360.

[82] Z. Xue, R. Poli, unpublished results.

[83] G. Bhandari, Y. Kim, J. M. McFarland, A. L. Rheingold, K. H. Theopold, *Organometallics* **1995**, *14*, 738–745.

[84] a) I. Cacelli, D. W. Keogh, R. Poli, A. Rizzo, *New J. Chem.* **1997**, *21*, 133–135; b) J. C. Fettinger, S. P. Mattamana, R. Poli, R. D. Rogers, *Organometallics* **1996**, *15*, 4211–4222; c) S. P. Mattamana, R. Poli, *Organometallics* **1997**, *16*, 2427–2433; d) E. Collange, D. Duret, R. Poli, *J. Chem. Soc., Dalton Trans.* **1999**, 875–880.

[85] G. W. Kirker, A. Bakac, J. H. Espenson, *J. Am. Chem. Soc.* **1982**, *104*, 1249–1255.

[86] A. V. Kramer, J. A. Osborn, *J. Am. Chem. Soc.* **1974**, *96*, 7832–7833.

[87] a) J. P. A. Heuts, D. J. Forster, T. P. Davis, B. Yamada, H. Yamazoe, M. Azukizawa, *Macromolecules* **1999**, *32*, 2511–2519; b) G. E. Roberts, J. P. A. Heuts, T. P. Davis, *Macromolecules* **2000**, *33*, 7765–7768; c) J. P. A. Heuts, G. E. Roberts, J. D. Biasutti, *Aust. J. Chem.* **2002**, *55*, 381–398.

[88] B. Milani, E. Stabon, E. Zangrando, G. Mestroni, A. Sommazzi, C. Zannoni, *Inorg. Chim. Acta* **2003**, *349*, 209–216.

[89] P. Yang, B. C. K. Chan, M. C. Baird, *Organometallics* **2004**, *23*, 2752–2761.

[90] A. A. Gridnev, S. D. Ittel, *Chem. Rev.* **2001**, *101*, 3611–3659.

[91] A. A. Gridnev, S. D. Ittel, B. B. Wayland, M. Fryd, *Organometallics* **1996**, *15*, 5116–5126.

[92] M. P. Shaver, L. E. N. Allan, V. C. Gibson, *Organometallics* **2007**, *26*, 4725–4730.

[93] a) B. Smirnov, I. Bel'govskii, G. Ponomarev, A. Marchenko, N. Enikolopian, *Dokl. Akad. Nauk SSSR* **1980**, *254*, 127–130; b) N. S. Enikolopyan, B. R. Smirnov, G. V. Ponomarev, I. M. Belgovskii, *J. Polym. Sci., Polym. Chem.* **1981**, *19*, 879–889; c) A. Y. Nokel, A. A. Gridnev, A. S. Semeikin, A. F. Mironov, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **1988**, *31*, 52–55; d) A. A. Gridnev, S. D. Ittel, M. Fryd, B. B. Wayland, *Organometallics* **1993**, *12*, 4871–4880; e) A. A. Gridnev, S. D. Ittel, M. Fryd, B. B. Wayland, *Organometallics* **1996**, *15*, 222–235.

[94] A. A. Gridnev, *Vysokomol. Soedin., Ser. A* **1989**, *31*, 2153–2159.

[95] a) G. P. Abramo, J. R. Norton, *Macromolecules* **2000**, *33*, 2790–2792; b) L. Tang, J. Norton, *Macromolecules* **2004**, *37*, 241–243; c) L. H. Tang, J. R. Norton, *Macromolecules* **2006**, *39*, 8229–8235; d) L. Tang, E. Papish, G. Abramo, J. Norton, M. Baik, R. Friesner, A. Rappe, *J. Am. Chem. Soc.* **2003**, *125*, 10093–10102; e) L. H. Tang, J. R. Norton, J. C. Edwards, *Macromolecules* **2003**, *36*, 9716–9720; f) J. Choi, L. H. Tang, J. R. Norton, *J. Am. Chem. Soc.* **2007**, *129*, 234–240.

