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Reductive Termination of Cyanoisopropyl Radicals by Copper(I) Complexes and Proton Donors: Organometallic Intermediates or Coupled Proton−Electron Transfer?

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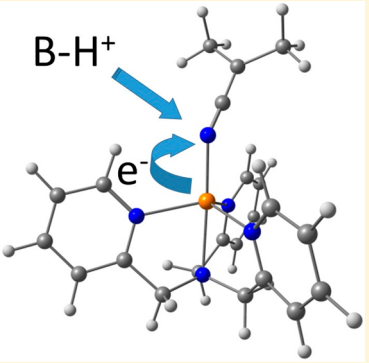
Supporting Information

ABSTRACT: Cyanoisopropyl radicals, generated thermally by the decomposition of azobis(isobutyronitrile) (AIBN), participate in reductive radical termination (RRT) under the combined effect of copper(I) complexes and proton donors (water, methanol, triethylammonium salts) in acetonitrile or benzene. The investigated copper complexes were formed in situ from $[Cu^{I}(MeCN)_4]^+BF_4^-$ in CD_3CN or $Cu^{I}Br$ in C_6D_6 using tris[2-(dimethylamino)ethyl]amine (Me_6TREN), tris(2-pyridylmethyl)amine (TPMA), and 2,2′-bipyridine (BIPY) ligands. Upon keeping all other conditions constants, the impact of RRT is much greater for the Me_6TREN and TPMA systems than for the BIPY system. RRT scales with the proton donor acidity ($Et_3NH^+ \gg H_2O > CH_3OH$), it is reduced by deuteration ($H_2O > D_2O$ and $CH_3OH > CD_3OD$), and it is more efficient in C_6D_6 than in CD_3CN. The collective evidence gathered in this study excludes the intervention of an outer-sphere proton-coupled electron transfer (OS-PCET), while an inner-sphere PCET (IS-PCET) cannot be excluded for coordinating proton donors (water and methanol). On the other hand, the strong impact of RRT for the noncoordinating Et_3NH^+ in CD_3CN results from the formation of an intermediate Cu^{I}-radical adduct, suggested by DFT calculations to involve binding via the N atom to yield keteniminato $[L/Cu{-}N{=}C{=}CMe_2]^+$ derivatives with only partial spin delocalization onto the Cu atom.



1. INTRODUCTION

Organic radicals can interact with transition metal complexes in a number of different ways.[1] Of particular interest to us are reversible reactions that yield dormant species, allowing radical polymerization processes to become controlled via the persistent radical effect.[2] These types of polymerization processes are known as "reversible deactivation radical polymerizations" (RDRPs).[3] Two such reactions are atom transfer from a halogen-containing oxidized metal complex, Y−Mt^{x+1}/L, to yield the reduced complex Mt^x/L and an alkyl halide R−Y (Scheme 1; Y = halogen, Mt = metal, L = coordinating ligand, R = organic radical, x and $x + 1$ = formal oxidation states) and direct metal−carbon bond formation to form an organometallic species, Scheme 2. The corresponding RDRP strategies are respectively known as "atom transfer radical polymerization" (ATRP)[4−9] and "organometallic-mediated radical polymerization" (OMRP).[10−12] These two mechanisms were shown to constructively interplay for certain metal systems.[13,14] One of the most versatile metals for ATRP is copper, shuttling between the oxidation states +1 and +2, whereas OMRP has so far been particularly successful using Co^{II}/Co^{III} systems and has not found successful implementations for copper complexes.[15]

In recent years, the use of copper complexes with greater catalytic activity in ATRP, i.e., greater K_{ATRP} (Scheme 1),[16,17] was shown to promote competitive radical trapping by the Cu^{I}/L ATRP catalyst with formation of the organometallic dormant species (i.e., sufficiently small K_{OMRP}, Scheme 2). However, rather than helping the system to gain better control,

Scheme 1. Reaction between an Organic Radical and a Halogen-Containing Metal Complex Leading to Atom Transfer

$$R^{\bullet} + Y\text{-}Mt^{x+1}/L \underset{k_{a,ATRP}}{\overset{k_{da,ATRP}}{\rightleftharpoons}} R\text{-}Y + Mt^{x}/L \qquad K_{ATRP} = \frac{k_{a,ATRP}}{k_{da,ATRP}}$$

Scheme 2. Reaction between an Organic Radical and a Metal Complex Leading to Metal−Carbon Bond Formation

$$R^{\bullet} + Mt^{x}/L \underset{k_{a,OMRP}}{\overset{k_{da,OMRP}}{\rightleftharpoons}} R\text{-}Mt^{x+1}/L \qquad K_{OMRP} = \frac{k_{a,OMRP}}{k_{da,OMRP}}$$

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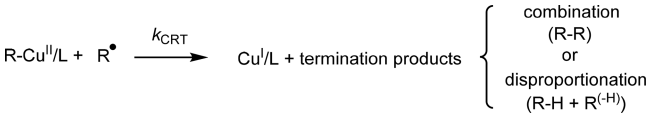
this phenomenon opened access to a metal-catalyzed radical termination pathway, termed "catalytic radical termination" (CRT, Scheme 3).[18−22] This process consists of a reaction

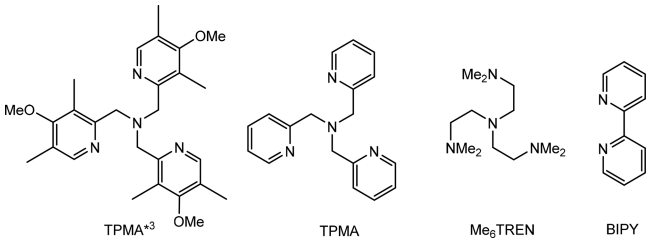
Scheme 3. Reaction between an Organocopper(II) complex and a Second Radical, Yielding Radical Termination and Regenerating the Copper(I) Complex



between the organometallic intermediate R−Cu^{II}/L and a second radical to yield termination products and regenerate the Cu^{I}/L catalyst, and it was found to be particularly prevalent when R$^{\bullet}$ is a growing polyacrylate chain.

Investigations aimed at learning about the intimate mechanism of the CRT process have been recently conducted. In an initial study,[19] well-defined bromine-capped polystyrene (PSt−Br) and poly(methyl acrylate) (PMA−Br) chains of known average molecular mass and low dispersity, prepared by ATRP, were activated by Cu^{I}Br/TPMA (TPMA = tris(2-pyridylmethyl)amine, see Scheme 4), and the

