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Copper (I/II) and Cobalt (II) Coordination Chemistry of Relevance to Controlled Radical Polymerization Processes

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ABSTRACT

The reaction of various alkyl halides (1-bromoethylbenzene, BEB; 1-chloroethylbenzene, CEB; methyl iodide; 1-bromoethylacetate, BEA; and ethyl-2-bromopropionate, EBP with CuBr/L (L = bipy, Me₆TREN) has been investigated in the presence of [Co(acac)₂] or [Co(acac)₂]/py, with the goal of generating radicals by halogen atom transfer to Cu^I for subsequent trapping by Co^{II} and generation of an alkylcobalt(III) product. No evidence for the formation of the target product has been obtained. The various reactions, carried out under different conditions, have led to the crystallization of the following compounds: {[Cu(bipy)₂Br]⁺}₂{[Cu₂Br₄]²⁻}, **1**; [Cu(Me₆TREN)Br]Br; [Cu(Me₆TREN)Br_{0.37}Cl_{0.63}]Br, **2**; and *trans*-[Co(acac)₂(THF)₂], **3**; [Co(Me₆TREN)Br]Br, **4**; [Cu(Me₇TREN)I]{[Cu₂I₂-(Br_{0.628}I_{0.372})₂]_{0.9}[I]_{0.2}}, **5**; [C₆H₈N]₂[CoI₄], **6**; [Co(acac)₃]; and [Co(acac)₂(THF)₂CoBr₂], **7**. The structures of **1-7** have been determined by single-crystal X-ray diffraction.

KEYWORDS

Coordination Chemistry, Cobalt, Copper, Me₆TREN ligand, Controlled Radical Polymerization

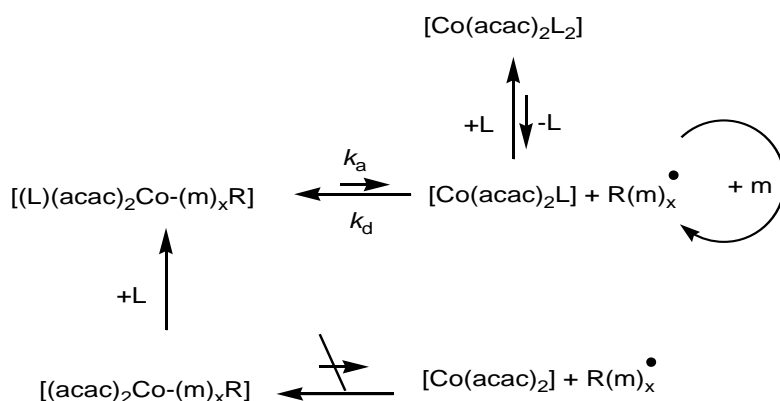
INTRODUCTION

Controlled radical polymerization (CRP) is the fastest developing field in modern polymer chemistry [1]. The scope and flexibility of this technique to access polymers with well-defined structure, chain length, and composition is unmatched by any other polymerization method. Although non-metal-based methods are also known, the coordination and organometallic chemistry of the transition metals involving one-electron processes (homolytic bond cleavage, atom transfer reactions) has been shown to be of fundamental importance in CRP [2].

There are three ways in which a transition metal complex can mediate CRP, all based on one-electron processes: (i) reversible halogen atom transfer to a reduced metal catalyst, termed atom transfer radical polymerization (ATRP) [3, 4]; (ii) homolytic cleavage of metal-carbon bonds, termed organometallic radical polymerization (OMRP) [5, 6]; (iii) degenerative transfer (DT), involving a rapid associative exchange between the active and dormant chains on a transition metal complex [7, 8]. Our group investigates the intimate details of coordination chemistry related to transition metal mediated CRP. We have developed a family of compounds capable of simultaneous control by ATRP and OMRP [9-11], rationalized the effect of certain Lewis acid promoters [12, 13] and explained reason for the observation of low initiator efficiencies under certain conditions [14]. The possible interplay of various one-electron processes in CRP has been recently outlined in a review [2].

Of current interest is the unique ability of compound $\text{Co}(\text{acac})_2$ to mediate the CRP of vinyl acetate (VAc), a challenging monomer for which previous attempts by ATRP and OMRP methods had failed. This compound was recently reported to provide excellent control by a proposed OMRP mechanism for a bulk polymerization (*i.e.* without solvent or additives) [15, 16], but our studies have in fact demonstrated its action through a DT mechanism under these conditions, though the mechanism switches to OMRP in the presence of neutral donors [17].

The reasons for this behavior are summarized in Scheme 1. Whereas the Co-C bond in the organometallic dormant chain is not weak enough to afford a significant free radical concentration in the absence of ligand, stabilization of the Co^{II} radical trap by further coordination of L to give 6-coordinate $[\text{Co}(\text{acac})_2\text{L}_2]$ shifts the radical formation equilibrium and allows the CRP to be sustained by the OMRP mechanism. The 6-coordinate, L-bonded Co^{III} dormant chain cannot undergo DT because it is coordinatively saturated, whereas the 5-coordinate ligand-free chain, $[(\text{acac})_2\text{Co}-(\text{m})_x\text{R}]$, is able to promote DT. In a more recent contribution, we have carried out computational investigations on the nature of the Co^{III} chain-end [18]. However, no simple alkylcobalt(III) compound that could represent a model of the OMRP dormant chain or DT transfer agent has so far been isolated and characterized with the acetylacetonate ligand environment, $[\text{RCo}(\text{acac})_2]$ or $[\text{RCo}(\text{acac})_2\text{L}]$. This is in contrast with other alkylcobalt(III) species, containing for instance a porphyrin ligand environment [19-21].



Scheme 1. Influence of ligand coordination to the mechanism of $[\text{Co}(\text{acac})_2]$ -mediated CPR of VAc.

We have therefore set out to prepare one such compound. This particular synthetic target does not appear straightforward. With supporting ligands such as porphyrin or Schiff bases, organylcobalt(III) products are easily accessed by first reducing $\text{Co}^{\text{II}}\text{L}$ to $[\text{Co}^{\text{I}}\text{L}]^-$, followed by

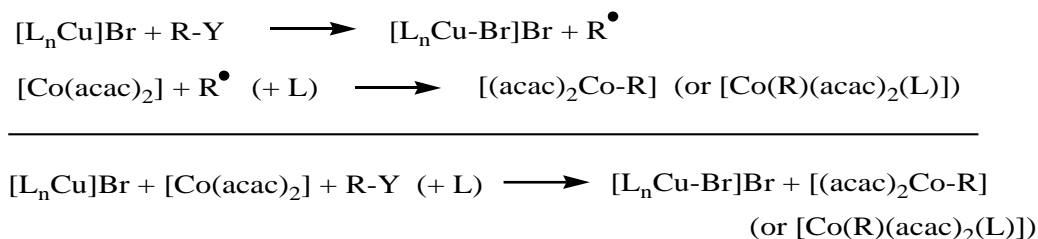
reaction with an alkyl halide [19, 20, 22]. The hard acac ligand, however, does not provide sufficient stability to the putative $[\text{Co}(\text{acac})_2]^-$ anion. A few derivatives have also been prepared by alkylation of halocobalt(III) reagents [23]. However, $[\text{Co}^{\text{III}}(\text{acac})_2\text{Y}]$ (Y = halogen) are non-existing compounds. A final method leading to organylcobalt(III) compounds is one-electron oxidative addition of alkyl halides to Co^{II} reagents [23], see Scheme 2, a drawback being that half of the Co^{II} reagent is sacrificed for making the $\text{Co}^{\text{III}}\text{-Y}$ by-product.



Scheme 2. Generation of R-Co^{III} products by one-electron oxidative addition of R-Y to Co^{II} precursors.

However, we find that no reaction takes place between $[\text{Co}(\text{acac})_2]$ and BEB, which is a quite active alkyl halide (weak C-Y bonds). The reason for this lack of reactivity may be thermodynamic: cobalt prefers to remain in the +II oxidation state with hard ligands such as acac, and the co-product $[\text{Co}(\text{acac})_2\text{Y}]$ (which is non-existent as already mentioned) does not provide sufficient thermodynamic help to achieve the oxidative addition process. A possible key to alleviate this problem is therefore to use a stronger halogen acceptor. We have considered the use of the Cu^{I} system CuBr/L (L = N-based ligand such as hexamethyl-tris(aminoethyl)amine (Me_6TREN) or 2,2'-bipyridine (bipy)). It has already been reported that CuBr/L systems abstract efficiently halide radicals from alkyl halides, forming the related Cu^{II} products [24-27], while Cu^{I} does not have sufficient affinity for carbon-based radicals [28]. Indeed, this is the basis for the high efficiency of this family of Cu^{I} systems as ATRP catalysts [3]. Some of these complexes, especially the *in situ* made $[(\text{Me}_6\text{TREN})\text{CuBr}]$, are very rapid under very mild conditions (room temperature or below) [29]. In this manner, we were hoping that alkyl radicals could be efficiently trapped by $[\text{Co}(\text{acac})_2]$. Scheme 3 shows the reaction pathway envisaged for

this transformation, which could be carried out in the presence of an additional monodentate ligand L, such as pyridine. Indeed, the organylcobalt(III) product should be stabilized by addition of a neutral ligand, with formation of a 6-coordinate $[\text{Co}(\text{R})(\text{acac})_2(\text{L})]$ complex, because low-spin Co^{III} is known to strongly prefer an octahedral coordination environment.



