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Halomethyl-cobalt(bis-acetylacetonate) for the controlled synthesis of functional polymers†

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Novel organocobalt complexes featuring weak C–CoL_2 bonds (L = acetylacetonate) are prepared and used as sources of halomethyl radicals. They permit the precision synthesis of α-halide functionalized and telechelic polymers in organic media or in water. Substitution of halide by azide allows derivatization of polymers using the CuAAC click reaction.

For decades, organocobalt(III) (R–Co) compounds have attracted attention because of the facile homolytic cleavage of the carbon–cobalt bond by thermal treatment or light irradiation[1] under mild conditions, being sources of carbon centered radicals in organic synthesis[1,2] and polymer chemistry.[3] When involved in reaction with olefins, these radicals add to the C–C double bond and, in some situations, the persistent Co^{II} complex may reversibly trap the newly formed radical adducts. Depending on both the substrate and the cobalt complex, either dehydrocobaltation occurs with the formation of unsaturated products,[3a] or the C–Co bond is homolytically cleaved in the presence of appropriate substrates, giving rise to well-defined addition products.[1,2e,3b,3c]

Four major processes can be found for the synthesis of R–Co. The first method consists in a reductive elimination/oxidative addition pathway for the synthesis of alkylcobaloximes (XCH_2–$Co^{III}L_2Py$; L = oxime and X = Br or Cl),[4] alkylcobalt derivatives of cobalt porphyrins[5] and vitamin B_{12}-derived alkyl-cobalamins.[6] In the second approach, organocobalts can be produced by hydrocobaltation of olefins.[7] The third pathway is the trapping of alkyl radicals by Co^{II} complexes such as bis(β-ketoaminato)cobalt(II).[8] The last route involves the oxidation of Co^{II} complexes ($Co^{II}L$; L = salen or porphyrin) in the presence of carbon monoxide and methanol to form (L)Co^{III}–CO_2CH_3 complexes.[9] The release of alkyl radicals from these different organocobalts requires an appropriate thermal treatment[7f,8,10] or irradiation with light (UV or visible).[9,11]

Organocobalt complexes with acetylacetonate (acac) bearing a weak C–Co bond (BDE < 20 kcal mol^{-1}) can however release alkyl radicals under mild conditions without requiring photoactivation.[12] The unique isolated specimen of this R–Co family is formed by the addition of a short oligo(vinyl acetate) radical to $Co(acac)_2$ at 30 °C.[13] We demonstrated that the high lability of the C–Co bond at 30–40 °C combined with the capacity of $Co(acac)_2$ to reversibly trap alkyl radicals, permitted the precision synthesis of unprecedented polymers by the so-called Organometallic-Mediated Radical Polymerization (OMRP)[12] technique. The growth of unstabilized growing radicals formed by the addition of $R^{\bullet}$ to unconjugated olefins (vinyl esters,[12] vinyl amides,[14] vinyl chloride,[15] *etc.*) is controlled by the reversible formation of a C–Co bond at the polymer chain end. The facile activation of this organometallic bond proved to be unique for radical addition to ethylene and its chain growth in the presence of polar monomers, with the construction of unprecedented functional poly(α-olefin)s.[16]

The lack of alternatives to this R–Co has until now placed limitations on further innovation in (macro)molecular design. While this organocobalt has proved to be extremely useful for the design of novel macromolecules with unique properties,[12] the presence of this R group at the α-polymer chain end is not always desired for the application. In the last few years, a lot of synthetic efforts were therefore devoted to the design and isolation of novel R–Co based on $Co(acac)_2$ with a precise and defined R group, but without any success. For instance, atom transfer radical addition (ATRA) of various alkyl halides to $Co(acac)_2$ was investigated but the target products were not obtained.[17] The main difficulties associated with the synthesis of novel R–$Co(acac)_2$ compounds concern the high lability of the C–Co bond,[12,18] the facile coordination of the vacant site of cobalt by coordinating solvents that affects the C–Co bond strength,[12,19] and their sensitivity to oxygen[12] and UV light.[20]

This communication describes an innovative synthetic route towards the preparation of new organocobalt compounds namely