Scheme 4. Ligands Used in This and Previous Studies

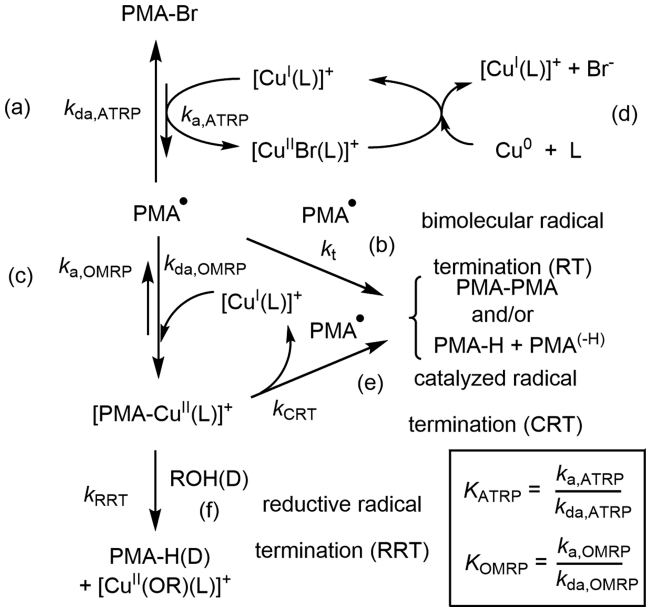


produced radicals were allowed to terminate in the absence of monomer. These studies were conducted in MeCN at 25 °C with the activating system formed in situ from Cu^{I}Br and TPMA, while Cu^{II}Br$_2$ was also present to moderate the activation equilibrium (Scheme 1). The PSt−Br activation was found to yield a double-molecular weight product, as expected from radical−radical coupling (combination). Since CRT is not efficient for these radicals,[23] the latter mostly undergo noncatalyzed bimolecular termination, which occurs predominantly by combination.[24] On the other hand, PMA−Br activation yielded a product with the same average molecular weight of the precursor, indicating the absence of combination. Since polyacrylate radicals are also known to terminate mostly by combination[25,26] (although this view has recently been challenged[27]), this result was attributed to the copper-catalyzed termination (Scheme 3).

In a subsequent study, a PMA−Br sample was activated by Cu^{I} systems made in situ from [Cu(MeCN)$_4$]$^+$OTf$^-$ and three different ligands (TPMA*^{3}, TPMA or Me$_6$TREN, Scheme 4), allowing termination reactions to occur in MeCN at 25 °C in the absence of monomer.[21] The recovered polymer had a bimodal distribution, the two components having respectively the same and a double average molecular weight relative to that of the macroinitiator. A key feature of this study was that the relative contribution of standard bimolecular (nonmetal-mediated) radical termination (RT) and copper-catalyzed radical termination (CRT) was tuned by a change of the initial Cu^{I}/Cu^{II} ratio. The observed trends and the accompanying kinetic simulation studies confirmed that RT yields nearly exclusively combination and suggested that the products with the same molar mass distribution as the macroinitiator originate from CRT.

A related investigation,[28] however, revealed a new phenomenon. In that study, a PMA−Br macroinitiator of narrow molar mass distribution was again used and activated by Cu^{I}Br/Me$_6$TREN in the absence of monomer. Two important differences relative to the investigations carried out in our laboratories were the use of (undried) toluene as solvent and metallic copper (Cu^0), which was added to the system rather than a Cu^{II} salt. The resulting polymer had again a bimodal molecular weight distribution (MWD), with the two contributing distributions having the same and double molecular weights, in agreement with our study. However, a detailed analysis of the recovered polymer by NMR and by mass spectrometry showed the absence of unsaturated chain, PMA$^{(-H)}$. Instead, the distribution with the same average molar mass as the PMA−Br precursor contained only saturated chain ends, PMA−H, thus excluding the possibility that it was generated by radical disproportionation. Furthermore, an additional experiment carried out in the presence of CH_3OD yielded the corresponding PMA−D while the double MWD completely disappeared. The saturated chains were proposed by the authors to originate from protonolysis (by adventitious water in the medium or by the added methanol) of the organometallic intermediate. The reaction scheme is summarized in Scheme 5.

Scheme 5. Possible Events in the Copper-Mediated Termination of Poly(methyl acrylate) Radicals in the Presence of Methanol



After activation of PMA−Br (a), the radicals can either terminate spontaneously in a bimolecular fashion according to path b or be trapped by [Cu^{I}(L)]$^+$ according to path c, while Cu^0, if present together with additional L, would convert the [Cu^{II}Br(L)]$^+$ product back to [Cu^{I}(L)]$^+$ by comproportionation according to path d. Subsequently, the generated OMRP dormant species [PMA−Cu^{II}(L)]$^+$ may react with a second

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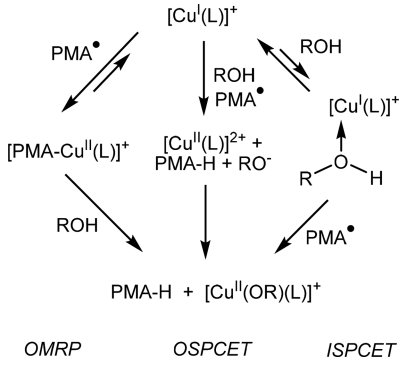
radical leading to CRT (e). Yamago et al. also proposed an alternative bimolecular CRT pathway involving interaction between two $[PMA-Cu^{II}(L)]^+$ complexes.[28] Competing with CRT, the $[PMA-Cu^{II}(L)]^+$ species may react with a proton donor to yield the observed PMA−H and a secondary Cu^{II} complex, $[Cu^{II}(OR)(L)]^+$ (f). We propose to name the latter process "reductive radical termination" (RRT). It is a stoichiometric process, not a catalytic one, because it does not regenerate a Cu^I complex. Incidentally, a recent report has also shown the ability of Cu^0 to catalyzed acrylate radical termination,[29] which is not included in Scheme 5.

While there is no doubt about the existence of RRT and on the nature of the resulting product, the intimate mechanisms and the nature of the bimolecular terminations (RT and CRT) products are controversial. Yamago et al. have claimed that RT results in disproportionation[27] and, since the unsaturated disproportionation product was not observed in the presence of the copper complex (even in the absence of proton donor), they proposed that RT (Scheme 5b) is totally suppressed by the faster OMRP trapping (c) and subsequent decompositions (e, f).[28] Hence, for the experiment run in the absence of deliberately added methanol, they deduced that the distribution with average molar mass equivalent to that of PMA−Br (PMA−H) results from RRT, while the double MWD (PMA−PMA) results from CRT, and proposed that this product is generated by reductive elimination from a dialkylcopper intermediate. However, our own above-mentioned study carried out with variable Cu^{II}/Cu^I ratios, run under very similar conditions to those of Yamago et al., gave essentially the same bimodal distribution and clearly demonstrated that the double molecular weight PMA−PMA product is generated by RT.[21] Our reinterpretation of the results from the study by Yamago et al. is that the double MWD observed at low [ROH] results from RT (Scheme 5b) and that an increasing concentration of the proton donor skews the product distribution in favor of RRT (Scheme 5, c and f). Complete suppression of RT is expected at high [ROH] because the RRT rate ($v_{RRT} = K_{OMRP}k_{RRT}[Cu^I(L)^+][PMA^\bullet][ROH]$) would become dominant relative to that of RT ($v_t = k_t[PMA^\bullet]^2$). At low [ROH], even though OMRP trapping (Scheme 5c, $k_{da,OMRP}[Cu^I(L)^+][PMA^\bullet]$) can compete with RT, the reversibility of the former allows RT and CRT to remain in competition.