Scheme 3. Possible reaction pathway for alkyl halides in the presence of $[\{\text{Me}_6\text{TREN}\}\text{Cu}]\text{Br}$ and $[\text{Co}(\text{acac})_2]$.

In this contribution, we present the results of synthetic efforts along these lines. Unfortunately, we have not attained our desired goal, because many side reactions take place as will be discussed in detail in the Results and Discussion section. However, the isolated and characterized compounds present some novelty in $\text{Cu}^{\text{I/II}}$ and Co^{II} coordination chemistry and may therefore represent useful reference for future work in CRP by the use of these metal systems.

RESULTS AND DISCUSSION

Reaction of $[\text{Cu}(\text{bipy})_2]\text{Br}$ and 1-bromoethylbenzene

We started our studies with the CuBr/bipy system, since the ligand is easily available. This is known to form the salt-like compound $[\text{Cu}(\text{bipy})_2]^+\text{Br}^-$ in solution [30]. However, this compound is not one of the fastest activators for ATRP (*i.e.* capable of generating free radicals

from an alkyl halide at a high rate under mild conditions) [29]. The rate of radical generation depends on the C-Y bond strength of the halide compound used [31], therefore we restricted our studies with this copper complex to the relatively active initiator 1-bromoethylbenzene (BEB). The reaction was carried out in MeOH at room temperature, leading to the immediate formation of a red precipitate after the addition of CuBr, signaling the formation of a Cu(II) product. This compound was crystallized and characterized by X-ray diffraction.

The X-ray determination revealed the formation of the mixed valence Cu(I)/Cu(II) salt $\{[\text{Cu}(\text{bipy})_2\text{Br}]^+\}_2\{[\text{Cu}_2\text{Br}_6]^{2-}\}$ (**1**) (Figure 1). Selected bond lengths and distances are shown in Table 1. The structure of **1** features a centrosymmetric $[\text{Cu}_2\text{Br}_6]^{2-}$ ion, which sits on twofold axis, and two symmetry-related $[\text{Cu}(\text{bipy})_2\text{Br}]^+$ cations. The Cu(II) cation is in a distorted trigonal bipyramidal coordination, with axial Cu-N bonds of 1.981(2) and 1.987(2) Å while longer Cu-N bonds of 2.070(2) and 2.083(3) Å occur in the equatorial positions as well as the Cu-Br bond with 2.4936(9) Å. The monovalent Cu2 site adopts a trigonal planar CuBr_3 coordination, with Cu2-Br2 (bridging) bonds of 2.4689(10) Å and Cu2-Br3 (terminal) bonds of 2.3215(12) Å. The structure of the cation has already been reported in the simpler $[\text{Cu}(\text{bipy})_2\text{Br}]\text{Br}$ salt [32], as well as with other anions [33-36] and the $[\text{Cu}_2\text{Br}_6]^{2-}$ dianion has also been crystallographically characterized in other compounds [37-45]. All bond distances are in good agreement with those reported in the above cited structures.

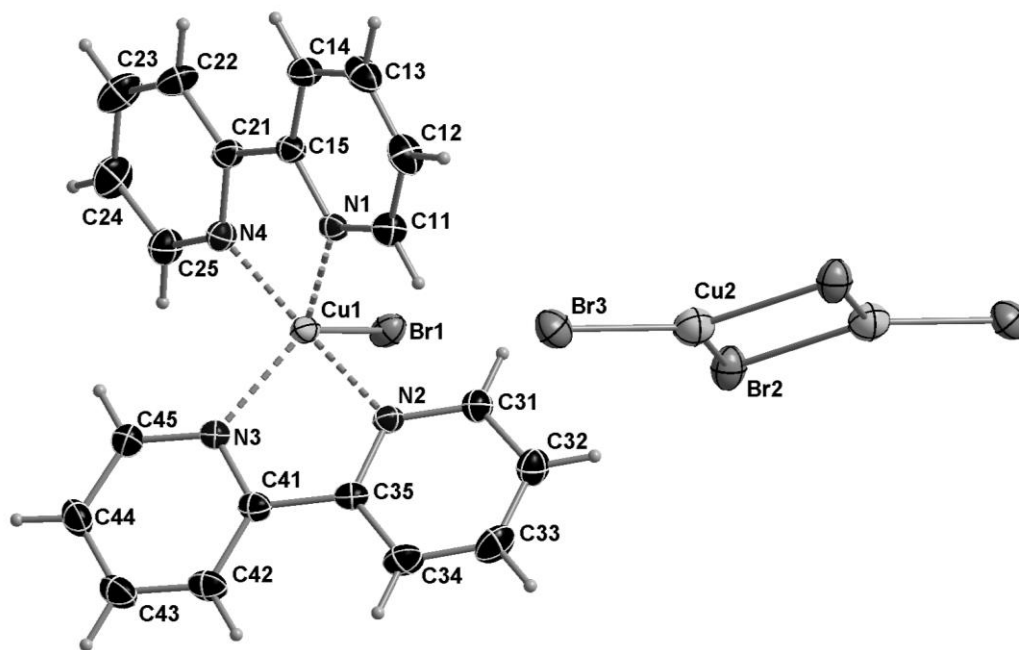


Figure 1. Molecular structure of **1** at 180 K (50% probability ellipsoids).

The formation of this compound can be understood on the basis of bromine atom transfer from BEB to $[\text{Cu}(\text{bipy})_2]^+$ to generate the Cu^{II} cation $[\text{Cu}(\text{bipy})_2\text{Br}]^+$, while the Br^- ion is trapped by additional CuBr to yield the Cu^{I} dianion $[\text{Cu}_2\text{Br}_4]^{2-}$. Thus, not all CuBr has reacted with bipy, or perhaps bipy coordination is reversible and these particular crystallization conditions favor the precipitation of this ion combination. Other mixed-valence $\text{Cu}^{\text{I}}/\text{Cu}^{\text{II}}$ salts have previously been obtained, for instance $[\text{Cu}^{\text{II}}(\text{dNpby})_2\text{Br}]^+[\text{Cu}^{\text{I}}\text{Br}_2]^-$ where $\text{dNpby} = 4,4'$ -di(5-nonyl)-2,2'-bipyridine [46], but the anion is a linear mononuclear $[\text{Br}-\text{Cu}-\text{Br}]^-$ complex in this compound. It seems that small subtleties tip the choice of the Cu^{I} anion for a mononuclear ($[\text{CuBr}_2]^-$) or dinuclear ($[\text{Cu}_2\text{Br}_4]^{2-}$) form.

Table 1. Selected bond distances (Å) and angles (deg) for $[\text{Cu}(\text{bipy})_2\text{Br}]_2[\text{Cu}_2\text{Br}_4]$, **1**.^a

Cu1—N2	1.981(2)	N4—Cu1—N1	80.29(9)	Br2 ⁱ —Cu2—Cu2 ⁱ	55.64(3)
Cu1—N4	1.987(2)	N2—Cu1—N3	80.01(10)	Br2—Cu2—Cu2 ⁱ	53.27(3)

Cu1—N1	2.070(2)	N4—Cu1—N3	100.68(10)	Cu2 ⁱ —Br2—Cu2	71.09(4)
Cu1—N3	2.083(3)	N1—Cu1—N3	123.74(9)	C11—N1—Cu1	128.16(19)
Cu1—Br1	2.4936(9)	N2—Cu1—Br1	92.16(7)	C15—N1—Cu1	113.28(18)
Cu2—Cu2 ⁱ	2.8295(16)	N4—Cu1—Br1	90.86(8)	C35—N2—Cu1	116.64(19)
Cu2—Br3	2.3215(12)	N1—Cu1—Br1	117.65(7)	C31—N2—Cu1	123.69(19)
Cu2—Br2 ⁱ	2.3973(8)	N3—Cu1—Br1	118.57(7)	C45—N3—Cu1	128.89(19)
Cu2 ⁱ —Br2	2.3972(8)	Br3—Cu2—Br2 ⁱ	127.39(3)	C41—N3—Cu1	112.92(19)
Cu2—Br2	2.4689(10)	Br3—Cu2—Br2	123.70(4)	C25—N4—Cu1	124.6(2)
N2—Cu1—N4	176.1(1)	Br2 ⁱ —Cu2—Br2	108.91(4)	C21—N4—Cu1	116.07(18)
N2—Cu1—N1	96.12(9)	Br3—Cu2—Cu2 ⁱ	176.96(3)		

^a(i): 3-x, -y, 2-z

The formation of compound **1** suggests that CH₃(Ph)CH[•] radicals are being produced, therefore this reaction was repeated in the presence of [Co(acac)₂]. However, the course of the reaction did not change and there was no spectroscopic evidence for the formation of an alkylcobalt(III) derivative. It is possible that the Co-CH(CH₃)Ph bond is too weak to be formed in an irreversible fashion at room temperature. Therefore, we have tried to generate these radicals at lower temperatures with a more active Cu complex.

Reaction of CuBr(Me₆TREN) and 1-bromoethylbenzene or 1-chloroethylbenzene

Me₆TREN, in combination with CuBr, provides one of the fastest initiating systems in copper mediated CRP. In order to insure sufficient solubility of all materials at low temperature, we switched solvent to THF. As already described [47], complexes [Cu(Me₆TREN)X] (X = Cl, Br, I) that form by combination of CuX and Me₆TREN are not stable at room temperature, yielding fast disproportionation into Cu⁰ and [Cu^{II}(Me₆TREN)X]X and are also quite sensitive to aerial oxidation. This has been confirmed in our study: the disproportionation can be easily observed by the development of a green color, characteristic of the Cu^{II} system, from the colorless solution of the Cu^I complex. At lower temperatures and under strict exclusion of air and moisture the solution remains colorless.