[96] a) H. M. Feder, J. Halpern, *J. Am. Chem. Soc.* **1975**, *97*, 7186–7188; b) F. Ungváry, L. Markó, *Organometallics* **1982**, *1*, 1120–1125.

[97] R. L. Sweany, J. Halpern, *J. Am. Chem. Soc.* **1977**, *99*, 8335–8337.

[98] R. L. Sweany, D. S. Comberrel, M. F. Dombourian, N. A. Peters, *J. Organomet. Chem.* **1981**, *216*, 57–63.

[99] a) J. H. Espenson, J. S. Shveima, *J. Am. Chem. Soc.* **1973**, *95*, 4468–4469; b) J. H. Espenson, T. D. Sellers, *J. Am. Chem. Soc.* **1974**, *96*, 94–97; c) A. Bakac, J. H. Espenson, *J. Am. Chem. Soc.* **1984**, *106*, 5197–5202.

[100] a) A. Vandenbe, B. O. West, *J. Organomet. Chem.* **1974**, *64*, 125–134; b) J. Z. Chrzastowski, C. J. Cooksey, M. D. Johnson, B. L. Lockman, P. N. Steggles, *J. Am. Chem. Soc.* **1975**, *97*, 932–934; c) D. Dodd, M. D. Johnson, B. L. Lockman, *J. Am. Chem. Soc.* **1977**, *99*, 3664–3673; d) J. F. Endicott, C. L. Wong, J. M. Ciskowski, K. P. Balakrishnan, *J. Am. Chem. Soc.* **1980**, *102*, 2100–2103; e) A. M. Stolzenberg, Y. Cao, *J. Am. Chem. Soc.* **2001**, *123*, 9078–9090.

[101] M. S. Ram, C. G. Riordan, *J. Am. Chem. Soc.* **1995**, *117*, 2365–2366.

[102] B. H. Song, H. M. Goff, *Inorg. Chim. Acta* **1994**, *226*, 231–235.

[103] R. C. McHatton, J. H. Espenson, A. Bakac, *J. Am. Chem. Soc.* **1982**, *104*, 3531–3533.

[104] R. C. McHatton, J. H. Espenson, A. Bakac, *J. Am. Chem. Soc.* **1986**, *108*, 5885–5890.

[105] a) A. E. Sherry, B. B. Wayland, *J. Am. Chem. Soc.* **1990**, *112*, 1259–1261; b) B. B. Wayland, S. Ba, A. E. Sherry, *J. Am. Chem. Soc.* **1991**, *113*, 5305–5311; c) S. Sarkar, S. Li, B. B. Wayland, *J. Am. Chem. Soc.* **2010**, *132*, 13569–13571.

[106] a) W. H. Cui, X. P. Zhang, B. B. Wayland, *J. Am. Chem. Soc.* **2003**, *125*, 4994–4995; b) W. H. Cui, B. B. Wayland, *J. Am. Chem. Soc.* **2004**, *126*, 8266–8274.

[107] C. A. Merlic, M. M. Miller, B. N. Hietbrink, K. N. Houk, *J. Am. Chem. Soc.* **2001**, *123*, 4904–4918.

[108] a) H. G. Schmalz, S. Siegel, A. Schwarz, *Tetrahedron Lett.* **1996**, *37*, 2947–2950; b) H. G. Schmalz, S. Siegel, J. W. Bats, *Angew. Chem.* **1995**, *107*, 2597; *Angew. Chem. Int. Ed. Engl.*

1995, *34*, 2383–2385; c) C. A. Merlic, J. C. Walsh, *J. Org. Chem.* **2001**, *66*, 2265–2274; d) J. H. Byers, N. R. Neale, J. B. Alexander, S. P. Gangemi, *Tetrahedron Lett.* **2007**, *48*, 7903–7905.

[109] H. C. Lin, H. J. Zhang, L. Yang, C. Z. Li, *Org. Lett.* **2002**, *4*, 823–825.

[110] E. Samuel, D. Caurant, D. Gourier, C. Elschenbroich, K. Agbaria, *J. Am. Chem. Soc.* **1998**, *120*, 8088–8092.

[111] E. Baciocchi, B. Floris, E. Muraglia, *J. Org. Chem.* **1993**, *58*, 2013–2016.