One specific result of the contribution by Yamago et al.,[28] however, requires further analysis. In the absence of any added $CH_3OH(D)$, unsaturated chains expected from disproportionation were still absent in the lower molecular weight fraction, ruling out any pathway leading to disproportionation products. While the double MWD (PMA−PMA) may result from either RT (according to us)[21] or from CRT (according to Yamago et al.),[28] the selective production of PMA−H in the absence of ROH is puzzling. Yamago et al. attributed this phenomenon to the efficient OMRP trapping (Scheme 5c) followed by RRT as a consequence of the water impurities in the solvent. Another interesting question is whether the RRT pathway occurs via an organometallic species. Indeed, this termination process may also occur by outer-sphere or inner-sphere electron transfer processes, coupled with protonation, as shown in Scheme 6. On the left, the organometallic pathway already considered in Scheme 5 is represented, which we name OMRP because it involves the dormant species of an organometallic-mediated radical polymerization. In the middle, the scheme shows a termolecular outer-sphere proton-coupled electron transfer

Scheme 6. Possible Pathways for Reductive Radical Termination



(OS-PCET). Finally, the right-hand side shows the two-step process involving initial coordination of the proton donor to the $[Cu^I(L)]^+$ complex, followed by proton-coupled electron transfer, which we name inner-sphere PCET, or IS-PCET. The involvement of metal complexes to mediate PCET is well established[30] and an IS-PCET process was found to be kinetically competent in a recent mechanistic study of $Fe(acac)_3$-catalyzed radical alkene cross-coupling.[31]

It is also relevant to mention the seminal work of Meyerstein, who has investigated the interaction between organic radicals and transition metal complexes, including those of Cu^I, carrying out their studies in water or aqueous media.[32−44] The resulting organocopper transients usually decomposed by protonolysis.[45] Those investigations, however, did not pay particular attention to the competition between trapping by Cu^I and spontaneous bimolecular termination and have mostly dealt with relatively reactive (nonstabilized) radicals, which have a strong tendency to generate organocopper(II) species. Exceptions are $^\bullet CH_2COOH$ and $^\bullet CH_2COO^-$,[43] where the unpaired electron is stabilized by delocalization onto the carboxylic function. The neutral $^\bullet CH_2COOH$ radical gives the organocopper(II) adduct with Cu^+_{aq} at a rate comparable to those of the more reactive radicals $^\bullet CH_3$ and $^\bullet CH_2CH_2COOH$ ($>10^9$ M^{-1} s^{-1}), whereas the anionic $^\bullet CH_2COO^-$ radical adds 1 order of magnitude slower than $^\bullet CH_3$ to a $[Cu^I(L)]^+$ complex (L = 2,5,8,11-tetramethyl-2,5,8,11-tetraazadodecane), but still formed an organocopper(II) transient. The decomposition of the $[Cu^{II}-CH_2COOH]^+_{aq}$ and $[(L)Cu^{II}-CH_2COO]$ transients was found to occur by protonolysis to yield CH_3COOH or CH_3COO^- and Cu^{2+}_{aq} or $[Cu^{II}(L)]^{2+}$, respectively.

In order to learn more about the RRT mechanism and about its impact in an ATRP/OMRP process, we have embarked in a detailed investigation of the nature of the termination products for stabilized radicals interacting with a variety of Cu^I complexes in nonaqueous solvents and in the presence of controlled amounts of proton donors. The interaction between carbon-based radicals and copper complexes in nonaqueous solvents is a relatively unexplored area of investigations.[45] The guiding principle is to probe radicals with a greater or smaller aptitude to generate an organometallic intermediate (thus probing the OMRP pathway in Scheme 6 relative to the other possible PCET pathways). In this report, we focus on the stabilized cyanoisopropyl radical ($Me_2(CN)C^\bullet$), with the idea in mind that this radical may be unable to generate an organocopper(II) intermediate because of an insufficiently strong $Cu^{II}-C$ bond.

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2. EXPERIMENTAL SECTION

2.a. Material and Methods. Copper(I) bromide (CuBr, Sigma-Aldrich, 99.8%), copper(0) powder (<425 μm, Sigma-Aldrich, 99.5%), tris[2-(dimethylamino)ethyl]amine (Me_6TREN, Alfa Aesar, 99%), tris(2-pyridylmethyl)amine (TPMA, AmBeed or Koei Chemical Co. Ltd., 98%), and 2,2′-bipyridine (BIPY, Sigma-Aldrich, 99%) were used as received without any purification. 2,2′-Azobis(isobutyronitrile) (AIBN, Sigma-Aldrich, 98%) was recrystallized from methylene chloride at −32 °C. Tetrakis(acetonitrile)copper(I) tetrafluoroborate ($[Cu^I(MeCN)_4]BF_4$, Acros Organics, 99%) was recrystallized from MeCN. Anhydrous deuterated acetonitrile (CD_3CN, Eurisotop, 99.8% D) was distilled over CaH_2 under an inert atmosphere and stored in a sealed flask. Anhydrous deuterated benzene (C_6D_6, Eurisotop, 99.5% D) was distilled over NaK alloy under an inert atmosphere and stored in a sealed flask. Methanol (MeOH, Carlo Erba, analytical grade) and deuterated methanol (CD_3OD, Eurisotop, 99.9% D) were dried over activated 4 Å molecular sieves and stored under an inert atmosphere in a sealed flask. Triethylammonium tetrafluoroborate ($[Et_3NH]BF_4$ was synthesized according to the literature.[46] The ^{1}H NMR spectra were recorded on a Bruker Avance III 300 or 400 MHz spectrometer at ambient temperature; chemical shifts (δ) are reported in ppm vs $SiMe_4$ and were determined by reference to the residual ^{1}H solvent peaks. The coupling constants are reported in hertz.

2.b. General Procedure for the AIBN Termination in CD_3CN. A degassed solution of CD_3CN containing the ligand (8.6×10^{-2} mmol, 2 equiv relative to Cu) and AIBN (3.6 mg, 2.1×10^{-2} mmol, 0.5 equiv relative to Cu) was transferred via cannula to a screw-capped NMR tube containing $[Cu(MeCN)_4]^+BF_4^-$ (13.5 mg, 4.3×10^{-2} mmol). The solution was heated at 80 °C for 8 h and then cooled to room temperature and analyzed by ^{1}H NMR spectroscopy.

2.c. General Procedure for the AIBN Termination in C_6D_6. A degassed solution of C_6D_6 containing the ligand (8.6×10^{-2} mmol, 1.7 equiv relative to Cu^I) and AIBN (8.2 mg, 5.1×10^{-2} mmol, 1 equiv relative to Cu^I) was transferred via cannula to a screw-capped NMR tube containing CuBr (7.3 mg, 5.1×10^{-2} mmol) and Cu^0 (12 mg, 20.4×10^{-2} mmol, 4 equiv relative to Cu^I). The solution was heated at 75 °C for 8 h and then cooled to room temperature and analyzed by ^{1}H NMR spectroscopy.

2.d. Computational Details. The DFT calculations were carried out using the Gaussian09 suite of programs.[47] Geometry optimizations were performed for the isolated molecules without any symmetry constraint using the BP86 functional[48] and the 6-311G(d,p) basis functions for all the light atoms (O, N, C, H) and the LANL2DZ functions for Cu, to which was added an *f* polarization function (α = 3.325 Cu).[49] The unrestricted formulation was used for open-shell spin doublets, yielding only minor spin contamination ($\langle S^2 \rangle$ at convergence was very close to the expected value of 0.75, the maximum deviation being 0.758 for the free cyanoisopropyl radical, $(CH_3)_2(CN)C^\bullet$). 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 BP86 optimized geometries using Grimme's D3 empirical method (BP86-D3), using S6 = 1, SR6 = 1.1390, and S8 = 1.6830.[50] A solvation correction in acetonitrile (ε = 35.688) was carried out using the SMD polarizable continuum model.[51] A further correction of 1.95 kcal/mol was applied to bring the G values from the gas phase (1 atm) to the solution (1 mol/L) standard state.[52]