Addition of BEB (1 equiv.) and [Co(acac)₂] led to the isolation of light green single-crystals, which were identified as the already reported [48] [Cu(Me₆TREN)Br]Br. The same reaction was worked out using 1-chloroethylbenzene (CEB) instead of BEB, with similar results. Single-crystal structure determination of the green crystals revealed the formation of [Cu(Me₆TREN)Br_{0.37}Cl_{0.63}]Br (**2**). Selected bond lengths and angles for compound **2** are shown in Table 2 and the molecular structure is shown in Figure 2. This structure is isomorphous with that of the all-Br analogue. The only difference is a compositional Cl/Br disorder in the Cu-bonded position, but not in the free anion. This selectivity is probably related to the lower solubility of the bromide salt, joint with the lower activation barrier for nucleation and crystal growth relative to the barrier for Cl/Br exchange between the coordinated and free position. The Cu atom adopts a trigonal bipyramidal coordination geometry, with the axial Cu-N1 and Cu-Cl/Br bonds coinciding with the crystallographic threefold axis. The axial Cu-N bond is significantly shorter than the equatorial one. Because of the mixed Cl/Br position, the Cu-Cl/Br distance does not carry any chemical meaning. As expected, it is shorter compared to the Cu-Br bond in the all-Br analogue (2.393(3) Å) [48] while it is longer than the Cu-Cl distance in [Cu(Me₆TREN)Cl]⁺ (2.234(2) Å) [47]. The trigonal bipyramidal environment is only slightly distorted with N1-Cu-N2 angles of 84.19(9)° and N2-Cu-N2ⁱ angles of 118.99(3)°.

Table 2. Selected bond distances (Å) and angles (deg) of [Cu(Me₆TREN)Br_{0.37}Cl_{0.63}]Br, **2**.^a

Cu1—N1	2.062(6)	N1—Cu1—Cl1 Br1	180.00(8)	C1—N1—C1 ⁱ	109.9(2)
Cu1—N2	2.149(3)	N2—Cu1—Cl1 Br1	95.81(9)	C2—N2—Cu1	104.5(2)
Cu1—Cl1 Br1	2.3170(14)	N1—Cu1—N2	84.19(9)	C3—N2—Cu1	114.7(2)
N1—C1	1.493(4)	N2—Cu1—N2 ⁱ	118.99(3)	C4—N2—Cu1	111.7(2)
N2—C2	1.477(5)	N1—C1—C2	110.1(3)	C3—N2—C2	109.5(3)
N2—C3	1.476(5)	N2—C2—C1	109.5(3)	C4—N2—C3	107.0(3)
N2—C4	1.472(5)	C1—N1—Cu1	109.0(2)	C4—N2—C2	109.4(3)

^a(i) 0.5+y, 0.5-z, 1-x

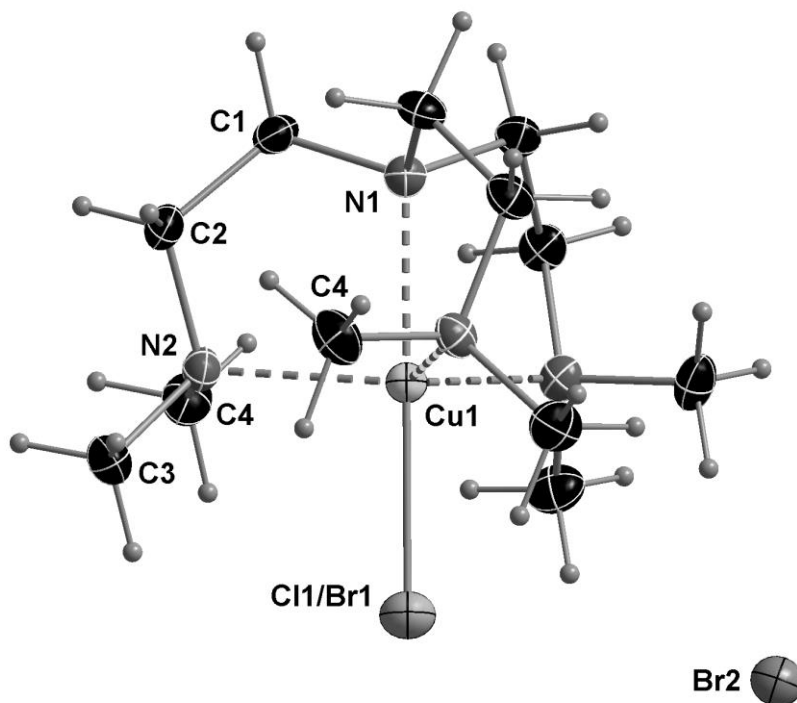


Figure 2. Molecular structure of **2** at 180 K (50% probability ellipsoids).

The formation of these Cu^{II} complexes confirms the fast and effective oxidation of Cu^{I} by halogen atom transfer from the organic halide molecule, therefore implying the formation of $\text{CH}_3(\text{Ph})\text{CH}^\bullet$ radicals in solution. The above reactions yielded a pink/red THF solution as the mother solution of the isolated crystals. There was no indications from spectroscopic analyses that the formation of an alkylcobalt(III) compound had taken place, while attempts to crystallize the pink/red component soluble in THF were not successful. We conclude that, even at lower temperatures, the $\text{Co}^{\text{III}}\text{-CH}(\text{CH}_3)\text{Ph}$ bond is probably too weak to withstand reversible homolytic rupture and ultimately leads to decomposition with formation of the typical radical decomposition products (coupling to $\text{PhCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{Ph}$ and disproportionation to ethylbenzene and styrene).

Reaction of CuBr(Me₆TREN) and ethyl-2-bromopropionate

Using this organic halide, no apparent reaction occurred at low temperature, indicating that the C-Br bond is less susceptible to atom transfer than that of BEB. Warming the solution to room temperature led to the development of a green color, which yielded crystals of Co(acac)₃. When the same reaction was repeated and maintained at low temperature for an extended period, red crystals were isolated, corresponding to the THF solvate complex [Co(acac)₂(THF)₂], **3**.

Compound **3** is only stable at low temperature and decomposes by solvent loss upon standing for longer than 5 min under mineral oil at ambient temperature. The Co^{II} ion has an octahedral coordination with the two acac ligands in equatorial positions and THF in the axial positions. A two-fold axis is situated in the metal centre of the molecule (Figure 3). Many X-ray structures of *trans*-[Co(acac)₂(L)₂] derivatives have been previously published (L = py, H₂O, CH₃OH, imidazole, etc.) [49-54], but that with THF had not yet been reported. The THF molecules show disorder with half of the molecules oriented in two different envelope conformations. Selected bond distances and angles are shown in Table 3. The Co-O(acac) bond lengths are in good agreement with those reported for the above mentioned other solvent adducts, as well as with those of solvent-free [Co(acac)₂] [51, 55], where in fact the coordination environment is pseudo-octahedral due to skewed stacking with neighboring molecules. The Co-O(THF) distances are significantly longer than the Co-O(acac) bonds. This result is quite logical considering that a neutral solvent molecule should be more weakly bonded to the metal centre compared to the anionic acac ligand.

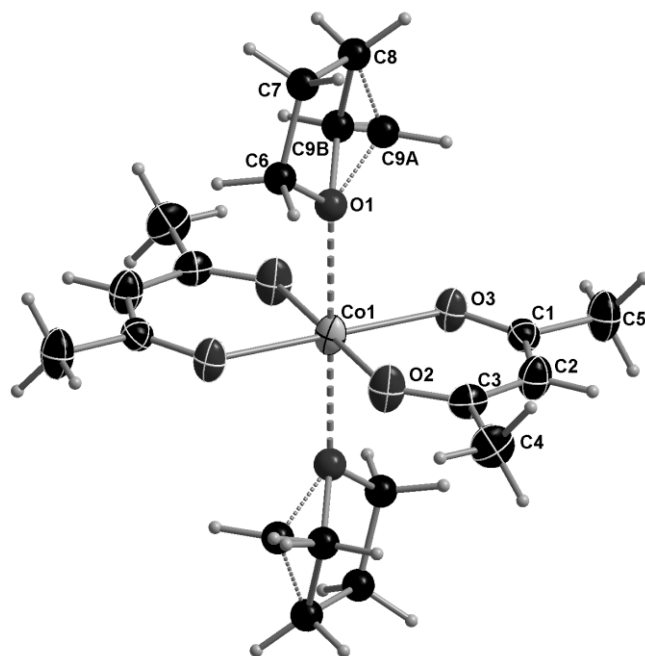


Figure 3. Molecular structure of **7** at 160 K (50% probability ellipsoids).

