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Homolytic bond strength and radical generation from (1-carbomethoxyethyl)pentacarbonylmanganese(I)

Roberto Morales-Cerrada,[a,b] Christophe Fliedel,[a] Florence Gayet,[a] Vincent Ladmiral,[b] Bruno Améduri,*[b] and Rinaldo Poli*[a]

Abstract: Compound (1-carbomethoxyethyl)pentacarbonyl-manganese(I), [MnR(CO)$_5$] (R = CHMeCOOMe, **1**), was synthesized from K$^+$[Mn(CO)$_5$]$^-$ and methyl 2-bromopropionate and isolated in pure form. Upon thermal activation, the Mn-R bond is homolytically cleaved and the resulting 1-carbomethoxyethyl radical is able to initiate the polymerization of methyl acrylate (MA). A kinetic study of the decomposition of **1** in the presence of tris(trimethylsilyl)silane, TTMSS (10 equiv, saturation conditions) at 70, 65 and 60 °C yielded the T-dependent activation rate constant, k_a, which allowed the calculation of the activation enthalpy ($\Delta H^{\ddagger} = 35.3\pm2.8$ kcal·mol^{-1}) and entropy ($\Delta S^{\ddagger} = 27.2\pm8.1$ cal·mol^{-1}·K^{-1}) through the use of the Eyring relationship. The $\Delta H^{\ddagger}$ value can be taken as an upper limit for the thermodynamic bond dissociation enthalpy, which was estimated as 36.9 kcal·mol^{-1} by DFT calculations. The higher thermal stability of **1** relative to that of simpler R derivatives that form stronger Mn-R bonds can be attributed to more difficult CO dissociation, precluding the decomposition by β-H elimination.

Introduction

We have recently become interested in using organometallic compounds of transition metals with homolytically weak metal-carbon bonds as initiators for controlled radical polymerization, also known as Reversible Deactivation Radical Polymerization (RDRP).[1] A dynamic equilibrium between the growing radical chain (P$_n$•) and a dormant species (P$_n$-T), formed by reversible trapping with a moderating agent (T), as shown in Scheme 1, decreases the likelihood of bimolecular radical terminations (persistent radical effect),[2] leading to a more predominant monomer (M) addition and controlled chain growth. The strategies that use a transition metal complex as moderating agent have been termed "organometallic-mediated radical polymerizations" (OMRP).[3] We have been particularly attracted to the controlled polymerization of challenging monomers such as vinylidene fluoride (VDF).[4] As is well-known from basic polymer chemistry,

the reactivity of the free radicals of growing chains scales inversely to that of their associated monomers. Therefore, radicals produced from less reactive monomers lead to stronger bonds with the moderating agent and the resulting dormant species are consequently less easily reactivated.
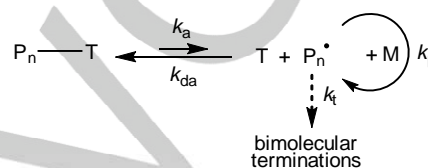
Scheme 1. Moderating equilibrium for a controlled radical polymerization.

It was previously shown that the controlled polymerization of VDF by another RDRP method termed "iodine transfer polymerization" (ITP),[5] which generally suffers from irreversible deactivation of the iodine-capped chains,[5-6] can be improved by the presence of [Mn(CO)$_5$•] radicals generated from [Mn$_2$(CO)$_{10}$] and visible light.[7] This phenomenon suggested the likelihood that [Mn(CO)$_5$]• may also directly trap the growing PVDF• chains, generating organometallic [(CO)$_5$Mn-PVDF] dormant species of type [(CO)$_5$Mn-CF$_2$CH$_2$PVDF] (for regular growing chains) or [(CO)$_5$Mn-CH$_2$CF$_2$PVDF] (for chains obtained after an inverted monomer addition). To learn about this possibility, we recently investigated model compounds with a variety of F-containing alkyl groups, [Mn(R$_F$)(CO)$_5$] (R$_F$ = CF$_3$, CHF$_2$, CH$_2$CF$_3$) in terms of their homolytic bond strength and aptitude to generate R$_F$• radicals under thermal or photochemical (visible, UV) conditions.[8] The experimental studies were carried out by a kinetic approach, trapping the thermally generated radicals with tris(trimethyl-silyl)silane (TTMSS) to produce R$_F$-H. These investigations yielded estimates for the bond dissociation enthalpies (BDEs) that are in agreement with those of previous[9] and more recent[10] DFT investigations. Furthermore, these investigations have shown that the Mn-R$_F$ bond cannot be thermally cleaved at significant rates under the conditions previously used for the ITP of VDF in the presence of [Mn$_2$(CO)$_{10}$] (50 °C). On the other hand, cleavage with production of R$_F$• radicals occurs at higher temperature or under visible or UV light irradiation and, under these conditions, these compounds successfully initiated the polymerization of VDF.[8]