3. RESULTS AND DISCUSSION

3.a. Control Experiments. The cyanoisopropyl radical was conveniently generated by thermal decomposition of azobis(isobutyronitrile) (AIBN; $Me_2C(CN)-N{=}N-C(CN)-Me_2$) in either CD_3CN or C_6D_6 and the nature and amount of the formed products were determined by ^{1}H NMR integration (see Supporting Information, section S1). All decomposition experiments in CD_3CN were conducted, unless otherwise stated, at 80 °C (where the half-life is reported as ca. 70 min or 1.2 h) for 8 h, whereas all those in C_6D_6 were set at 75 °C ($t_{1/2}$ = ca. 150 min or 2.5 h), also for 8 h. The observed fraction of decomposed AIBN is consistent with the reported decomposition rates in the presence of Cu^I complexes,[53] with some variability caused by the imperfect control of the heating bath temperature and/or occasional induction periods because of oxygen contamination. The product distributions reported in all tables below are relative to the converted AIBN fraction. Control experiments conducted in the absence of both copper complex and proton donor (Table 1, entries 1 and 2) yield

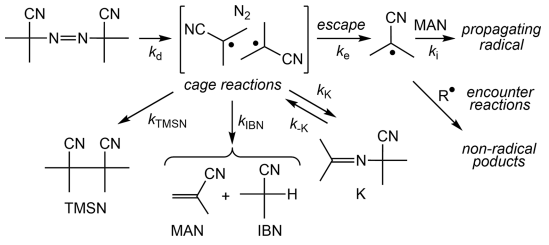
Table 1. Results of the Thermal Decomposition of AIBN in the Absence of Copper Complexes[a]

entry	solvent	additive/AIBN	iBN/dimer[b]	% D[c]
1	CD_3CN	–	0.11	
2	C_6D_6	–	0.07	
3	CD_3CN	H_2O (200)	0.11[d]	
4	CD_3CN	D_2O (200)	0.11[d]	n.d.
5	CD_3CN	CH_3OH (40)	0.12	
6	CD_3CN	CD_3OD (40)	0.13	n.d.
7	C_6D_6	CH_3OH (200)	0.08	
8	C_6D_6	CD_3OD (200)	0.09	n.d.

[a]Experiments in CD_3CN: T = 80 °C, 8 h. Experiments in C_6D_6: T = 75 °C, 8 h. [b]Ratio of the two Me_2C resonances (see Supporting Information), hence equivalent to the moral ratio of AIBN leading to each product. [c]Key: n.d. = not detectable (the integral of the two peaks of the iBN(H) doublet are identical within experimental error). [d]A small amount of amide ($Me_2CHCONH_2$ or $Me_2CHCOND_2$, < 1%) was also detected.

mainly tetramethylsuccinonitrile, $Me_2C(CN)-C(CN)Me_2$ (indicated as "dimer") and a minor amount of isobutyronitrile (iBN) as secondary product (Scheme 7). This is in line with a

Scheme 7. AIBN Decomposition in the Absence of Cu^I Complex



previous investigation[54] and with the known termination mode in the polymerization of acrylonitrile and methacrylonitrile, which occurs predominantly by combination.[55] The observed iBN probably derives from a small amount of disproportionation, but the expected methacylonitrile coproduct was not observed in this specific control experiment, because it is subsequently consumed by radical addition with formation of oligomers as previously demonstrated.[54] Small amounts of vinyl protons were indeed occasionally observed in the ^{1}H NMR spectra for other experiments during the investigation. Since the putative oligomers could not be quantified, the percent of coupling and saturated product reported in Table 1 cannot be taken as precise measures of the percent coupling and disproportionation for the cyanoisopropyl radical. The

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Table 2. Results of the Thermal Decomposition of AIBN in the Presence of the Cu^I/Me_6TREN System[a]

entry	solvent	Cu^I complex	additive/AIBN	iBN/dimer[b]	% D in iBN[c]
9	CD_3CN	$[Cu^I(Me_6TREN)]^+BF_4^-$	–	0.16	
10	C_6D_6	CuBr/Me_6TREN	–	0.09	
11[d]	C_6D_6	CuBr/Me_6TREN	–	0.06	
12	CD_3CN	$[Cu^I(Me_6TREN)]^+BF_4^-$	H_2O (200)	4.28[e]	
13	CD_3CN	$[Cu^I(Me_6TREN)]^+BF_4^-$	D_2O (200)	1.09	85.0
14	CD_3CN	$[Cu^I(Me_6TREN)]^+BF_4^-$	CH_3OH (2)	0.20	
15	CD_3CN	$[Cu^I(Me_6TREN)]^+BF_4^-$	CH_3OH (40)	1.65	
16	CD_3CN	$[Cu^I(Me_6TREN)]^+BF_4^-$	CH_3OH (200)	3.17	
17	CD_3CN	$[Cu^I(Me_6TREN)]^+BF_4^-$	CD_3OD (2)	0.23	17.2
18	CD_3CN	$[Cu^I(Me_6TREN)]^+BF_4^-$	CD_3OD (40)	0.15	13.8
19	CD_3CN	$[Cu^I(Me_6TREN)]^+BF_4^-$	CD_3OD (200)	0.94[e]	65.3
20	C_6D_6	CuBr/Me_6TREN	CH_3OH (20)	1.78	
21	C_6D_6	CuBr/Me_6TREN	CH_3OH (100)	8.64	
22[d]	C_6D_6	CuBr/Me_6TREN	CH_3OH (100)	7.81	
23	C_6D_6	CuBr/Me_6TREN	CD_3OD (20)	0.35	54.7
24	C_6D_6	CuBr/Me_6TREN	CD_3OD (100)	3.30	68.7
25[d]	C_6D_6	CuBr/Me_6TREN	CD_3OD (100)	4.36	68.9

[a]Experiments in CD_3CN: $[Cu^I(MeCN)_4]BF_4$/Me_6TREN/AIBN = 1:2:0.5, T = 80 °C, 8 h. Experiments in C_6D_6: [CuBr]/Cu^0/Me_6TREN/AIBN = 1:4:1.7:1, T = 75 °C, 8 h (unless otherwise stated). [b]Ratio of the two Me_2C resonances (see Supporting Information), hence equivalent to the moral ratio of AIBN leading to each product. [c]Fraction of $Me_2CD(CN)$ in the iBN product, determined by ^1H NMR integration. [d]Thermal decomposition for 24 h in C_6D_6 that was dried and distilled over Na/K. [e]A small amount of amide ($Me_2CHCONH_2$ or $Me_2CHCOND_2$, <1%) was also detected.

observed dimer/iBN product ratio was about the same (ca. 10:1) in both CD_3CN and C_6D_6. Additional control experiments were carried out in the presence of proton donors, still in the absence of any copper complex. Both water and methanol (regular or deuterated) were used in CD_3CN, whereas only methanol could be used in C_6D_6 for miscibility reasons. The results (entries 3–6 in CD_3CN, entries 7 and 8 in C_6D_6) do not greatly differ from those obtained in the absence of these proton-donor additives. The only slight difference was the detection of minor amounts of isobutyramide, $Me_2CHCONH_2$, resulting from hydrolysis of the isobutyronitrile, for the experiments carried out in the presence of water.

3.b. Decomposition in the Presence of Cu^I Complexes with Me_6TREN. The Me_6TREN ligand was selected for the initial studies in the presence of Cu^I (Table 2). Termination experiments were first carried out without any proton donor additive (entries 9 and 10 in CD_3CN and C_6D_6, respectively). The results, in both solvents, are again quite similar to those obtained in the absence of copper complex, showing that the presence of the complex alone does not significantly affect the radical decomposition mode. A marginal increase of the iBN production in CD_3CN may result from the presence of small amounts of water in the deuterated solvent (which was found to be ca. 0.05 equiv relative to AIBN by ^1H NMR integration), but the difference is barely significant. The deuterated benzene is much drier—no detectable H_2O by ^1H NMR—and the results (entry 10) are essentially identical to those of the control in entry 2 (Table 1). An additional control experiment run in C_6D_6 that had been dried and distilled over Na/K (entry 11) gave a marginally lower iBN/dimer ratio.