Table 3. Selected bond distances (Å) and angles (deg) of [Co(acac)₂THF₂], **3**.^a

Co1—O1	2.163(2)	O2—Co1—O2 ⁱ	180.00(14)	O2—Co1—O1 ⁱ	89.4(1)
Co1—O2	2.012(2)	O2—Co1—O3 ⁱ	90.38(9)	O2 ⁱ —Co1—O1 ⁱ	90.6(1)
Co1—O3	2.025(2)	O2 ⁱ —Co1—O3 ⁱ	89.62(9)	O3 ⁱ —Co1—O1 ⁱ	90.16(9)
O1—C6	1.414(4)	O2—Co1—O3	89.62(9)	O3—Co1—O1 ⁱ	89.84(9)
O1—C9A	1.452(14)	O2 ⁱ —Co1—O3	90.38(9)	C6—O1—Co1	126.4(2)
O1—C9B	1.440(14)	O2—Co1—O1	90.6(1)	C9B—O1—Co1	120.1(6)
O2—C3	1.253(4)	O2 ⁱ —Co1—O1	89.4(1)	C9A—O1—Co1	122.5(6)
O3—C1	1.258(3)	O3 ⁱ —Co1—O1	89.84(9)	C3—O2—Co1	126.5(2)
		O3—Co1—O1	90.16(9)	C1—O3—Co1	125.58(19)

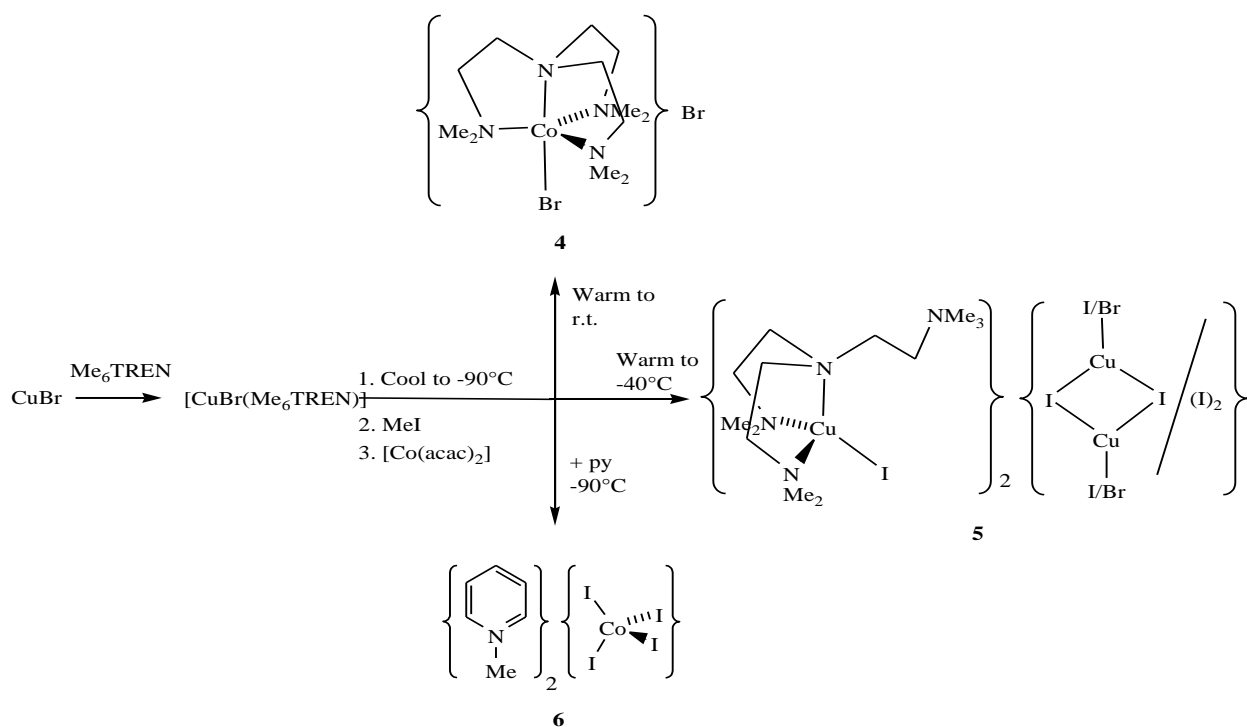
^a(i) -x, -y, 1-z

The isolation of compound **3** is not to be considered surprising, since the solution contains [Co(acac)₂] in THF, thus the bis-adduct is certainly present, at least in equilibrium amounts,

especially at low temperatures. The recovery of **3** gives no indication as to whether or not the Cu^I reagent has abstracted a halogen atom.

Reaction of CuBr(Me₆TREN) and methyl iodide

We have next turned our attention to an alkyl halide that would yield a stronger Co-C bond. The homolytic bond dissociation energy of R-X bonds for a variety of R groups and for X = Cl, Br, I has been the subject of a computational study [18]. Methyl is the alkyl group at the top of the list. Although not yet supported by an extensive computational investigation on an homologous series of organometallic compounds, it may be anticipated that the strength of M-R bonds should roughly parallel that of R-X bonds, thus the (acac)₂Co-CH₃ bond is expected to have a reasonable strength. Indeed, recent calculations have shown that (acac)₂Co-R bonds with R = CH₃(X)CH[•] (X = CH₃O, CH₃COO and CH₃OOC) are weaker than with R = CH₃ [18]. On the other hand, the strength of CH₃-X increases in the order X = I < Br < Cl. Thus, Me₃Cl should be difficult to activate. We have chosen to work with CH₃I, also in consideration of the fact that this compound is a volatile liquid and therefore easier to handle. Several reactions were carried out at different temperatures and with different order of reagent addition, but no alkylcobalt(III) compound was crystallized under any circumstances. The products that were crystallized are summarized in Scheme 4.



Scheme 4. Products generated by the reaction of $[\text{Co}(\text{acac})_2]$ with MeI in the presence of $[\text{Cu}(\text{Me}_6\text{TREN})\text{Br}]$.

*Structure of $[\{\text{Me}_6\text{TREN}\}\text{CoBr}]\text{Br}$, **4***

The violet crystals of **4** reveal a trigonal bipyramidal coordination geometry around the Co^{II} center with axial Co-N and Co-Br bonds and three equatorial Co-N bonds. The most important distances and angles are listed in Table 4, whereas the molecular structure is shown in Figure 4. This structure is already reported in the literature, but based on data collected at room temperature and much less precisely determined [56]. The structure is also isomorphous with those of **2** and the all-Br analogue, $[\text{Cu}(\text{Me}_6\text{TREN})\text{Br}]\text{Br}$, discussed above. As expected, all distances are slightly longer in **3** than in the Cu analogue, because of the slightly larger ionic radius of Co^{II} .

Table 4. Selected bond distances (\AA) and angles (deg) of $[\text{Co}(\text{Me}_6\text{TREN})\text{Br}]\text{Br}$, **4**.^a

Co1-N1	2.137(2)	N1-Co1-Br2	98.83(6)	C3-N2-Co1	108.15(17)
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Co1—N2	2.215(4)	N2—Co1—Br2	180.00(6)	N1—C2—C3	110.2(2)
Co1—Br2	2.4471(7)	N1—Co1—N1 ⁱ	117.69(3)	N2—C3—C2	110.1(2)
N1—C1	1.488(4)	N1—Co1—N2	81.17(6)	C1—N1—C4	106.9(2)
N1—C2	1.484(3)	C1—N1—Co1	113.21(17)	C2—N1—C1	109.4(2)
N1—C4	1.491(3)	C2—N1—Co1	107.67(17)	C2—N1—C4	109.6(2)
N2—C3	1.484(3)	C4—N1—Co1	109.91(16)	C3—N2—C3 ⁱ	110.76(16)

^a(i) 0.5-z, 1-x, -0.5+y

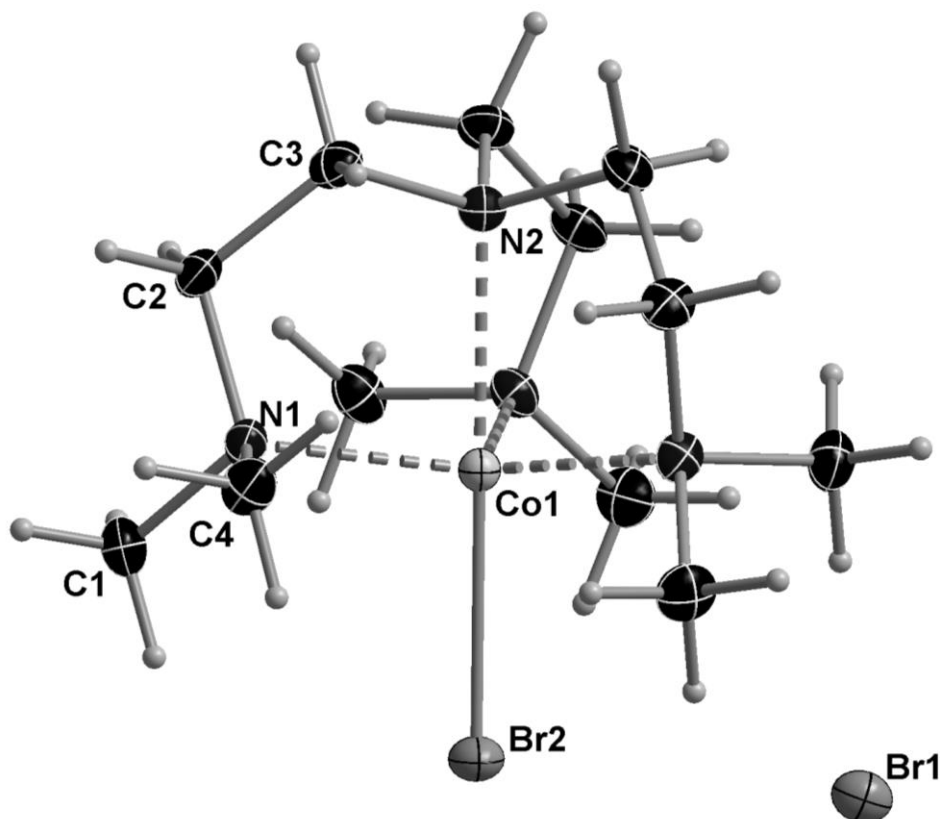
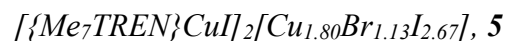


Figure 4. Molecular structure of **4** at 150 K (50% probability ellipsoids).