[112] a) G. E. Herberich, E. Bauer, *J. Organomet. Chem.* **1969**, *16*, 301–307; b) G. E. Herberich, J. Schwarzer, *Angew. Chem.* **1970**, *82*, 883; *Angew. Chem. Int. Ed. Engl.* **1970**, *9*, 897.

[113] a) G. L. Casty, J. M. Stryker, *J. Am. Chem. Soc.* **1995**, *117*, 7814–7815; b) S. Ogoshi, J. M. Stryker, *J. Am. Chem. Soc.* **1998**, *120*, 3514–3515; c) C. A. G. Carter, R. McDonald, J. M. Stryker, *Organometallics* **1999**, *18*, 820–822.

[114] W. T. Boese, A. S. Goldman, *J. Am. Chem. Soc.* **1992**, *114*, 350–351.

[115] N. H. Nsouli, I. Mouawad, F. Hasanayn, *Organometallics* **2008**, *27*, 2004–2012.

[116] F. Hasanayn, N. H. Nsouli, A. Al-Ayoubi, A. S. Goldman, *J. Am. Chem. Soc.* **2008**, *130*, 511–521.

[117] J. H. Byers, N. J. Janson, *Org. Lett.* **2006**, *8*, 3453–3455.

[118] a) C. A. Merlic, D. Q. Xu, *J. Am. Chem. Soc.* **1991**, *113*, 9855–9856; b) C. A. Merlic, D. Q. Xu, M. C. Nguyen, V. Truong, *Tetrahedron Lett.* **1993**, *34*, 227–230.

[119] a) G. G. Melikyan, R. C. Combs, J. Lamirand, M. Khan, K. M. Nicholas, *Tetrahedron Lett.* **1994**, *35*, 363–366; b) G. G. Melikyan, O. Vostrowsky, W. Bauer, H. J. Bestmann, M. Khan, K. M. Nicholas, *J. Org. Chem.* **1994**, *59*, 222–229.

[120] S. C. Bart, K. Chlopek, E. Bill, M. W. Bouwkamp, E. Lobkovsky, F. Neese, K. Wieghardt, P. J. Chirik, *J. Am. Chem. Soc.* **2006**, *128*, 13901–13912.

[121] R. J. Trovitch, E. Lobkovsky, M. W. Bouwkamp, P. J. Chirik, *Organometallics* **2008**, *27*, 6264–6278.

[122] J. Scott, S. Gambarotta, I. Korobkov, P. H. M. Budzelaar, *J. Am. Chem. Soc.* **2005**, *127*, 13019–13029.

[123] M. W. Bouwkamp, S. C. Bart, E. J. Hawrelak, R. J. Trovitch, E. Lobkovsky, P. J. Chirik, *Chem. Commun.* **2005**, 3406–3408.

[124] a) K. Vyakaranam, J. B. Barbour, J. Michl, *J. Am. Chem. Soc.* **2006**, *128*, 5610–5611; b) K. Vyakaranam, S. Koerbe, J. Michl, *J. Am. Chem. Soc.* **2006**, *128*, 5680–5686.

[125] T. Clark, *J. Am. Chem. Soc.* **2006**, *128*, 11278–11285.

[126] a) F. Hasanayn, S. Gozem, *Organometallics* **2008**, *27*, 5426–5429; b) F. Hasanayn, M. S. El-Makkaoui, *Organometallics* **2009**, *28*, 6469–6479.

[127] J. R. Bryant, J. M. Mayer, *J. Am. Chem. Soc.* **2003**, *125*, 10351–10361.

[128] J. P. Roth, J. M. Mayer, *Inorg. Chem.* **1999**, *38*, 2760–2761.

[129] a) J. M. Mayer, *Acc. Chem. Res.* **2010**, *43*, 36–46; b) J. J. Warren, T. A. Tronic, J. M. Mayer, *Chem. Rev.* **2010**, *110*, 6961–7001.

[130] R. Sharma, A. Goyal, J. M. Caruthers, Y. Y. Won, *Macromolecules* **2006**, *39*, 4680–4689.

Received: December 30, 2010