The deliberate addition of 200 equiv of water (relative to AIBN, or 100 equiv relative to the Cu complex) in MeCN dramatically changed the product distribution in favor of iBN (Table 2, entry 12). Replacement of water with the same amount of D_2O (entry 13) yielded a lower amount of iBN relative to entry 12, but it is still much greater than in the control experiment of entry 9, and nearly 90% of this product was deuterated ($Me_2CD(CN)$). The relative amount of this product could be rather precisely determined by ^1H NMR integration of the Me proton resonances (1:1:1 triplet for the deuterated product, vs doublet for the nondeuterated compound; see section S1 in the Supporting Information). The dimer/iBN difference for H_2O and D_2O may be attributed to a kinetic isotope effect (KIE) in the reaction leading to the iBN product, while the imperfect deuteration of iBN may be attributed to the incorporation of the residual H in D_2O, plus the H_2O originally present in the CD_3CN solvent, in the presence of the KIE bias.

Use of regular and deuterated methanol (entries 14–16 and 17–19, respectively) as a proton donor gave the same trends. In this case, a finer study as a function of proton donor concentration was carried out, showing that the iBN/dimer ratio increases with the methanol/AIBN ratio. This ratio is greater with CH_3OH than with CD_3OD under identical conditions, again consistent with the presence of a KIE. It is however smaller than with the same amount of water (*cf.* entries 16 and 12, or 19 and 13). This shows that water is slightly more effective than methanol for generating the reduced iBN product. The observed deuterium incorporation was smaller with CD_3OD than with D_2O, reflecting a greater impact of the residual H in the deuterated reagent or in the solvent.

The same trends are also found for the experiments run with the $Cu^IBr/Cu^0/Me_6$TREN/methanol combination in C_6D_6 (entries 20–25 in Table 2). There is again a greater fraction of iBN with an increased amount of proton donor, and the iBN fraction is greater with CH_3OH than with CD_3OD. In order to tell whether the residual H in iBN originates from the CD_3OD reagent or from the solvent, the experiments were repeated with dried C_6D_6 (entries 22 and 25). The results, particularly the percent D incorporation in iBN, are essentially identical to those obtain in untreated C_6D_6, pointing to the CD_3OD reagent as the most probable H source.

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Table 3. Results of the Thermal Decomposition of AIBN in the Presence of Cu^I/TPMA Systems[a]

entry	solvent	Cu^I complex	additive/AIBN	iBN/dimer[b]	% D in iBN[c]
26	CD_3CN	$[Cu^I(TPMA)]^+BF_4^-$	–	0.09	
27	C_6D_6	CuBr/TPMA	–	0.10	
28	CD_3CN	$[Cu^I(TPMA)]^+BF_4^-$	CH_3OH (2)	0.10	
29	CD_3CN	$[Cu^I(TPMA)]^+BF_4^-$	CH_3OH (40)	0.14	
30	CD_3CN	$[Cu^I(TPMA)]^+BF_4^-$	CH_3OH (200)	3.6	
31	CD_3CN	$[Cu^I(TPMA)]^+BF_4^-$	CD_3OD (2)	0.11	1.3
32	CD_3CN	$[Cu^I(TPMA)]^+BF_4^-$	CD_3OD (40)	0.12	9.7
33	CD_3CN	$[Cu^I(TPMA)]^+BF_4^-$	CD_3OD (200)	2.35	70.5
34	C_6D_6	CuBr/TPMA	CH_3OH (100)	4.66	
35	C_6D_6	CuBr/TPMA	CD_3OD (100)	2.85	87.4

[a]Experiments in CD_3CN: $[Cu^I(MeCN)_4]BF_4$/TPMA/AIBN = 1:2:0.5, T = 80 °C, 8 h. Experiments in C_6D_6: [CuBr]/Cu^0/TPMA/AIBN = 1:4:1.7:1, T = 75 °C, 8 h. [b]Ratio of the two Me_2C resonances (see Supporting Information), hence equivalent to the moral ratio of AIBN leading to each product. [c]Fraction of $Me_2CD(CN)$ in the iBN product, determined by ^1H NMR integration.

Table 4. Results of the Thermal Decomposition of AIBN in the Presence of Cu^I/BIPY Systems[a]

entry	solvent	Cu^I complex	additive/AIBN	iBN/dimer[b]	% D in iBN[c]
36	CD_3CN	$[Cu^I(BIPY)_2]^+BF_4^-$	–	0.11	
37	C_6D_6	CuBr/BIPY	–	0.07	
38	CD_3CN	$[Cu^I(BIPY)_2]^+BF_4^-$	CH_3OH (2)	0.10	
39	CD_3CN	$[Cu^I(BIPY)_2]^+BF_4^-$	CH_3OH (40)	0.08	
40	CD_3CN	$[Cu^I(BIPY)_2]^+BF_4^-$	CH_3OH (200)	0.11	
41	CD_3CN	$[Cu^I(BIPY)_2]^+BF_4^-$	CD_3OD (2)	0.11	2.4
42	CD_3CN	$[Cu^I(BIPY)_2]^+BF_4^-$	CD_3OD (40)	0.12	3.6
43	CD_3CN	$[Cu^I(BIPY)_2]^+BF_4^-$	CD_3OD (200)	0.15	4.2
44	C_6D_6	CuBr/BIPY	CH_3OH (100)	0.13	
45	C_6D_6	CuBr/BIPY	CD_3OD (100)	0.13	38.2

[a]Experiments in CD_3CN: $[Cu^I(MeCN)_4]BF_4$/BIPY/AIBN = 1:4:0.5, T = 80 °C, 8 h. Experiments in C_6D_6: [CuBr]/Cu^0/BIPY/AIBN = 1:4:3.4:1, T = 75 °C, 8 h. [b]Ratio of the two Me_2C resonances (see Supporting Information), hence equivalent to the moral ratio of AIBN leading to each product. [c]Fraction of $Me_2CD(CN)$ in the iBN product, determined by ^1H NMR integration.

A comparison of the results obtained in the two different solvents shows that a greater iBN fraction was obtained in C_6D_6 (for instance, *cf.* entries 21 and 16 or entries 24 and 19), even though with a lower methanol/AIBN ratio. It is notable, however, that small amounts of the radical–radical coupling product (dimer) were always present, even when using 100 equiv of CH_3OH. This result is in stark contrast with the results reported by Yamago et al.,[28] where the PMA$^\bullet$ radicals produced by PMA–Br activation were fully quenched to PMA–H by Cu^I in the presence of only 10 equiv of CH_3OH or CD_3OD, with no visible detection of coupling product.