The present contribution extends the homolytic BDE determination to the alkyl compound [Mn(CHMeCOOMe)(CO)$_5$], **1**, which generates the ester-stabilized radical •CHMe(COOMe) (a model of the growing poly(methyl acrylate) radical chain). We were also interested in establishing whether this compound could function as a suitable initiator for the radical polymerization of methyl acrylate.

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Results

(a) Synthesis
The title compound has been previously described,[11] but was only obtained as an alkyl rearrangement by-product during the decarbonylation of [Mn(COCH$_2$CH$_2$COOCH$_3$)(CO)$_5$], which yields the expected [Mn(CH$_2$CH$_2$COOCH$_3$)(CO)$_5$] as the main product by reverse migratory insertion. We have synthesized compound **1**, following a well-established general procedure,[12] by nucleophilic substitution of bromide in methyl 2-bromopropionate by pentacarbonylmanganate, which was made *in situ* by reduction of [Mn$_2$(CO)$_{10}$] with Na-K alloy, see Scheme 2. We prefer this reducing agent[8] over the more commonly employed sodium amalgam.
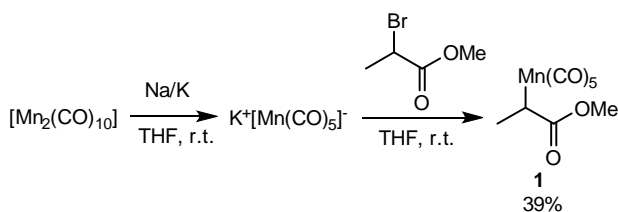
Scheme 2. Synthesis of compound **1**.

Compound [Mn(CHMeCOOEt)(CO)$_5$], which is rather similar to **1** (ethyl instead of methyl in the ester group), was previously synthesized using the same strategy.[13] In that contribution, the influence of the halogen nature (X) in the R-X substrate on the product yield was investigated in detail. It was established that the bromide substrate gives the best yields, whereas Cl led to better results for analogous primary alkyl derivatives. These syntheses are affected by side reactions with generation of [Mn$_2$(CO)$_{10}$] and [MnX(CO)$_5$], in addition to the desired [MnR(CO)$_5$]. The reactions of Na$^+$[Mn(CO)$_5$]$^-$ or PPN$^+$[Mn(CO)$_5$]$^-$ with MeCH(Br)COOEt in THF at 25 °C gave respectively 63% and 76% spectroscopic (^{55}Mn NMR) yields of [Mn(CHMeCOOEt)(CO)$_5$], but no isolated yields were reported.[13] In our hands, K$^+$[Mn(CO)$_5$]$^-$ and methyl 2-bromopriopionate gave, after chromatographic purification, a fair 39% yield of pure product. The spectroscopic properties of the isolated compound matched those reported in the previous contribution (see SI, Figures S1 and S2).[13]

(b) Experimental investigation of the Mn-C bond cleavage
The Mn-C homolytic bond strength in compound **1** was investigated by monitoring the rate of its disappearance at different temperatures in the presence of a sufficient amount of trapping agent for the produced •CHMe(COOMe) radical to insure saturation conditions. Using the ubiquitous TEMPO as a trapping agent[14] turned out unsuitable for this type of system, whereas TTMSS gave good results.[8] The proposed sequence of reactions for the produced [Mn(CO)$_5$]• and (Me$_3$Si)Si• radicals, which is based on literature reports,[15] is shown in reactions 1-5 (Scheme 3).