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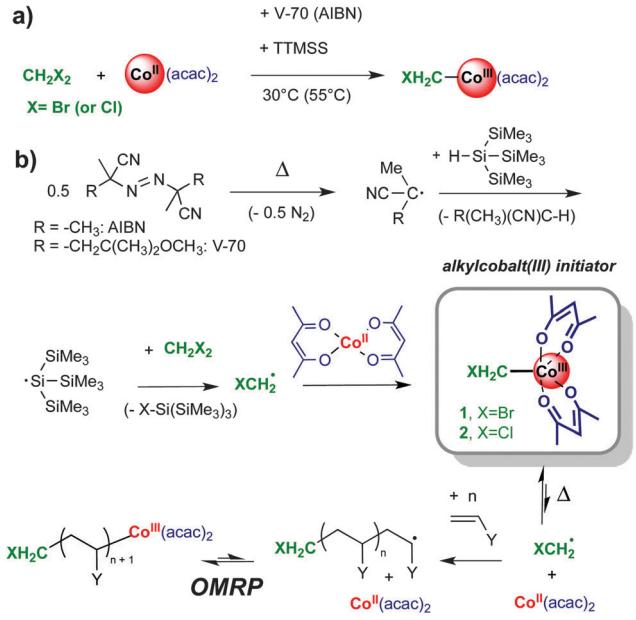


Scheme 1 (a) General reaction scheme for bromo- and chloro-methyl cobalt(bisacetylacetonate), (b) proposed mechanism for the formation of complexes **1** and **2**, and their use in the OMRP process.

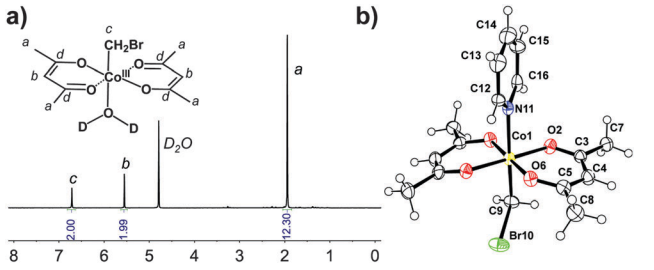


Fig. 1 (a) ^{1}H NMR spectrum of compound **1** in D_2O, (b) ORTEP representation of $BrCH_2$–$Co(acac)_2Py$ showing displacement ellipsoids drawn at the 50% probability level.

XCH_2–$Co(acac)_2$ (X = Cl or Br) having a weak C–Co bond (Scheme 1a). Their capacity to release halomethyl radicals ($XCH_2^{\bullet}$) under mild conditions is explored. Finally we investigate their ability to control the radical polymerization of vinyl monomers and to bring a terminal functionality to the polymers. In contrast to previously reported organocobalt species, the halomethyl–$Co(acac)_2$ complexes are soluble in solvents of very different polarities, from benzene to water, allowing reactions in various media.

Compounds **1** and **2** are produced *via* a one-pot multicomponent radical route involving an equimolar amount of $Co(acac)_2$ and a radical source such as 2,2′-azobis(4-methoxy-2.4-dimethyl valeronitrile) (V-70) or azobisisobutyronitrile (AIBN), 1.25 equiv. of tris-(trimethylsilyl)silane (TTMSS) and an excess of CH_2Cl_2 or CH_2Br_2 as both the solvent and the alkylating agent (Scheme 1a).

Scheme 1b illustrates the proposed reaction mechanism. TTMSS, a greener alternative to Bu_3SnH, is used here as a radical reducing agent that found utility in radical dehalogenation reactions of halogenated compounds.[21] Its reaction with the tertiary alkyl radicals formed by the decomposition of AIBN or V70 leads to tris(trimethylsilyl) radicals ($(Me_3Si)_3Si^{\bullet}$) by hydrogen abstraction that subsequently abstracts a halogen atom from CH_2X_2 to provide $XCH_2^{\bullet}$. The targeted organocobalt, XCH_2–$Co(acac)_2$, is then formed by trapping $XCH_2^{\bullet}$ by $Co(acac)_2$.

Compound **1** is best prepared with 26% yield by using V70 as the radical source at 30 °C. EI-MS analysis of the crude reaction product shows a signal at *m*/*z* 326/328 (Fig. S1, ESI†) assigned to $(Me_3Si)_3Si$–Br formed during the reaction (Scheme 1b); the isotopic distribution unambiguously confirms the presence of a bromine atom. The identification of this side product confirms the crucial role of TTMSS, *i.e.* the formation of $BrCH_2^{\bullet}$ that is ultimately intercepted by $Co(acac)_2$ to provide **1**. Importantly, compound **1** is not formed in the absence of TTMSS.