This structure features ordered $[Cu(Me_7TREN)I]^+$ ions in the cationic sites, whereas the anionic sites are occupied by a compositional disorder of $[Cu_2I_2(I/Br)_2]^{2-}$ and free I^- ions. There are two cations per each anionic site, with one full cation and half the dianion in the asymmetric unit around an inversion center. Overall, all Cu species are in the oxidation state I, explaining the almost colorless aspect of the crystals. Figure 5 shows a representation of the molecule with

the dinuclear Cu^I dianion. Whereas the I3 site is fully occupied, the Cu2 and Br2/I2 sites refine with 90% occupancy. Moreover, the terminal halide position is a compositional disorder of atoms Br2 and I2 in a 62.8:37.2 ratio. Thus, the structure may be described as [Cu(Me₇TREN)-I] {[Cu₂I₂(Br_{0.628}I_{0.372})₂]_{0.9}[I]_{0.2}}, with 90% of the molecules having the disordered [Cu₂I₂(Br_{0.628}I_{0.372})₂]²⁻ ion and 10% having two I⁻ ions. This kind of crystallographic defect is well known for its ability to change the color of a correct structure significantly [57]. Selected distances and angles for this compound are listed in Table 5.

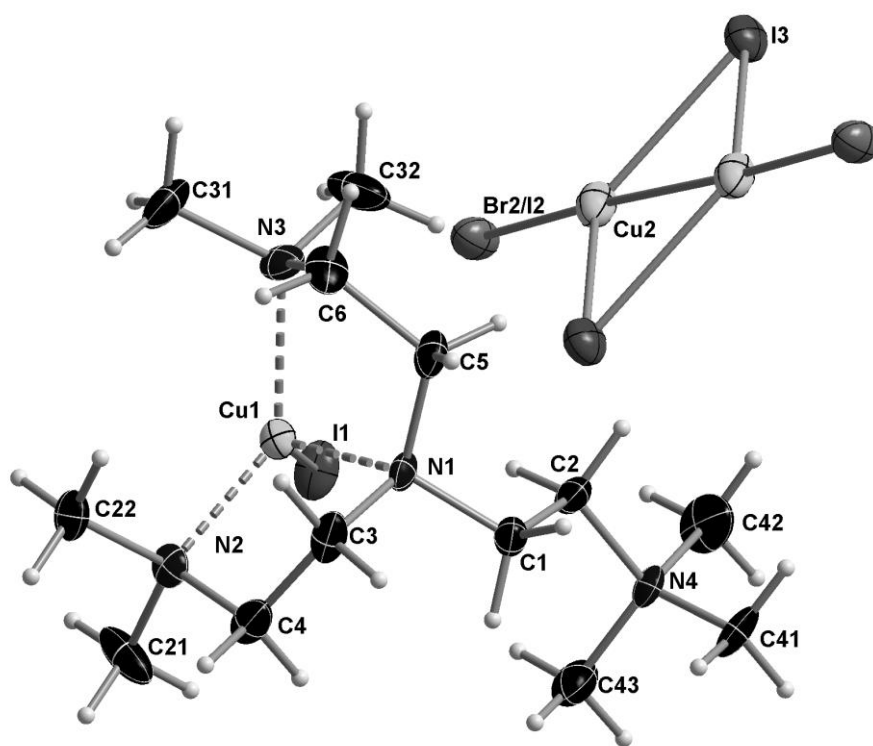


Figure 5. Molecular structure of **5** at 160 K (50% probability ellipsoids).

Table 5. Selected bond distances (Å) and angles (deg) of [Cu(Me₇TREN)I]₂[Cu_{1.8}Br_{1.13}I_{2.67}], **5**.^a

Cu1—N3	2.123(9)	N3—Cu1—N2	119.9(4)	I ⁱ —Cu2—Cu ⁱ	58.99(7)
Cu1—N2	2.131(9)	N3—Cu1—N1	83.7(4)	Cu2—I3—Cu ⁱ	61.80(7)

Cu1—N1	2.270(9)	N2—Cu1—N1	84.3(4)	C1—N1—Cu1	119.1(7)
Cu1—I1	2.5034(16)	N3—Cu1—I1	116.6(3)	C5—N1—Cu1	105.3(7)
Cu2—Br2/I2	2.432(2)	N2—Cu1—I1	117.3(3)	C3—N1—Cu1	102.2(7)
Cu2—I3	2.535(2)	N1—Cu1—I1	127.4(2)	C21—N2—Cu1	112.5(7)
Cu2—I3 ⁱ	2.541(2)	Br2/I2—Cu2—I3	120.69(8)	C22—N2—Cu1	114.4(7)
Cu2—Cu2 ⁱ	2.607(4)	Br2/I2—Cu2—I3 ⁱ	121.01(8)	C4—N2—Cu1	103.4(7)
I3—Cu2 ⁱ	2.541(2)	I3—Cu2—I3 ⁱ	118.20(7)	C31—N3—Cu1	114.0(8)
		Br2/I2—Cu2—Cu2 ⁱ	176.96(12)	C6—N3—Cu1	105.0(7)
		I3—Cu2—Cu2 ⁱ	59.21(7)	C32—N3—Cu1	108.4(7)

^a(i) -x, -2-y, 1-z

The Cu(I) cation is better described as a distorted trigonal pyramid than as a tetrahedron, with the Cu1-N3, Cu1-N2 and Cu1-I1 bonds being close to a trigonal planar arrangement with angles close to 120° (sum of the three angles = 353.8°), while a longer Cu1-N1 bond is located on the apex of the pyramid. This distortion is caused by the tridentate nature of the N₃ ligand, forcing the *cis*-N-Cu-N angles to be significantly smaller than the ideal tetrahedral value (N2-Cu1-N1: 84.3(4)°; N1-Cu1-N3: 83.7(4)°). Other cations with the same CuN₃I coordination environment around 4-coordinate Cu^I and with similar open tridentate N₃ ligands show the same distortion [58-62], while complexes with three monodentate N-donors or with symmetric *cyclo*-N₃ ligands adopt a more regular tetrahedral geometry [39, 63-69]. The Cu2 site is in a trigonal planar coordination, like the [Cu₂Br₄]²⁻ ion of compound **1**. A number of structures containing the [Cu₂I₄]²⁻ ion have been previously reported [63-66], but no related structure with a compositional Br/I disorder has been described so far, to the best of our knowledge. The localization of the disorder in the terminal position suggests that the softer iodide anion has a stronger preference for the bridging site.

[C₅H₅NMe]₂[CoI₄], 6

When the reaction was carried out as outlined above at -90 °C, except that pyridine was added in the hope of stabilizing an alkylcobalt(III) product in the form of a 6-coordinate

complex, methylation of pyridine took place, as shown by the X-ray structure of a new compound with the composition $[\text{C}_6\text{H}_8\text{N}]_2[\text{CoI}_4]$, **6**. A view of the molecule is shown in Figure 6. The entire molecule, which is composed by two N-methylpyridinium cations and by a tetrahedral $[\text{CoI}_4]^{2-}$ dianion, is contained in the asymmetric unit. Selected bond lengths and distances are listed in Table 6. The geometry around Co^{II} is very close to ideal tetrahedral, with all I-Co-I angles laying between 107.3 and 112.8° . The Co-I bond distances of $2.583 - 2.608 \text{ \AA}$ coincide very well with those found in other compounds containing the same dianion [70-73].

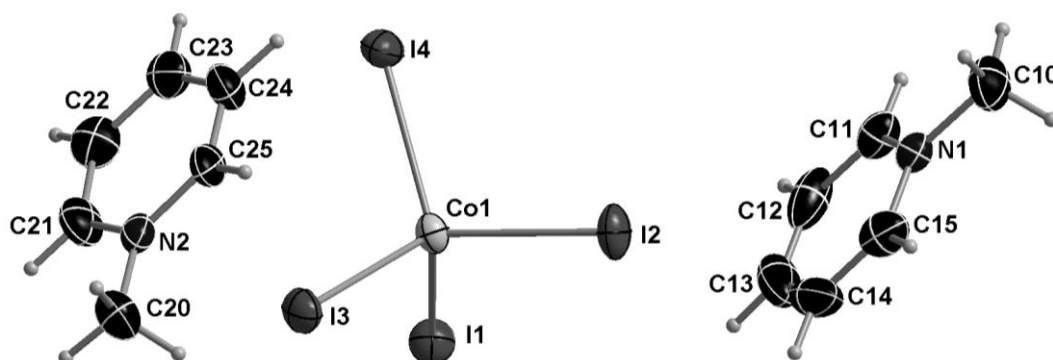


Figure 6. Molecular structure of **6** at 180 K (50% probability ellipsoids).

Table 6. Selected bond distances (\AA) and angles (deg) of $[\text{C}_6\text{H}_8\text{N}]_2[\text{CoI}_4]$, **6**.