Saturation conditions are achieved when the rate of the trapping process (k_{trap} in equation 2) is much faster than that of the reverse radical recombination (k_{da} in equation 1). Hence, the latter may be neglected and the experimentally measured pseudo-first order rate constant for the decay of the starting complex (k_{obs}) corresponds to the rate constant of the Mn-C bond homolytic cleavage (k_a in equation 1). It was established that 10 equivalents of TTMSS per Mn are sufficient, even for the strongest bond with CF$_3$, to achieve saturation conditions.[8]
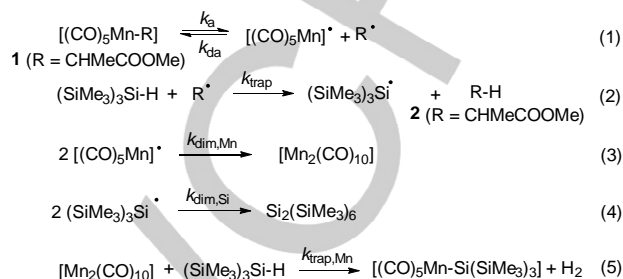
Scheme 3. Thermal decomposition of alkylpentacarbonylmanganese(I) compounds in the presence of TTMSS as a radical trap. In the present study, R = CH(CH$_3$)COOCH$_3$.

The experimental protocol used for **1** (see Experimental Section) was the same as in our recent study of the Mn-R$_F$ bond strengths in compounds [(CO)$_5$Mn-R$_F$] (R$_F$ = CF$_3$, CHF$_2$ and CH$_2$CF$_3$),[8] except that the increased thermal lability of the Mn-C bond in **1** allowed using lower temperatures. The kinetic monitoring was based on ^{1}H NMR measurements in C$_6$D$_6$. The expected main product is methyl propanoate, CH$_3$CH$_2$COOCH$_3$ (**2**). However, several by-products were also formed, leading to resonance overlap and complicating the extraction of rate data. The formation of the expected **2** was suggested by the observation of a growing triplet at δ 0.96 with J = 6 Hz (*cf.* δ 1.17, J = 7.5 Hz in CDCl$_3$).[16] The relative amounts of compound **1** at different times were calculated from the relative integral of the signals of the 1,3,5-trioxane internal standard (δ 4.45 to 4.55) and the CHCH_3 proton doublet (δ 1.40 to 1.55), which is located in a clean spectral region with no overlap with the resonances of other species, see SI, Figure S3. The first-order decay plots at 70, 65 and 60 °C are shown in Figure 1 and the resulting k_a values are reported in Table 1. Analysis of these data by the Eyring equation (Figure 2) yields the activation parameters $\Delta H_a^{\ddagger}$ = 35.3±2.8 kcal·mol^{-1} and $\Delta S_a^{\ddagger}$ = 27.2±8.1 cal·mol^{-1}·K^{-1}.

Table 1. Kinetics parameters and half-lives for the decay of compound **1** in the presence of TTMSS (10 equiv) in C$_6$D$_6$.

T/°C	60	65	70
k_{obs}/s^{-1}	(4.1±0.4)·10^{-5}	(9.6±0.5)·10^{-5}	(2.00±0.03)·10^{-4}
$t_{1/2}$/min	282±27	120±6	58±1

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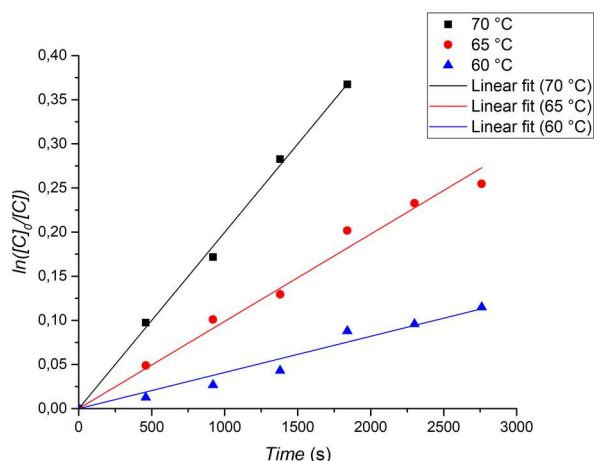