Compound **1** is then purified by elution on the silica column under an inert atmosphere. ^{1}H and ^{13}C NMR characterization of **1** in a non-coordinating solvent, C_6D_6, are however not exploitable as a result of NMR peak broadening. The solution magnetic moment of **1** in C_6D_6 (determined by the Evan's method[22]) reaches a value of 2.15, and therefore suggests that the paramagnetic nature of **1** in this solvent is responsible for the previously observed NMR peak broadening. In contrast, when **1** is analyzed in a coordinating solvent, D_2O, the ^{1}H-, ^{13}C APT- and HSQC NMR spectra exhibit fine singlet resonances for the methine (δ = 5.55 ppm, 2H) and methyl protons (δ = 1.94 ppm, 12H) of acac ligands, and $-CH_2Br$ (6.71 ppm, 2H) (Fig. 1a, Fig. S2 and S3, ESI†). Several methods (vapour diffusion, layering, evaporation, slow cooling) were then used for the tentative crystallization of compound **1** in order to analyze it using single crystal X-ray crystallography, but no crystal was recovered.

The addition of pyridine (py) to the solution of compound **1** in benzene was the only possibility for inducing crystallization. This aminated ligand was expected to stabilize the structure in an octahedral geometry, thus favoring the crystallization of the corresponding complex, XCH_2–$Co(acac)_2(py)$. Experimentally, the addition of pyridine induces an immediate change of coloration of the solution from dark green to red. After the addition of pentane, dark red needles are collected after storing the solution at 6 °C for 72 h. The structure of the complex was then determined by X-ray crystallography (Table S1, ESI†). Fig. 1b shows an ORTEP representation of the complex. The Co atom shows an octahedral coordination with two acetylacetonate (acac) ligands found in the equatorial plane, crystallographically linked by a mirror plane passing through the central metal atom; pyridine and a $BrCH_2$– group which hold the axial positions are found on this mirror plane. The C–Co bond length in $BrCH_2$–$Co(acac)_2(py)$ is 1.935 Å (Table S2, ESI†), which is thus similar to that found in other reported bromomethyl–alkylcobalt(III) such as cobaloxime complexes bearing triphenylphosphine ligands and $-CH_2Br$ in the axial position (C–Co bond length = 1.998 Å).[4d] ^{1}H-, ^{13}C APT- and HSQC NMR analyses of our pyridinated complex in C_6D_6 are shown in Fig. S4, S5 and S6 (ESI†), respectively. Experimental elemental analysis is also in agreement with the theoretical values.

The capacity of compound **1** to generate radicals under mild conditions is demonstrated by the Electron Spin Resonance (ESR) spin trapping experiment. The addition of *N-tert*-butyl-α-phenylnitrone (PBN) to the solution of **1** in *tert*-butylbenzene at 40 °C leads to the immediate appearance of an ESR signal with a_N of 14.32 G and a_H of 2.74 G (Fig. S7, ESI†). This signal is characteristic of the

nitroxide formed by the trapping of the bromomethyl radical ($Br–CH_2^•$) by PBN, confirming the lability of the C–Co bond under these conditions.

The synthetic route described in Scheme 1 can also be applied to CH_2Cl_2, thus to a di-haloalkane with a stronger C–halogen bond, to form compound **2**. The latter is prepared with 26% yield at 55 °C, using AIBN as the free radical source. Compound **2** is also analyzed in deuterated water by ^{1}H-, ^{13}C APT- and HSQC NMR and shows similar resonances (Fig. S8–S10, ESI†). The addition of pyridine to the solution of **2** in a mixture of benzene and pentane enables the crystallization of the corresponding complex, $Cl–CH_2–Co(acac)_2(py)$. The proposed pyridinated structure is confirmed by XRD (Fig. S11 and Tables S3 and S4, ESI†), NMR (Fig. S12–S14 ESI†) and elemental analysis. Because compounds **1** and **2** are air sensitive, all syntheses and purifications were carried out under an inert atmosphere.