Co1—I1	2.6084(8)	I1—Co1—I2	108.64(3)	C10—N1—C11	119.6(5)
Co1—I2	2.6030(8)	I1—Co1—I3	107.40(3)	C10—N1—C15	120.6(5)
Co1—I3	2.5828(7)	I1—Co1—I4	112.10(3)	C11—N1—C15	119.8(5)
Co1—I4	2.5943(8)	I2—Co1—I3	112.80(3)	C20—N2—C21	120.5(5)
N1—C10	1.477(7)	I2—Co1—I4	107.29(3)	C20—N2—C25	119.1(5)
N2—C20	1.463(7)	I3—Co1—I4	108.68(3)	C21—N2—C25	120.2(5)
N1—C11	1.344(6)			N1—C11—C12	120.8(6)
N1—C15	1.339(7)			N1—C15—C14	120.7(6)
N2—C21	1.336(7)			N2—C21—C22	120.6(5)
N2—C25	1.333(6)			N2—C25—C24	120.6(5)

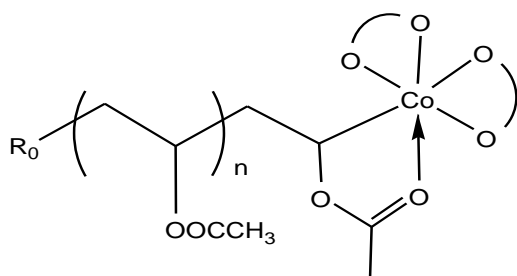
[18]

The nature of the identified compounds resulting from this reaction (Scheme 4) brings us to the following conclusions. First, it is quite surprising to see how readily the acac ligand is displaced from Co^{II} , in spite of the chelate effect associated with this ligand. Two of the characterized compounds feature the Co^{II} ion surrounded by other ligands, in the 5-coordinate $[\text{Co}(\text{Me}_6\text{TREN})\text{Br}]^+$ cation and in the 4-coordinate $[\text{CoI}_4]^{2-}$ dianion. Second, the electrophilic reactivity of MeI prevails on the homolytic rupture of the C-I bond and yields methylation of the Me_6TREN and py ligands, affording products that contain the $(\text{Me}_7\text{TREN})^+$ and $(\text{C}_5\text{H}_5\text{NMe})^+$ ions. One curious observation is that compound **4** contains only bromide and no iodide, including as free anion, even though it is obtained under very similar conditions as compound **5** where plenty of iodide enters the coordination sphere of the metal in both cation and anion.

Reaction of $\text{CuBr}(\text{Me}_6\text{TREN})$ and 1-bromoethylacetate

Until now, we have found that the $\text{CH}_3(\text{Ph})\text{CH}^\bullet$ radicals are too stabilized to afford sufficiently strong R-Co^{III} bonds, whereas MeI, which should lead in principle to a stable $\text{Me-Co}^{\text{III}}$ derivative, prefers to yield complex products of nucleophilic substitution at carbon and subsequent halide and neutral ligand exchange processes between copper and cobalt. In light of these results, our last attempt involved a halide molecule that is precursor of a radical of intermediate strength: $\text{CH}_3(\text{CH}_3\text{COO})\text{CH}^\bullet$. Indeed, the $[\text{Co}(\text{acac})_2]$ complex controls the VAc polymerization by reversibly trapping the PVAc^\bullet growing chain, $\text{R}_0\{\text{CH}_2\text{CH}(\text{OOCCH}_3)\}_n\text{CH}_2(\text{CH}_3\text{COO})\text{CH}^\bullet$, forming a Co^{III} -capped dormant chain as represented in Scheme 5 (R_0 = radical derived from the initiator) [15, 17]. Another indication that the above-mentioned radical should lead to a stable adduct is the recent isolation of a mixture of cobalt-capped short oligomers by thermally decomposing the mild radical initiator V-70 in the

presence of VAc and a large excess of $[\text{Co}(\text{acac})_2]$. The product was assigned the structure shown in Scheme 5, where $\text{R}_0 = (\text{CH}_3)_2(\text{CH}_3\text{O})\text{CCH}_2\text{C}(\text{CN})(\text{CH}_3)^*$, with an average n value of ca. 3 [18], on the basis of NMR and IR spectroscopy and derivatizations. The chelating mode indicated in Scheme 5 for the Co-bonded monomer unit is suggested by a DFT calculation on the model $[\text{Co}(\text{acac})_2\{\text{CH}(\text{OOCCH}_3)\text{CH}_3\}]$ system and by the known preference of Co^{III} for an octahedral coordination. Thus, we have chosen compound $\text{CH}_3(\text{CH}_3\text{COO})\text{CHBr}$ (1-bromoethylacetate, BEA) as halide precursor. Bromine rather than iodine was selected as halogen atom in order to disfavor the reactivity towards nucleophilic attack. Also, in order to minimize nucleophilic substitution problems, pyridine was not used in these reactions.



Scheme 5. Proposed structure of the dormant chain for the $[\text{Co}(\text{acac})_2]$ -controlled polymerization of VAc.

Using this organic halide, no apparent reaction occurred at low temperature, whereas only compound $\text{Co}(\text{acac})_3$ was identified amongst the product obtained after warming the solution to room temperature, as already observed for the reaction with BEP. If the reaction solution was not allowed to warm up but rather kept at $-80\text{ }^\circ\text{C}$, the formation of blue crystals was observed over a period of 10 days. This product was identified as a new binuclear $\text{Co}(\text{II})$ complex $[\text{Co}(\text{acac})_2(\text{THF})_2\text{CoBr}_2]$, **7**. The molecular structure of this compound is depicted in Figure 7 and selected bond lengths and distances are listed in Table 7. The corresponding dichloride compound, $[\text{Co}(\text{acac})_2(\text{THF})_2\text{CoCl}_2]$, displaying the same coordination geometry, has previously

been described [74]. The molecule is composed of two bivalent Co atoms, connected to each other by two bridging oxygen atoms O11 and O22. Atom Co1 adopts an octahedral coordination mode, with two chelating acetylacetonate ligands and two *trans* THF molecules, whereas Co2 has a tetrahedral coordination environment, defined by the bridging atoms O11 and O22 of two different acetylacetonato ligands and two Br atoms. Due to the bridging oxygen atoms O11 and O22 which impose a small O11-Co2-O22 angle, the angle Br-Co-Br is widened relative to the tetrahedral value. The Co1-O bonds to the non-bridging atoms O12 and O21 are shorter than those to the bridging ones. The Co2-O bonds are even shorter, as expected from the lower coordination. All bond distances and angles involving the O atoms correspond very closely to those reported for the chloride analogue [74]. The Co-Br bonds agree well with values reported in the literature for other tetrahedrally coordinated Co^{II} bromides .

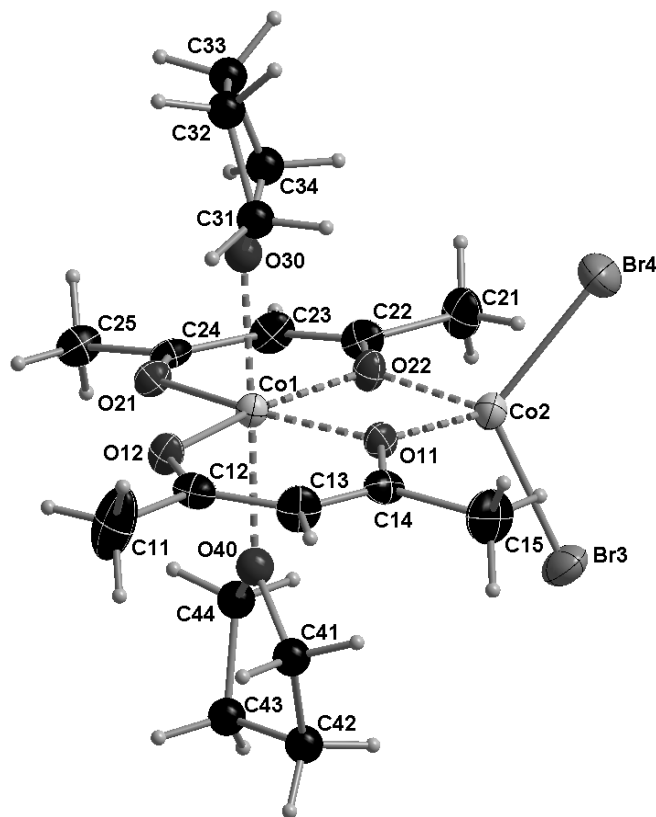


Figure 7. Molecular structure of **7** at 180 K (50% probability ellipsoids).

Table 7. Selected bond distances (Å) and angles (deg) of [Co(acac)₂(THF)₂CoBr₂], **7**.