Figure 1. First order decay of [Mn(CHMeCOOMe)(CO)$_5$] (**1**) in C$_6$D$_6$ at 70, 65 and 60 °C in the presence of TTMSS.
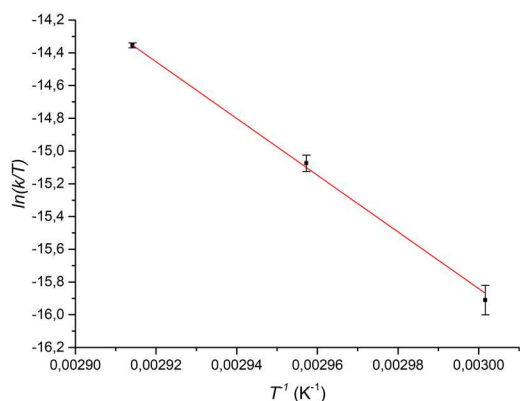

Figure 2. Eyring plot of k$_{obs}$ as function of temperature for the decomposition of compound **1**.

Under the reasonable hypothesis that the radical recombination process (k_{da} in equation 1, Scheme 3) has an associated negligible activation enthalpy, the determined $\Delta H_a^{\ddagger}$ parameter may be taken as a reasonable upper estimate of the thermodynamic bond dissociation enthalpy. This assumption is commonplace, made also in other studies of metal-carbon bond dissociation energies by a similar kinetic approach in non-coordinating solvents.[14a-d, 17] The value obtained for compound **1** is much lower than those obtained for the fluorinated alkyl analogues, see Table 2. This is consistent with the greater stabilization of the carbomethoxyethyl radical, which is a model of the poly(methyl acrylate) growing chain, relatively to fluorinated alkyl radicals. It must be underlined that using a coordinating solvent would not provide a legitimate approximation of the metal-carbon bond strength, because the thermodynamics and kinetics would be skewed by the solvent coordination process.[18] The [Mn(CO)$_5$] radical was shown to have a 5-coordinate C$_{4v}$ structure both in an Ar[19] and in a CO[20] low-temperature matrix, thus

indicating its low aptitude to add ligands as expected for a low-valent 17-electron complex.[21] Although this radical has never been studies in a benzene matrix, benzene is certainly a poorer ligand than CO for low-valent metal centers.

Table **2**. Comparison of experimental activation enthalpies and calculated BDEs for different [MnR(CO)$_5$] compounds, in kcal mol^{-1}.

R	$\Delta H_a^{\ddagger}$	Ref.	BDE^a	Ref.
CF$_3$	53.8±3.5	[8]	55.1	[10]
CH$_2$CF$_3$	50.6±0.8	[8]	50.5	[10]
CHF$_2$	46.3±1.6	[8]	48.0	[10]
CHMeCOOMe	35.3±2.8	This work	36.9	This work

^{a} Difference between the enthalpies of ([Mn(CO)$_5$]$^{\bullet}$ + R$^{\bullet}$) and [MnR(CO)$_5$] calculated by the DFT method.