An important application of compound **1** is illustrated in Fig. 2a for the synthesis of well-defined poly(vinyl acetate) (PVAc). Fig. 2b shows that compound **1** is able to initiate and control the vinyl acetate (VAc) polymerization at 40 °C in the bulk with no induction period being observed (Table S5, ESI†). The molar mass of the polymer increases with the monomer conversion and is easily tuned by adapting the monomer/**1** molar ratio (Fig. 2b). Importantly, PVAc with molar masses as high as 1.3 10^5 g mol^{-1} can be produced, although the molar mass distribution is increased. The SEC chromatograms are clearly shifted towards the higher molar mass side with the reaction progress, in line with a continuous growth of the polymer chains (Fig. S15, ESI†). The low dispersity of the polymer is a clear indication of the fast initiation of the chains compared to the propagation step, again confirming the fast release of the initiating bromomethyl radical from **1**. Under these conditions, compound **1** therefore acts both as an initiator, through the release of a bromomethyl radical, and as a control agent by $Co(acac)_2$ that reversibly traps the growing chains through a reversible termination mechanism (Scheme 1b).

We then prepared a low molar mass PVAc (M_n = 2200 g mol^{-1}; $Đ$ = 1.14) by using a VAc/**1** molar ratio of 328 in order to probe the structure of the chain ends by NMR (Fig. S16 ESI†) and mass spectrometry analyses (Fig. S17, ESI†). At the end of the polymerization process, excess of propanethiol is added to irreversibly deactivate the propagating radical[23] and to avoid any side reaction during the polymer purification (Scheme S1, ESI†). Fig. S16 (ESI†) shows that, besides the typical signals characteristics to the main chain, ^{1}H-NMR analysis of the purified PVAc reveals resonances corresponding to the presence of the $Br–CH_2–$ group at 3.36 ppm (for the α-chain end) and $–CH_2OAc$ at 4.07 ppm (for the ω-chain end). The molar mass of the polymer calculated from the α- and the ω-chain ends is identical ($M_{n,NMR}$ = 2000 g mol^{-1}), attesting the complete deactivation of the chain by propanethiol.

Fig. S17 (ESI†) shows the MALDI mass spectrum recorded for the PVAc sample previously analyzed by NMR. The number averaged molecular weight determined by mass spectrometry is around 2160 g mol^{-1} ($Đ$ = 1.06), in agreement with that calculated by ^{1}H-NMR based on the structure of the chain ends. The isotopic pattern for all signals of the distribution clearly confirms the presence of the bromine atom in the polymer chains. As attested in Fig. S17c (ESI†), the comparison between the experimental data and the theoretical isotopic model confirms the presence of $Br–CH_2$ and hydrogen at α- and ω-chain ends, respectively.

In the same way, compound **2** also permits the control of the VAc polymerization (Fig. S18, ESI†). After quenching the reaction with propanethiol, well-defined PVAc chains are formed with $Cl–CH_2–$ and –H groups at the α- and ω-chain ends, respectively. The structure of these end-groups is corroborated by ^{1}H NMR (Fig. S19, ESI†) and MALDI-TOF analyses (Fig. S20, ESI†), with a very good agreement between molar mass calculated by NMR based on the α-chain ends ($M_{n,NMR}$ = 2100 g mol^{-1}) and by MALDI-TOF ($M_{n,MALDI}$ = 2110 g mol^{-1}).

These novel organocobalt compounds **1** and **2** give therefore access to polymer chains bearing the $X–CH_2–$ group at the α-chain end (Fig. 2a and Scheme S2, ESI†). The high lability of the C–Co bond at the ω-chain end can then be exploited for the facile design of telechelic polymers by cobalt-mediated radical coupling (CMRC).[24] Indeed, the addition of isoprene to PVAc produced by **2** quantitatively couples Cl–PVAc, forming the telechelic polymer (Cl–PVAc–Cl) with the doubling of the polymer molar mass (Fig. 3). MALDI-TOF analysis confirms the presence of the chloromethyl groups at both chain-ends and the doubling of M_n (Fig. S21, ESI†). As expected, at least two isoprene units are incorporated at the middle of the chain (Fig. S21, ESI† and related discussion). Signal characteristics of isoprene units are also detected by ^{1}H NMR (Fig. S22, ESI†).