If RRT takes place according to the OMRP pathway (Scheme 6), the greater iBN fraction in C_6D_6 relative to CD_3CN may be attributed to either a more favorable formation of the organometallic intermediate or to the greater acidity of the proton donor in this solvent or to a contribution of both factors. The first hypothesis requires that a coordination site for the radical addition is more easily available in C_6D_6. The Cu^I complex in this solvent is likely to be pentacoordinated, [CuBr(κ^4-Me_6TREN)], like the crystallographically characterized related [CuBr(κ^4-TPMA)],[56] and the resulting organocopper(II) adduct is also likely to adopt a 5-coordinated structure. Thus, the radical addition requires either dissociation of the bromide ion, $[Cu\{C(CN)Me_2\}(\kappa^4\text{-}Me_6TREN)]^+Br^-$, which is unlikely in a nonpolar solvent, or dissociation of one of the Me_6TREN N donor atoms, $[CuBr\{C(CN)Me_2\}(\kappa^3\text{-}Me_6TREN)]$. On the other hand, in CD_3CN the Cu^I complex may be either tetracoordinated, $[Cu(\kappa^4\text{-}Me_6TREN)]^+BF_4^-$, or pentacoordinated as a solvent adduct, $[Cu(\kappa^4\text{-}Me_6TREN)(CD_3CN)]^+BF_4^-$, like the related crystallographically characterized $[Cu(\kappa^4\text{-TPMA})(CH_3CN)]^+BPh_4^-$.[57] Hence, radical addition would require in this case displacement of the solvent molecule. The relative acidity (pK_a) of methanol in C_6D_6 and CD_3CN does not appear to be known. Acid dissociation constants are available in polar solvents but cannot be easily assessed in nonpolar ones such as benzene.

If RRT follows the OS-PCET pathway, the reaction should be facilitated in the solvent with higher dielectric constant (acetonitrile), because of the better stabilization of charged species (the transients $[Cu^{II}Br(Me_6TREN)]^+$ and MeO^- would initially be produced, together with the product PMA–H, from neutral $[Cu^IBr(Me_6TREN)]$, PMA$^\bullet$, and MeOH), hence the observed greater fraction of iBN in C_6D_6 seems to exclude this pathway. Finally, if an IS-PCET pathway is followed, the observed trends when changing solvent would be consistent with more favorable methanol coordination to $[Cu^IBr(Me_6TREN)]$ in C_6D_6 than to $[Cu^I(Me_6TREN)]^+$ in CD_3CN. In terms of the water/methanol comparison in CD_3CN, either a more favorable coordination of water than methanol to $[Cu^I(Me_6TREN)]^+$ in CD_3CN or a greater aptitude of the coordinated water to undergo the PCET process would explain the observed trend.

3.c. Decomposition in the Presence of Cu^I Complexes with TPMA and BIPY. Additional experiments, using copper complexes stabilized by the TPMA and BIPY ligands, were restricted to methanol as the source of hydrogen or deuterium. The results obtained in the presence of TPMA are collected in

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Table 3. The control experiments run in the absence of proton donor (entries 26 and 27) yielded again results identical to those in the absence of copper complex. The addition of increasing amount of CH_3OH or CD_3OD in CD_3CN (entries 28−30 or 31−33, respectively) yields an increasing amount of iBN, with the biggest jump between 40 and 200 equiv per AIBN. The same trend holds for the percent of D incorporation in the iBN product. The KIE induced a greater fraction of iBN with CH_3OH relative to CD_3OD (*cf.* entries 30 and 33). Changing solvent from CD_3CN to C_6D_6 shows the same trends as for the Me_6TREN system, with more iBN generated in the C_6D_6 solution relative to the CD_3CN solution (*e.g.*, *cf.* entries 34 and 30 or entries 35 and 33).

Table 4 reports all the results obtained using copper complexes in combination with the BIPY ligand. In this case, increasing the amount of methanol, whether regular or deuterated, whether in CD_3CN or in C_6D_6, did not significantly alter the iBN/dimer ratio relative to the control experiments run in the absence of copper complex. On the other hand, there was a slight D incorporation when using CD_3OD. This D incorporation was much less significant in CD_3CN than in C_6D_6.

3.d. Probing OS-PCET. If RRT occurs via OS-PCET (Scheme 6), the copper(I) complex is oxidized to $[Cu^{II}(L)]^{2+}$ and the radical is reduced to anion, with concurrent or subsequent proton transfer from ROH(D). Either way, the aptitude to follow this decomposition pathway relative to RT (or CRT) should scale with the standard reduction potentials (E°) of the copper complexes. The values of E° for the $[Cu^{II}(L)]^{2+}/[Cu^{I}(L)]^{+}$ redox couples with BIPY, TPMA, and Me_6TREN are 0.18, 0.02, and −0.07 V vs SCE in acetonitrile.[58] The iBN/dimer ratio, reflecting the aptitude to undergo RRT for the three complexes and 200 equiv of CH_3OH or CD_3OD in CD_3CN is shown in Figure 1. The

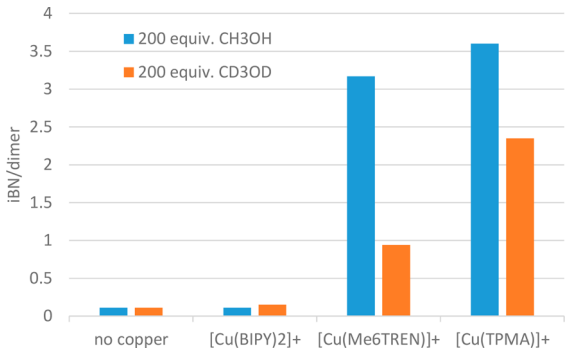

Figure 1. Observed isobutyronitrile(iBN)/tetramethylsuccinonitrile-(dimer) ratio for the AIBN decomposition in the presence of 200 equiv of CH_3OH or CD_3OD and the $[Cu^{I}(L)]^{+}$ complexes (L = $(BIPY)_2$, Me_6TREN, TPMA) in CD_3CN.

value of E° agrees with $[Cu^{I}(BIPY)]^{+}$ yielding the lowest degree of RRT, because it is the weakest reducing agent. However, the trend of reduction potentials for $[Cu^{I}(TPMA)]^{+}$ and $[Cu^{I}(Me_6TREN)]^{+}$ does not match the experimental degrees of RRT, which is greater for the weaker reducing agent $[Cu^{I}(TPMA)]^{+}$. Therefore, the electrochemical properties of the catalysts appear to rule out OS-PCET as the preferred mechanism for this decomposition pathway. Further evidence against the OS-PCET pathway is provided by the iBN/dimer ratio (hence the impact of RRT), which is greater in benzene than in MeCN, whereas reactions involving the generation of charged species from neutral (or less charged) ones should be facilitated in solvents with a greater dielectric constant. Finally, a concerted OS-PCET process would be a termolecular reaction with an inherently low probability.[59]