(c) DFT calculation of the Mn-C BDE in compound 1

Calculations of the BDE in compound **1** were based on the DFT approach with the BPW91* functional, which has given us excellent results in previous applications the thermochemistry of first-row paramagnetic complexes.[10, 22] This functional is a reparametrized version of B3PW91 with the same parameters previously optimized for B3LYP.[23] Geometry optimizations were run in the gas phase and the energies were corrected for dispersion forces. No solvation corrections were applied, since the experimental study was carried out in the low-polarity benzene solvent. This approach is identical to that of the recent study of the analogous [MnR(CO)$_5$] complexes with R = CF$_3$, CHF$_2$ and CH$_2$CF$_3$.[10] The BDE is the difference between the enthalpies of the [Mn(CO)$_5$]$^{\bullet}$ and $^{\bullet}$CH(CH$_3$)COOCH$_3$ fragments and that of the starting complex **1**. The calculated energies and the Cartesian coordinates of the three optimized geometries are given in the SI, Table S1, whereas views of the optimized structures and the bond breaking thermochemical parameters are given in Figure 3. The enthalpy value is also reported in Table 2. A comparison of the experimental activation enthalpy and the calculated BDE shows an excellent match, as for the previously published fluorinated alkyl derivatives.[8, 10]

[Mn(CHMeCOOMe)(CO)$_5$]   →   [Mn(CO)$_5$]$^{\bullet}$ + $^{\bullet}$CHMeCOOMe
(**1**)

ΔE = 28.7 kcal mol^{-1} $\Delta H_{298K,D3}$ = 36.9 kcal mol^{-1}
ΔE_{D3} = 39.8 kcal mol^{-1} ΔS_{298K} = 45.3 cal mol^{-1} K^{-1} ($\Delta G_{298K,D3}$ = 23.4 kcal mol^{-1})
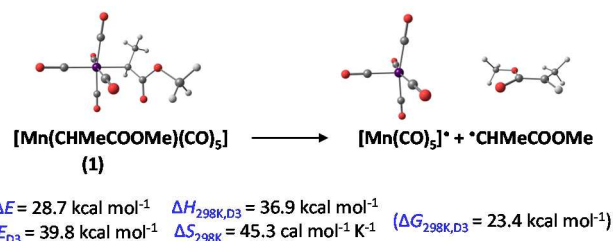
Figure 3. Views of the optimized geometries of [Mn(CH(CH$_3$)COOCH$_3$)(CO)$_5$] (**1**), [Mn(CO)$_5$]$^{\bullet}$ and $^{\bullet}$CH(CH$_3$)COOCH$_3$, and DFT-calculated thermochemical parameters.

(d) Initiation of methyl acrylate radical polymerization

Since compound **1** is soluble in methyl acrylate (MA), bulk polymerizations using **1** as initiator were initially carried out at different temperatures (75, 50 and 30 °C) with three different

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monomer/initiator ratios (70, 30 and 20). All tests led to rapid (0.5 - 1 h) viscosity increase and even to a solid, proving the occurrence of MA polymerization and the efficiency of **1** as a radical initiator. The high viscosity suggests the formation of very high molar mass macromolecules, which made it impossible to perform a detailed kinetic study. Therefore, an additional polymerization was carried out at 70 °C in a dilute C_6D_6 solution. This solvent was selected because it dissolves all components including the polymer, it does not promote chain transfer to solvent, and it allows direct monitoring by ^{1}H NMR spectroscopy. A polymerization also took place under these conditions (results in the SI, Table S2), although at a much slower rate as expected from the lower monomer concentration. The ^{1}H NMR spectrum of the polymer (SI, Figure S4) confirmed its identity as PMA by comparison with the published spectrum.[24] A conversion vs. time plot is shown in Figure S5. In agreement with the determined half-life of compound **1** at 70°C in C_6D_6 (ca. 1 h, Table 1), the polymerization essentially stops after 8 h (ca. 8 half-lives), when the polymer yield is only 14%. The recovered polymer samples have high average molar masses and high dispersities (results are also in Table S2), even for the first sample recovered after 1 h. This shows that the manganese complex does not exert any kind of control (*i.e.* a persistent radical effect, as in OMRP) for this polymerization. This result is quite expected, because the released $[Mn(CO)_5]^•$ radicals rapidly disappear by dimerization (equation 3, Scheme 3, $k_{dim,Mn} = 1.9 \cdot 10^9$ $M^{-1} \cdot s^{-1}$)[25] and, although they can be thermally generated in small equilibrium amounts at 70°C,[26] they are not able to add to methyl acrylate and initiate the polymerization. The SEC trace of the first polymer sample (SI, Figure S6) shows the immediate production of a high molar mass PMA. This remains essentially unchanged in the subsequent samples, while a new lower average molar mass component starts to grow, resulting in the decrease of the overall average molar mass and in a dispersity increase.