Since compound **1** is soluble in water, we investigated its efficiency for initiating and controlling the radical polymerization in water of a hydrosoluble monomer, 1-vinyl-3-ethylimidazolium bromide (VEtImBr) (Fig. S23, ESI†). Fig. S23 and S24 (ESI†) illustrate the polymerization of VEtImBr with good control over the molar mass and low dispersity of the polymer formed at 40 °C. The polymerization is fast with no induction period and no organic cosolvent is

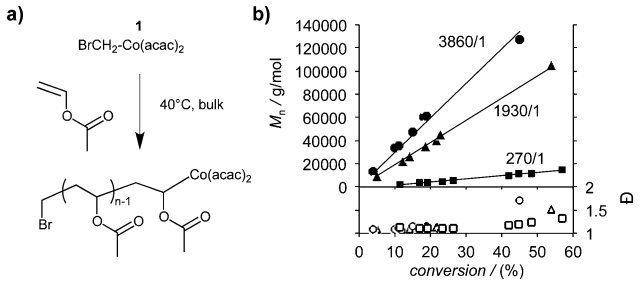


Fig. 2 OMRP of VAc initiated by **1** in the bulk at 40 °C: (a) reaction scheme and (b) plots of M_{nSEC} and $Đ$ evolutions *vs.* conversion for different [VAc]/[**1**] ratios. See S15 (ESI†) for SEC traces of [VAc]/[**1**] = 270, [VAc]/[**1**] = 1930 and [VAc]/[**1**] = 3860, and Table S5 (ESI†) for polymerization data.

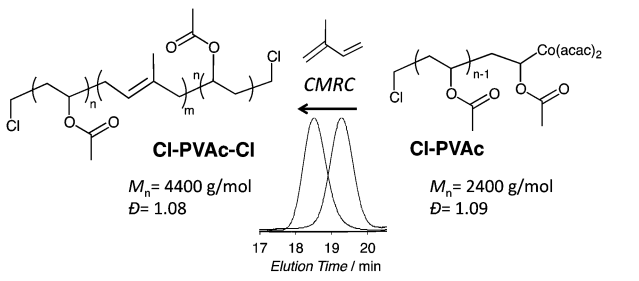
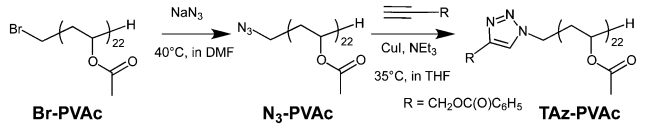


Fig. 3 Synthesis of telechelic PVAc and SEC chromatograms of PVAc before and after coupling with isoprene.



Scheme 2 Synthesis of α-azido PVAc, followed by the copper catalyzed azide–alkyne cycloaddition (CuAAC) reaction.

required. This experiment highlights the compatibility of compound **1** with water, opening new avenues for radical reactions in this important green solvent.

The utility of the halomethyl group at the α-chain end of the polymers is exemplified by the formation of novel α-azido functional PVAc, a keystone for the preparation of a plethora of end-functional PVAc (Scheme 2). Indeed, this azido group is extremely important for introducing various functional groups to polymer chain-end(s) or for preparing advanced polymer structures by exploiting the so-called copper catalyzed azide–alkyne cycloaddition (CuAAC) reaction.[25] Briefly, Br–PVAc prepared by **1** and deactivated by propanethiol is treated by NaN_3 in DMF to afford N_3–PVAc at 40 °C overnight. The completeness of the reaction is demonstrated by MALDI-TOF (Fig. S25, ESI†) and ^{1}H NMR analyses (Fig. S26, ESI†). A model alkyne, propargyl benzoate, is then successfully clicked by the CuAAC reaction using CuI as a catalyst in THF at 35 °C overnight (Fig. S25 for MALDI-TOF and Fig. S26 for ^{1}H NMR, ESI†).

In summary, we have developed an unprecedented one-pot silyl-radical assisted route to the synthesis of a novel family of organo-cobalts with nitrogen-free ligands and weak C–Co bonds. The XCH_2–$Co(acac)_2$ (X = Cl or Br) complexes are used for the fast generation of the halomethyl radical that enables the initiation of the controlled radical polymerization of less activated vinyl monomers under mild conditions, even when carried out in water. Well-defined polymers bearing a facile functionalizable halomethyl group at the α-chain end are now accessible and, by coupling the living chains, telechelic polymers are easily prepared. The halomethyl group at the chain end of the polymers is easily derivatized into azide functional polymers. Due to the importance of this functional group for click reactions with various alkynes, the synthesis of a multitude of novel end-functional polymers that are currently not accessible by OMRP can now be envisioned. Finally, besides numerous possible applications in macromolecular engineering, this unexplored family of organo-cobalt compounds presents a high potential in radical reactions in organic synthesis by the facile production of halomethyl radicals.

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