3.e. Investigation of Water and Methanol Coordination to $[Cu^{I}(L)]^{+}$. The IS-PCET pathway requires coordination of the proton donor to the Cu^{I}/L activator. Thus, the aptitude of the two proton donors (H_2O and CH_3OH in CD_3CN, CH_3OH in C_6D_6) to yield equilibrium amounts of Cu^{I} adducts was investigated by ^1H NMR spectroscopy, using the Me_6TREN system. These investigations, however, could not give unambiguous evidence in favor of an interaction. The ^1H NMR spectra recorded for the $[Cu^{I}(Me_6TREN)]^{+}/H_2O$ experiment in CD_3CN are shown in the Supporting Information, section S2. Before the addition of water, the spectrum shows the three expected signals of the Me_6TREN ligand in a 3:1:1 ratio, although broad, plus an additional small resonance at 2.23 ppm probably due to the water impurity that was already present in the NMR solvent. The observation of broad ^1H NMR resonances is a common phenomenon for Cu^{I} complexes, caused by the presence of paramagnetic Cu^{II} impurities. These possibly originate from disproportionation of the in situ-generated $[Cu^{I}(Me_6TREN)]^{+}$. However, this equilibrium is not extensive in MeCN ($K_{disp} = 10^{-3}$).[60] Addition of increasing amounts of H_2O results in a continuous downfield shift of the H_2O resonance while the Me_6TREN resonances further broaden. A rapid exchange between free and coordinated H_2O that would only involve the diamagnetic Cu^{I} complex would result instead in a signal sharpening and displacement toward the typical chemical shift value of free water in acetonitrile (2.13 ppm).[61] Therefore, the observed behavior rather suggests a rapid exchange with a paramagnetic $Cu^{II}(H_2O)$ adduct, which would be generated in increasing proportions by addition of water, because the latter favors disproportionation of the $[Cu^{I}(Me_6TREN)]^{+}$ complex. Similarly, electrochemical or spectrochemical titrations of Cu complexes in the presence of various amounts of water did not provide conclusive evidence on water binding to Cu^{I} (see Supporting Information, section S3). It is therefore impossible to obtain even qualitative evidence in favor of water binding to Cu^{I} from this experiment.

The analogous addition of CH_3OH to a $[Cu^{I}(Me_6TREN)]^{+}$ solution in CD_3CN provides analogous results, see Supporting Information, section S4. Notably, the Me_6TREN ligand resonances broaden upon addition of increasing methanol amounts. At the same time, the OH resonance, while remaining relatively sharp, diverges toward lower-field position rather than converging toward the value of free CH_3OH in CD_3CN. It is also notable that the coupling between the CH_3 (doublet) and OH (quartet) protons for free CH_3OH, which is visible in the absence of the Cu complex (spectrum also shown in the Supporting Information), is washed out in the presence of the metal complex. The corresponding study of the addition of CH_3OH to $[Cu^{I}Br(Me_6TREN)]$ in C_6D_6 exhibits again the same behavior. In this case, the methanol OH resonance is not clearly visible in the absence of copper, in agreement with the literature,[61] but becomes observable as a weak and broad resonance in the presence of the copper complex, once again broadening and shifting downfield as the methanol amount is increased (Supporting Information, section S5).

3.f. DFT Calculations. Since no experimental methods are available to assess the ability of the various copper systems to bind proton donor molecules on one side and the

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Table 5. DFT-Estimated Gibbs' Free Energies ($\Delta G_{298.15,MeCN,1M}$ in kcal/mol) for the Formation of $[Cu^{I}(L)_n(CH_3CN)]^+$, $[Cu^{I}(L)_n(H_2O)]^+$, and $[Cu^{II}\{CMe_2(CN)\}(L)_n]^+$ from $[Cu^{I}(L)_n]^+$ plus CH_3CN, H_2O, or $Me_2C^{\bullet}(CN)$, Respectively (L = Me_6TREN and TPMA, n = 1; L = BIPY, n = 2)

L	$[(L)_nCu^{I}-NCCH_3]^+$	$[(L)_nCu^{I}-OH_2]^+$	$[(L)_nCu^{II}-CMe_2(CN)]^+$	$[(L)_nCu^{II}-N{=}C{=}CMe_2]^+$
Me_6TREN, n = 1	−2.6	−1.1	−6.6	−12.9
TPMA, n = 1	−0.5	−5.9	−11.9	−12.6
BIPY, n = 2	+5.8	*a*	*a*	+2.9

[a]A stable adduct could not be optimized (see text).

Table 6. Selected Structural Parameters (Distances in Å, Angles in deg) for the Optimized $[Cu^{II}(L)_n(CMe_2CN)]^+$, $[Cu^{II}(L)_n(N{=}C{=}CMe_2)]^+$, $[Cu^{I}(L)_n((CH_3CN)]^+$, and $[Cu^{I}(L)_n((H_2O)]^+$ Structures

parameter	Me_3TREN	TPMA	$(BIPY)_2$
	$[Cu^{II}(L)_n(CMe_2CN)]^+$ systems		
Cu−C	2.160	2.134	
Cu−N_{ax}	2.260	2.223	
Cu−N_{eq}	2.384, 2.409, 2.363	2.210, 2.211, 2.207	
average Cu−N_{eq}	2.385	2.209	
C−Cu−N_{ax}	171.46	174.69	
C−Cu−N_{eq}	99.26, 101.40, 100.96	102.36, 104.82, 102.78	
	$[Cu^{II}(L)_n(N{=}C{=}CMe_2)]^+$ systems		
Cu−N	1.983	2.008	2.040
Cu−N_{ax}	2.227	2.307	2.168, 2.220 (eq)
Cu−N_{eq}	2.315, 2.321, 2.214	2.094, 2.150, 2.166	2.125, 2.164 (ax)
average Cu−N_{eq}	2.283	2.137	
N−Cu−N_{ax}			120.67, 137.39 (eq)
N−Cu−N_{eq}	93.72, 96,21, 105.17	106.98, 100.83, 100.20	95.04, 89.44 (ax)
	$[Cu^{I}(L)_n(CH_3CN)]^+$ systems		
Cu−N (MeCN)	1.976	2.038	1.984
Cu−N_{ax}	2.332	2.438	2.108, 2.108 (eq)
Cu−N_{eq}	2.336, 2.321, 2.342	2.142, 2.141, 2.143	2.325, 2.323 (ax)
N−Cu−N_{ex}	179.29	179.93	125.25, 125.41 (eq)
N−Cu−N_{eq}	100.79, 101.39, 100.53	105.08, 105.12, 105.04	93.75, 93.76 (ax)
	$[Cu^{I}(L)_n(CH_3CN)]^+$ systems		
Cu−O	2.435	2.458	
Cu−N_{ax}	2.280	2.315	
Cu−N_{eq}	2.225, 2.224, 2.233	2.071, 2.078, 2.065	
O−Cu−N_{ax}	179.69	164.97	
O−Cu−N_{eq}	96.64, 97.16, 97.09	93.94, 92.30, 114.76	

cyanoisopropyl radical on the other, we turned to computational studies. These were restricted to the cationic $[Cu^{I}(L)_n]^+$ complexes in acetonitrile solution and their interaction with water and with the cyanoisopropyl radical. However, since the complexes are likely to be solvated in acetonitrile, the 5-coordinate $[Cu^{I}(L)_n(CH_3CN)]^+$ system was also considered. The calculations were carried out using a DFT approach (see Computational Details), using the full molecular systems with dispersion and solvation corrections in acetonitrile. The calculated values are reported as Gibbs free energies at 298.15 K in the condensed phase 1 M standard state. On the basis of our previous work, we believe that the chosen functional/basis set combination gives relatively accurate energy estimates,[20] but we do not put a large amount of faith on the quantitative results. However, we believe that the calculated trends should accurately reproduce the experimental reality. The interaction energies are shown in Table 5, and selected optimized structural parameters are reported in Table 6, while views and Cartesian coordinates of all optimized geometries are reported in the Supporting Information (section S5).

The binding energies for CH_3CN are very small and negative (i.e., the interaction is favorable) only for the Me_6TREN and TPMA systems. The CH_3CN adduct for the BIPY system, although giving an optimized local energy minimum, is endoergic relative to the sum of the separate $[Cu^{I}(BIPY)_2]^+$ and MeCN. The lower binding aptitude of the BIPY system may be associated to the greater stability of the $[Cu^{I}(BIPY)_2]^+$ tetrahedral geometry, whereas the geometry of the complexes with tripodal ligands, $[Cu^{I}(Me_6TREN)]^+$ and $[Cu^{I}(TPMA)]^+$, is strained. The trigonal bipyramidal structure of the $[Cu^{I}(L)_n(CH_3CN)]^+$ product, on the other hand, can better adjust all ligands.