Discussion

While compound **1** has a homolytically weak Mn-R bond (see half-lives at different temperatures in Table 1), it is relatively stable at room temperature when protected under an inert atmosphere. Only slow darkening was witnessed when the compound was left as a solid at room temperature in air. This is in stark contrast with the high thermal instability of other alkylpentacarbonylmanganese(I) compounds, such as $[Mn(CO)_5(C_2H_5)]$ or $[Mn(CO)_5(n-C_3H_7)]$, which were reported to slowly decompose even at -10 °C in the dark under an inert atmosphere.[27] The increased thermal sensitivity of those compounds cannot be attributed to an easier homolytic bond cleavage, because ethyl and isopropyl are non-stabilized radicals that form stronger bonds than an acrylate radical. Indeed, the previously published DFT investigation of the Mn-R BDE in $[MnR(CO)_5]$ included the compound with R = C_2H_5 (BDE = 41.9 kcal/mol, *i.e.* 5.0 kcal/mol stronger than the Mn-C bond in **1**).[10] Such low thermal stability has been attributed to the available β-H elimination pathway following the dissociation of a CO ligand.[27b] In this respect, the stability of **1** is striking because this compound also contains β-H atoms. However, the formation of methyl acrylate (the expected β-H elimination product), was never observed in the degrading solutions of **1**. A faster β-H elimination from the ethyl and isopropyl derivatives, relative to **1**, may be caused by their greater aptitude to dissociate CO, a possible consequence of the stronger Mn-C bond and hence stronger *trans* effect of the Et and *i*Pr groups relative to the ester-substituted alkyl in **1**. It is also likely that the homolytic bond cleavage, which is easier for **1** than for the ethyl derivative according to the DFT predictions, is more favored than CO dissociation, thus precluding a decomposition pathway by β-H elimination for this compound.

Conclusions

The present contribution has proven that compound **1** is thermally activated to generate the stabilized radical, $^•CHMeCOOMe$, which is a model of a polyacrylate radical chain. This generated radical successfully initiates the radical polymerization of MA. The Mn-R homolytic bond dissociation enthalpy has been quantitatively assessed by a kinetic approach. Notably, the experimentally measured activation enthalpy matches rather closely the DFT estimate of the BDE. The same was recently found for similar compounds with fluorinated R groups,[8] for which the BDEs are 10-20 kcal/mol higher than that of **1**. These comparisons confirm that the chosen DFT methodology may be used as a predictive tool for further thermochemical studies of Mn-C bond breaking in $[MnR(CO)_5]$ complexes.

The recently introduced[8] protocol for the experimental determination of the metal-carbon homolytic bond cleavage rate using TTMSS as radical trapping agent, developed for the strong Mn-R bonds in $[MnR(CO)_5]$ (R = CF_3, CHF_2, CH_2CF_3), has been extended here to compound **1**, which contains a more weakly bonded alkyl group leading to the ester-stabilized acrylate radical $^•CHMeCOOMe$. The experimentally determined activation enthalpy is in close agreement with the predicted thermodynamic BDE from DFT calculations. The compound was proved to successfully initiate the radical polymerization of methyl acrylate under thermal activation conditions. A comparison of the thermal stability of **1** with that of other thermally fragile pentacarbonyl-manganese(I) alkyl derivatives shows that **1** is less susceptible to decompose by initial CO dissociation followed by β-H elimination, leaving the homolytic bond breaking as the dominant decomposition pathway. Further developments on the complex scaffold are now under investigation to improve the OMRP equilibrium / polymerization control.