Co1—O11	2.082(5)	O11—Co1—O12	87.5(2)	O11—Co2—Br4	112.49(16)
Co1—O12	2.022(5)	O11—Co1—O21	166.1(2)	O22—Co2—Br3	111.26(17)
Co1—O21	2.008(5)	O11—Co1—O30	92.9(2)	O22—Co2—Br4	115.54(17)
Co1—O22	2.082(5)	O11—Co1—O40	89.3(2)	Br3—Co2—Br4	118.69(6)
Co1—O30	2.145(5)	O12—Co1—O21	106.1(2)	Co1—O11—C14	127.4(5)
Co1—O40	2.146(6)	O12—Co1—O22	166.1(2)	Co1—O12—C12	128.9(5)
Co2—O11	2.027(5)	O12—Co1—O30	89.8(2)	Co1—O21—C24	129.0(5)
Co2—O22	1.998(6)	O12—Co1—O40	90.1(2)	Co1—O22—C22	128.9(5)
Co2—Br4	2.3559(15)	O21—Co1—O22	87.8(2)	Co1—O30—C31	125.3(5)
Co2—Br3	2.3666(14)	O21—Co1—O30	89.7(2)	Co1—O30—C34	124.7(5)
		O21—Co1—O40	88.2(2)	Co1—O40—C44	125.5(5)
Co1—O11—Co2	99.1(2)	O22—Co1—O30	89.6(2)	Co1—O40—C41	126.7(5)
Co1—O22—Co2	100.0(2)	O22—Co1—O40	91.0(2)	Co2—O11—C14	131.8(5)
O11—Co1—O22	78.7(2)	O30—Co1—O40	177.8(2)	Co2—O22—C22	130.6(5)
O11—Co2—O22	82.0(2)	O11—Co2—Br3	111.20(16)		

[17, 18]

Compound **7** forms under similar operating conditions that led to the isolation of **3** by using the reagent BEP. Both products are coordination compounds of Co^{II}. However, whereas compound **3** may be obtained by direct interaction of [Co(acac)₂] and the solvent, without the intervention of the halide reagent, the incorporation of bromine atoms in compound **7** requires the intervention of the BEA reagent, therefore giving indirect evidence of the production of CH₃(CH₃COO)CH[•] radicals. Recall that no disproportionation occurs for [Cu(Me₆TREN)Br] when this is kept at low temperatures. The formation of compound **7** may be envisaged as follows. Bromine atom transfer to [CuBr(Me₆TREN)] affords [Cu(Me₆TREN)Br]⁺Br[−] and CH₃(CH₃COO)CH[•]. Ligand exchange between [Co(acac)₂] and the bromide ion generates “Co(acac)Br”, which may dimerize and undergo ligand redistribution, to yield **7** with the help of further coordination of two THF molecules. According to our previous findings [17, 18], the CH₃(CH₃COO)CH[•] radicals should be efficiently trapped by [Co(acac)₂]. However, our best efforts to identify an organometallic species by ¹H NMR in the mother solution of the crystals

have not met with success. We cannot exclude that such a species is formed, but we do not have any evidence to support this possibility at the moment.

CONCLUSION

[Co(acac)₂] has so far resisted the synthesis of a simple alkyl derivative, [RCo^{III}(acac)₂] or [RCo^{III}(acac)₂(L)]. All attempts made in our laboratory and reported herein have resulted in side reactions that reveal the limitations of this synthetic strategy and the challenge of this synthetic target: the R-Co^{III} is weak for the unreactive radicals, namely those that can be generated most easily; R-X precursors with reactive radicals engage more readily in other reaction pathways (nucleophilic halide displacement by neutral ligands) whereas the simple one-electron oxidative addition is thermodynamically unfavorable. However, we still believe that it may be possible, given an appropriate method of rapidly generating a large amount of reactive radicals under very mild conditions, to synthesize a sufficiently stable organylcobalt(III) complex supported by two acetylacetonate groups, which would represent a model for the chain end in the dormant form of PVAc grown by [Co(acac)₂]-mediated CRP.

EXPERIMENTAL SECTION

General. All manipulations were carried out under strict oxygen-free and dry argon atmosphere. Reaction vessels were flame-dried under vacuum before use and standard Schlenk techniques were used to carry out all reactions. Toluene and THF were purified by distillation under argon after drying over sodium/benzophenone ketyl. *n*-Pentane and CH₂Cl₂ were dried over LiAlH₄ and P₄O₁₀ and then freshly distilled under argon prior to use. MeI, ethyl-2-bromopropionate (EBP), 1-bromoethylbenzene (BEB), and 1-chloroethylbenzene (CEB) were dried over molecular sieve and distilled under reduced pressure before use. Me₆TREN [75] and

1-bromoethylacetate (BEA) [76, 77] were synthesized according to literature methods. [Co(acac)₂] was purchased from Alfa Aesar and sublimed under reduced pressure and filled into glass ampoules under argon atmosphere. CuBr (99.9%) was purchased from Alfa Aesar. All other reagents used were of commercially available reagent-grade quality and were used without further purification.

Syntheses.

Formation of compound $\{[\text{Cu}(\text{bipy})_2\text{Br}]^+\}_2\{[\text{Cu}_2\text{Br}_4]^{2-}\}$, **1.** A Schlenk tube equipped with a magnetic stirrer was charged with 2 mL of freshly distilled methanol, 0.043 g 2,2'-bipyridine (0.272 mmol), and 35 μL BEB (0.262 mmol). CuBr (0.019 g; 0.13 mmol) was added subsequently at room temperature, leading to an immediate color change to intense brown-red. Stirring overnight yielded a red precipitate, which was isolated and dissolved in acetone. Single-crystals of **1** were produced upon storing the solution at 4 °C for 2 days.

Formation of $[\text{Cu}(\text{Me}_6\text{TREN})\text{Br}]\text{Br}$. CuBr (0.05 g, 0.35 mmol) was placed into a Schlenk tube equipped with a magnetic stirrer and 3 mL of freshly distilled toluene was added. Three freeze-pump-thaw cycles guaranteed an oxygen free atmosphere. 124 μL Me₆TREN (0.52 mmol) were added at room temperature and the mixture was stirred until a colorless solution was obtained. The solution was then cooled to -90 °C using acetone and liquid nitrogen. Subsequently, BEB (71 μL , 0.052 mmol) was added and the solution was stirred for another 30 min. In a separate Schlenk tube [Co(acac)₂] (0.09 g, 0.35 mmol) was dissolved in 2 mL of THF and the solution was cooled to -90 °C. Three freeze-pump-thaw procedures guaranteed an oxygen-free atmosphere. While cooling down, the violet [Co(acac)₂] solution became red. Then, the [Co(acac)₂] solution was added to the other solution at -90 °C using a cannula and the reaction was stirred for another 2 hours and then placed in a -20°C freezer. Crystallization took

place in 3 days. The crystalline green solid was redissolved in CH_2Cl_2 and crystallized placing the solution again into the freezer (-20°C). Suitable light green single-crystals were obtained, which were identified as the already reported [48] $[\text{Cu}(\text{Me}_6\text{TREN})\text{Br}]\text{Br}$ by comparison of the unit cell parameters.

Formation of compound $[\text{Cu}(\text{Me}_6\text{TREN}) \text{Br}_{0.37}\text{Cl}_{0.63}]\text{Br}$, 2. CuBr (0.134 g, 0.93 mmol) was placed into a Schlenk tube equipped with a magnetic stirrer and 3 mL of freshly distilled THF was added. Three freeze-pump-thaw cycles guaranteed an oxygen free atmosphere. Me_6TREN (220 μL , 0.93 mmol) was added at room temperature and the mixture was stirred until a colorless solution was obtained. The solution was then cooled down to -90°C using acetone and liquid nitrogen. Subsequently, CEB (97 μL , 0.93 mmol) was added and the solution was stirred for another 30 min. In a separate Schlenk tube $[\text{Co}(\text{acac})_2]$ (0.09 g, 0.35 mmol) was dissolved in 2 mL of THF and the solution was cooled to -90°C . Three freeze-pump-thaw procedures guaranteed an oxygen-free atmosphere. While cooling down, the violet $[\text{Co}(\text{acac})_2]$ solution became red. Then, the $[\text{Co}(\text{acac})_2]$ solution was slowly added to the other solution at -90°C using a cannula and the reaction was stirred for another 7 hours. Crystallization took place after addition of 0.5 mL n-pentane and yielded tetrahedral shaped dark green single-crystals of **2**.

Reaction of CuBr , Me_6TREN , $[\text{Co}(\text{acac})_2]$ and EBP. Formation of compound $[\text{Co}(\text{acac})_3]$. $[\{\text{Me}_6\text{TREN}\}\text{CuBr}]$ was prepared freshly at -90°C in THF by addition of Me_6TREN (139 μL , 0.6 mmol) to a mixture of CuBr (0.086 g, 0.6 mmol) in 3 mL THF. Addition of equimolar amounts of $[\text{Co}(\text{acac})_2]$ (0.152 g), EBP (0.072 mL) and acetonitrile (0.060 mL) took place subsequently. After addition of $[\text{Co}(\text{acac})_2]$ the solution turned red and after addition of EBP no change of color was observed. The solution was warmed up slowly to room temperature, leading to a green solution. This was evaporated to dryness and the residue was redissolved in acetone. The solution was placed into the fridge at 4°C and dark green crystals

were obtained after two weeks. X-ray diffraction experiments identified this compound as $[\text{Co}(\text{acac})_3]$ by comparison of the unit cell parameters with those already available in the literature [78, 79].

Formation of compound $[\text{Co}(\text{acac})_2(\text{THF})_2]$, 3. $[\{\text{Me}_6\text{TREN}\}\text{CuBr}]$ was prepared freshly at $-90\text{ }^\circ\text{C}$ in THF by addition of Me_6TREN (90 μL , 0.35 mmol) to a mixture of CuBr (0.050 g, 0.35 mmol) in 3 mL THF. In a separate Schlenk tube $[\text{Co}(\text{acac})_2]$ (0.100 g, 0.39 mmol) was dissolved in 3 mL of THF and EBP (0.038 mL, 0.35 mmol) was added dropwise to the pink solution. The two solutions were combined at $-80\text{ }^\circ\text{C}$ using a cannula. The resulting intense red solution was kept stirring for 3 h and then stored at $-80\text{ }^\circ\text{C}$. After 1 week a blue solution had formed and red crystals of **3** had formed at the bottom of the Schlenk tube.