Experimental Section

General. All operations were carried out under an atmosphere of argon except for the column chromatography purification, which was carried out in air. Compounds $[Mn_2(CO)_{10}]$ (98%, Strem Chemicals), methyl 2-bromopropionate (98%, Sigma-Aldrich), tris(trimethylsilyl)silane (TTMSS, 97%, Fluorochem), 1,3,5-trioxane (99%, Fluorochem), benzene-d_6 (99.5% D, Euriso-top), acetone-d_6 (99.5% D, Euriso-top) and silica gel (40-63 μm, VMR Chemicals) were used as received. Methyl acrylate (99%, Sigma-Aldrich) was filtered through activated basic alumina Brockmann I (Sigma-

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Aldrich) prior to use to remove the monomethyl ether hydroquinone inhibitor. Laboratory Reagent grade (≥ 99.5%) diethyl ether, pentane and THF were purchased from Sigma-Aldrich. THF was purified by percolation through a dry activated alumina column. Potassium (98%, Aldrich) and sodium (≥ 99.8%, Aldrich) were washed in *n*-pentane to remove the mineral oil prior to use. The nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance™ III 400 MHz spectrometer. The instrumental parameters for recording ^{1}H NMR spectra were as follows: flip angle 30°, acquisition time 5.7 s, pulse delay 2 s, number of scans 64 (4 for the kinetic study), and a pulse width of 3.05 μs. The Fourier transform infrared (FTIR) spectra on the pentane solutions were recorded in transmission mode with a PerkinElmer Spectrum One FT-IR Spectrophotometer using a CaF$_2$ window with a 4 mm thick and 0.05 mm path length. The apparent number average molar masses and dispersities (Đ) of the synthesized polymers were determined using a PL-GPC 50 Plus apparatus from Polymer Laboratories (Varian Inc.) equipped with two 300 mm PL-gel 5 μm, mixed D (200–300000 g mol–1) columns thermostated at 35 °C and a refractive index detector. Calibration was performed with PMMA standards. THF was used as the eluent at a flow rate of 1 mL·min^{-1}. The GPC system was calibrated using narrow poly(methyl methacrylate) (PMMA) standards ranging from 550 to 1,568,000 g mol-1 (EasiVial-Agilent). The typical sample concentration was 10 mg/mL.

Synthesis of (1-carbomethoxyethyl)pentacarbonylmanganese(I), 1. In a Schlenk tube were introduced 400 mg (10.23 mmol) of metallic potassium and 250 mg (10.87 mmol) of metallic sodium under argon. They were crushed together to generate the liquid "NaK" alloy. A solution of dimanganese decacarbonyl (2.00 g, 5.13 mmol) in 25 mL of dry THF was added and the resulting mixture was stirred for 3 h at room temperature. The mixture was then filtered through Celite to yield a greenish-brown solution, rinsing the Celite with 10 mL of dry THF. Then, methyl 2-bromopropionate (1.71 g, 10.24 mmol) was added dropwise at room temperature, generating a brown solution, which subsequently turned to yellow. After stirring at room temperature for 3 h, the solvent was evaporated under reduced pressure to yield on oily residue. The product was purified by column chromatography through a silica gel column. To facilitate the transfer of the oily product onto the chromatographic column, a small amount of silica gel was added to the solution from the synthesis before solvent removal. After evaporation, the silica gel containing the complex was laid on top of the column chromatography as a solid deposit. The chromatography was carried out using *n*-pentane as the initial mobile phase. After elimination of a first yellow fraction corresponding to [Mn$_2$(CO)$_{10}$], the mobile phase polarity was increased using a 9:1 mixture of *n*-pentane and diethyl ether. A light-yellow fraction was collected, followed by evaporation to dryness under reduced pressure to afford the product as a yellow oil 1.13 g, 4.00 mmol, yield 39%). The spectroscopic properties of the isolated product (^{1}H NMR, FTIR in pentane) matched those previously reported by Casey *et al.* ^{1}H NMR (actone-*d*$_6$, δ): 3.62 (3H, s, OC*H*$_3$), 2.35 (1H, q, ^{3}J$_{HH}$ = 7 Hz, MnC*H*), 1.55 (3H, d, ^{3}J$_{HH}$ = 7 Hz, CHC*H*$_3$) [*cf.* 3.65, 2.31 and 1.58 (J = 7.5 Hz) in CDCl$_3$]$^{[11]}$. The FTIR in pentane is essentially identical to the previously reported one in hexane, but previously unreported weak bands, attributed to ^{13}C isotopomers, are also observed in our spectrum (see Figure S2). The product is not very stable at room temperature in air, slowly darkening to brown. Thus, it is recommended to store it under argon at low temperature and in the dark.

Investigation of the Homolytic Mn-R Bond Cleavage. All experiments were carried out using the same procedure. [Mn(CHMeCO$_2$Me)(CO)$_5$] (213 mg, 0.76 mmol) was dissolved in 2.0 mL of C$_6$D$_6$ together with 30 mg (0.33 mmol) of 1,3,5-trioxane as internal standard. Aliquots of this solution (0.3 mL) were transferred into NMR tubes, then the desired amount of TTMSS was added (282 mg, 1.13 mmol for 10 equivalents) and the thermal decomposition was monitored at the desired temperatures by ^{1}H NMR scpectroscopy. The signal of 1,3,5-trioxane (internal standard) was

integrated from 4.65 ppm to 4.85 ppm and the resulting value was set to 1 in all spectra. Then, the complex signal was integrated from 1.39 ppm to 1.53 ppm. Knowing the initial concentration of the manganese complex in each tube (C$_0$), the concentration at time t (C$_t$) was determined as C$_t$ = C$_0$I$_t$/I$_0$, where I$_0$ and I$_t$ stand for the integral value of the NMR signal of the complex at t = 0 and at t, respectively. The ln[C$_0$/C$_t$] vs. time plots led to straight lines, the slopes of which represents k.

Computational Details. The computational work was carried out using the Gaussian09 suite of programs.$^{[28]}$ Gas-phase geometry optimizations were performed without any symmetry constraint using the BPW91* functional, which is a reparametrized version of B3PW91 with the same parameters previously optimized for B3LYP.$^{[23]}$ The basis sets used were 6-31G(d,p) for all light atoms (H, C, F, O, S) and SDD, augmented by an f polarization function (α = 2.195),$^{[29]}$ for the Mn atom. The unrestricted formulation was used for open-shell molecules, yielding only minor spin contamination (<S^2> at convergence was very close to the expected value of 0.75 for the radical species). All final geometries were characterized as local minima by verifying that all second derivatives of the energy were positive. Thermochemical corrections were obtained at 298.15 K on the basis of frequency calculations, using the standard approximations (ideal gas, rigid rotor and harmonic oscillator). Corrections for dispersion were carried out at the fixed BPW91* optimized geometries using Grimme's D3 empirical method (BPW91*-D3) with SR6 and S8 parameters identical to those optimized for B3PW91.$^{[30]}$

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The metal-carbon bond in [Mn(CHMeCOOMe)(CO)$_5$] is sufficiently weak to be homolytic cleaved, releasing the acrylate radical under mild conditions ($\Delta H_a^\ddagger$ = 35.3±2.8 kcal mol^{-1}, $\Delta S_a^\ddagger$ = 27.2±8.1 cal mol^{-1} K^{-1}) to initiate the radical polymerization of methyl acrylate.
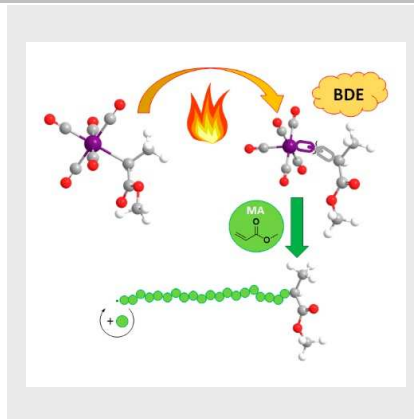
Weak Mn-carbon bond

Roberto Morales-Cerrada, Christophe Fliedel, Florence Gayet, Vincent Ladmiral, Bruno Améduri,* and Rinaldo Poli*

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Homolytic bond strength and radical generation from (1-carbomethoxy-ethyl)pentacarbonylmanganese(I)