Formation of compound $[\{\text{Me}_6\text{TREN}\}\text{CoBr}]\text{Br}$, 4. CuBr (0.066 g, 0.46 mmol) was placed in a Schlenk tube equipped with a magnetic stirrer and 2 mL of freshly distilled THF was added. Three freeze-pump-thaw cycles guaranteed an oxygen free atmosphere. Me_6TREN (107 μL , 0.46 mmol) were added at room temperature and the mixture was stirred until a colorless solution was obtained. The solution was then cooled down to $-90\text{ }^\circ\text{C}$. Subsequently, methyl iodide (62 μL , 0.46 mmol) and immediately afterwards $[\text{Co}(\text{acac})_2]$ (0.118 g, 0.46 mmol) were added to the solution. Warming up the reaction mixture to room temperature led to a brown solution over a large amount of amorphous white precipitate. The solid was separated and washed with a mixture of toluene/acetone. All toluene/acetone fractions were united and left standing on a vibration-free place. After one week both a white precipitate and violet crystals had formed at the bottom of the Schlenk tube. The crystals were separated and redissolved in CH_2Cl_2 . Cooling the solution to $4\text{ }^\circ\text{C}$ yielded tetrahedral shaped violet crystals of compound **4**.

Formation of compound $[\{\text{Me}_7\text{TREN}\}\text{CuI}]_2[\text{Cu}_{1.80}\text{Br}_{1.13}\text{I}_{2.67}]$, 5. CuBr (0.1 g, 0.70 mmol) was placed into a Schlenk tube equipped with a magnetic stirrer and 3 mL of freshly

distilled THF was added. Three freeze-pump-thaw cycles guaranteed an oxygen free atmosphere. Me₆TREN (165 μ L, 0.70 mmol) were added at room temperature and the mixture was stirred until a colorless solution was obtained. The solution was then cooled to -90 $^{\circ}$ C. Subsequently, methyl iodide (100 μ L, 1.2 mmol) and immediately afterwards [Co(acac)₂] (0.02 g, 0.08 mmol) were added to the solution. Warming up the reaction mixture to -40 $^{\circ}$ C led to a green solution over a colorless precipitate. The solution was separated from the solid and evaporated to dryness under reduced pressure. The solid was dissolved in dry acetone, yielding a green solution. Addition of *n*-pentane and crystallization at -80 $^{\circ}$ C with pentane layered on top of the CH₂Cl₂ solution yielded almost colorless (slightly greenish) air and moisture sensitive crystals of compound **5** at the bottom of the Schlenk tube.

Formation of compound [C₅H₅NMe]₂[CoI₄], 6. CuBr (0.021 g, 0.15 mmol) was placed in a Schlenk tube equipped with a magnetic stirrer and 3 mL of freshly distilled THF was added. Three freeze-pump-thaw cycles guaranteed an oxygen free atmosphere. Me₆TREN (35 μ L, 0.15 mmol) were added at room temperature and the mixture was stirred until a colorless solution was obtained. The solution was then cooled to -90 $^{\circ}$ C. [Co(acac)₂] (0.080 g, 0.31 mmol) were added and dissolved, followed by methyl iodide (39 μ L, 0.62 mmol) and pyridine (25 μ L, 0.31 mmol). Storing the resulting red solution at -80 $^{\circ}$ C for one week yielded green plate-like crystals of compound **6**.

Formation of compound [Co(acac)₂(THF)₂CoBr₂], 7. [{Me₆TREN}CuBr] was prepared freshly at -90 $^{\circ}$ C in THF by addition of Me₆TREN (135 μ L, 0.58 mmol) to a mixture of CuBr (0.080 g, 0.56 mmol) in 3 mL THF. In a separate Schlenk tube [Co(acac)₂] (0.150 g, 0.58 mmol) was dissolved in 2 mL of THF. Equimolar amounts of BEA (0.072 mL) and acetonitrile (0.060 mL) were subsequently added. The two solutions were combined at -80 $^{\circ}$ C using a cannula. The

resulting brown-red solution was stirred for 3 h and then stored at -80 °C. After 5 weeks, blue crystals of compound **7** had formed on the bottom of the Schlenk tube.

X-ray Structural Studies. A single-crystal of each compound was mounted under inert perfluoropolyether on the tip of a cactus spike and cooled immediately in the cryostream of an Oxford-Diffraction XCALIBUR CCD diffractometer. The structures were solved by direct methods (SHELXS-97 [80]) and refined by least-square procedures on F^2 using SHELXL-97 [81]. All H atoms attached to carbon atoms were introduced in ideal positions and treated as riding models. Absolute structures were confirmed by the refinement of Flack's enantiopole parameter [82] and by careful examination of the sensitive reflections. Crystal data and refinement parameters are shown in Table 8. Crystallographic information files (CIF) were also deposited with the Cambridge Crystallographic Data Centre. CCDC 674118-674124 contains the supplementary crystallographic data for compounds **1-7**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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Table 8. Crystallographic data for all compounds.

Compound	1	2	3	4	5	6	7
Empirical formula	C ₂₀ H ₁₆ Br ₃ Cu ₂ N ₄	C ₁₂ H ₃₀ Br _{1.37} Cl _{0.63} CuN ₄	C ₁₈ H ₃₀ CoO ₆	C ₁₂ H ₃₀ Br ₂ CoN ₄	C ₂₆ H ₆₆ Br _{1.13} Cu _{3.80} I _{4.67} N ₈	C ₁₈ H ₃₀ Br ₂ Co ₂ O ₆	C ₁₈ H ₃₀ Br ₂ Co ₂ O ₆
Formula Mass [g mol ⁻¹]	679.18	425.53	401.35	449.15	1415.17	754.80	620.10
Temperature <i>T</i> [K]	180	180	160	150	160	180	180
Wavelength λ [Å]	0.71073 (Mo-K α)						
Crystal system	triclinic	cubic	monoclinic	cubic	triclinic	orthorhombic	orthorhombic
Space group	<i>P</i> 1	<i>P</i> 2 ₁ /3	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ /3	<i>P</i> 1	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> (Å)	8.7884(18)	11.9666(6)	15.485(2)	12.0768(3)	8.2697(10)	28.376(4)	9.5934(7)
<i>b</i> (Å)	11.449(2)		11.1151(14)		8.5175(10)	9.2662(9)	14.5601(11)
<i>c</i> (Å)	12.346(3)		12.9790(13)		18.607(2)	16.5472(14)	17.1601(13)
α (deg)	64.95(3)				77.337(10)		
β (deg)	84.89(3)		116.091(10)		86.862(15)	109.953(9)	
γ (deg)	77.64(3)				66.140(11)		
Cell volume (Å ³)	1099.3(5)	1713.61(15)	2006.3(4)	1761.39(8)	1168.6(3)	4089.7(8)	2396.9(3)
Formula units / cell <i>Z</i>	2	4	4	4	1	8	4
ρ_{calc} (g cm ⁻³)	2.052	1.649	1.329	1.694	2.011	2.452	1.718
μ (mm ⁻¹)	7.401	4.551	0.883	5.506	5.783	6.869	4.746
<i>F</i> (000)	654	870	852	908	675	2728	1240
crystal size (mm ³)	0.38×0.29×0.24	0.34×0.31×0.30	0.24×0.12×0.09	0.29×0.26×0.25	0.81×0.47×0.40	0.19×0.18×0.04	0.12×0.11×0.06
Diffraction device	Oxford-Diffraction XCALIBUR						
Scan type	omega scan						
2 θ range (deg)	3.43 – 32.11	2.41 – 27.45	2.51 – 25.00	2.92 – 32.04	2.67 – 27.50	2.62 – 32.02	2.76 – 27.50
Reflections connected	11900	14609	5996	19109	10011	15764	18634
Unique reflections (<i>R</i> _{int})	6967 (0.0230)	1314 (0.0417)	1774 (0.0332)	2007 (0.0263)	5337 (0.0697)	6264 (0.0336)	5518 (0.0722)
Reflectns with <i>F</i> ₀ ² ≥ 2 σ (<i>F</i> ₀ ²)	5230	1253	1275	1890	1854	3471	3311
Completeness to θ (%)	90.5 (32.11°)	100 (27.45°)	99.9 (25.00°)	98.4 (32.04°)	99.6 (27.5°)	87.9 (32.02°)	99.8 (27.50°)
Absorption correction	semiempirical						
Min. – max. trans.	0.086, 0.1708	0.189, 0.257	0.7871, 0.9200	0.1961, 0.2500	0.5411, 0.7952	0.3384, 0.7900	0.6085, 0.7741
Refinement method	full-matrix least squares on <i>F</i> ²						
Data/restraints/parameters	6967/0/262	1314/0/60	1774/0/125	2007/0/59	5337/0/201	6264/0/173	5518/0/254
Goodness-of-fit on <i>F</i> ²	1.067	1.315	1.038	1.374	0.781	0.901	0.922
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0366	0.0307	0.0379	0.0253	0.0446	0.0267	0.0392
<i>wR</i> ₂	0.0850	0.0861	0.1117	0.0626	0.0925	0.0677	0.0763
Absolute structure param.		-0.05(2)		0.008(14)			
Max, min resid. density (eÅ ⁻³)	1.043, -0.960	1.618, -0.487	0.465, -0.302	2.746, -0.695	1.429, -0.975	0.983, -1.121	0.830, -0.947

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Material for the Table of Contents

Text

The reaction between CuBr/L_n ($\text{L}_n = 2$ bipy or Me_6TREN) and a variety of alkyl halides in the presence of $[\text{Co}(\text{acac})_2]$ leads to a variety of products originating from atom transfer and ligand redistribution reactions. The formation of a stable alkylcobalt(III) derivative was not observed.

Graphics