Water binding also appears weak according to the calculations. For the Me_6TREN system, binding water is less favorable than acetonitrile, though still slightly exoergic relative to the 4-coordinated unsaturated complex. For the TPMA system, on the other hand, the calculations indicate that water binds better than acetonitrile. For the BIPY system, a local minimum for a Cu^{I}-bound water adduct could not even be located, yielding instead a van der Waals $[Cu^{I}(BIPY)_2\cdots OH_2]^+$ adduct that features a loose interaction between the O atom and a CH group of one of the BIPY aromatic rings.

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The interaction with the cyanoisopropyl radical was found possible in two different ways, leading to C-bonded and N-bonded isomers. In the free radical, the spin density resides mostly on the tertiary C atom (0.731), but a significant amount (0.342) is also located on the cyano N atom. The most relevant spin density values for all paramagnetic systems are shown in Figure 2. Metal binding through the C atom, even

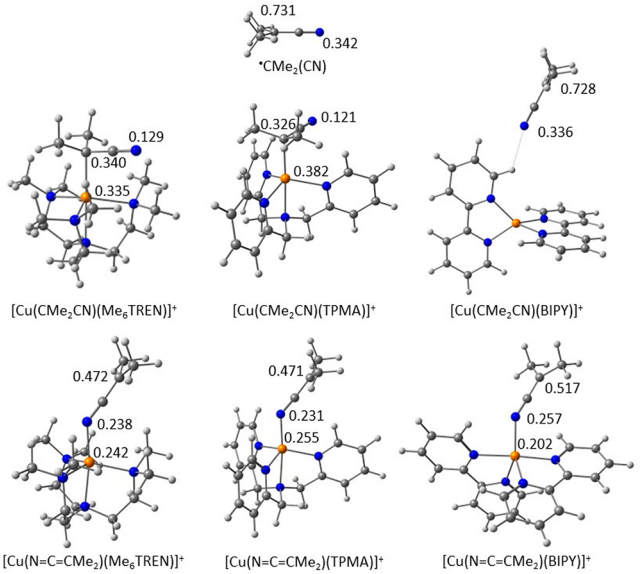

Figure 2. Views of all optimized paramagnetic structures with the main Mulliken spin densities.

though the radical is stabilized and tertiary, is energetically favored for the most reactive Me_6TREN and TPMA systems. On the other hand, no stable energy minimum could be located for the less reactive BIPY system. Instead, the geometry optimization for this system converged to a van der Waals $[Cu^I(BIPY)_2\cdots NC(CMe_2)]^+$ adduct, similar to that already described with water (loose interaction between the N atom and a CH group of a BIPY aromatic rings). In this adduct, which is located at +3.7 kcal/mol relative from the two separate reagents, the spin density is entirely located on the cyanoisopropyl group, with values on the C and N atoms very close to those of the free radical, while the Cu atom has no spin density. On the other hand, the organocopper(II) products with the two tripodal ligands show an approximately equal share of the spin density between the Cu atom and the Cu-bonded C atom, in agreement with the weak bonding interaction, plus a comparatively reduced but nonzero spin density on the cyanoisopropyl N atom; see Figure 2.

Strikingly, the alternative binding of the cyanopropyl radical through the N atom, leading to the keteniminato $[(L)_n(Cu^{II}-N{=}C{=}CMe_2]^+$ isomer, is even more favorable. It is worth noting that metal binding of a cyano-stabilized radical via the N atom has been previously proposed for the addition of the $^{\bullet}C(CN)(Me)CH_2C(OMe)Me_2$ radical generated from 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70) to Co(acac)$_2$ (acac = acetylacetonate), on the basis of both experimental and computational evidence.[62] Other keteniminato complexes of transition metals are also known, such as $[IrCp^*(N{=}C{=}CPh_2)(Ph)(PMe_3)]$ (Cp^* = pentamethylcyclopentadienyl)[63] and $[Ru(dmpe)_2(H)(N{=}C{=}CHAr)]$ (Ar = Ph, p-$C_6H_4CF_3$; dmpe = 1,2-bis(dimethylphosphino)-ethane),[64,65] although they were not obtained by radical routes.

The energetic advantage for N-binding is greater for the Me_6TREN system (6.3 kcal/mol) than for the TPMA system, for which the N-bonded complex is more stable than the C-bonded isomer by only 0.7 kcal/mol. The reason for this difference in relative stabilization can be appreciated from the structural parameters in Table 6. The NMe_2 groups of Me_6TREN generate a significantly greater steric repulsion than the TPMA pyridine rings on the C-bonded tertiary radical, which is greater than the steric repulsion exerted on the isomeric N-bonded fragment. This can be judged by the greater increase of the Cu−N_{eq} distances from the N-bound to the C-bound isomer (the average Cu^{II}−N_{eq} distance increases from 2.227 to 2.385 Å, a 0.158 Å increase, for the Me_6TREN system, vs an increase from 2.137 to 2.209 Å, only a 0.072 Å increase, for the TPMA system). The N-bound isomer yields a stable minimum also for the less reactive BIPY system, but this is endoergic relative to the separate reagents. In these three keteniminato Cu^{II} derivatives, the spin density is predominantly located on the isopropyl C atom (0.472, 0.471, and 0.517 for Me_6TREN, TPMA, and BIPY systems, respectively) with the rest equally shared by the directly bonded Cu and N atoms. In this respect, the assignment of the oxidation state II to the copper atom in these radical adducts is just a formality, because the majority of the spin density, particularly for the N-bound keteniminato isomer, still resides on the cyanoisopropyl group. It is of interest to note that the related cyanomethyl group (CH_2CN) was found bonded in a Cu^{II} complex as a cyano-substituted alkyl ligand via the C atom, rather than as a keteniminato ligand via the N atom.[66]

In conclusion, the DFT calculations indicate that there is substantial difference between the two tripodal ligands

Table 7. Results of the Thermal Decomposition of AIBN in the Presence of $[Et_3NH]^+$ Salts as Proton Donors and Different Cu^I/L Systems[a]

entry	anion	Cu^I complex	$[Et_3NH]^+$/AIBN	iBN/dimer[b]
46	BF_4^-	–	[c]	0.05
47	BF_4^-	$[Cu^I(Me_6TREN)]^+BF_4^-$	2	5.11
48	BF_4^-	$[Cu^I(Me_6TREN)]^+BF_4^-$	40	7.68
49	Br^-	$[Cu^I(Me_6TREN)]^+BF_4^-$	2	5.56
50	BF_4^-	$[Cu^I(TPMA)]^+BF_4^-$	2	2.58
51	BF_4^-	$[Cu^I(TPMA)]^+BF_4^-$	40	9.81
52	BF_4^-	$[Cu^I(BIPY)_2]^+BF_4^-$	2	0.15
53	BF_4^-	$[Cu^I(BIPY)_2]^+BF_4^-$	40	1.18

[a] $[Cu^I(MeCN)_4]BF_4$/L/AIBN = 1:(2 for L = Me_6TREN and TPMA; 4 for L = BIPY):0.5, T = 80 °C, 8 h. [b] Ratio of the two Me_2C resonances (see Supporting Information), hence equivalent to the moral ratio of AIBN leading to each product. [c] $[Et_3NH]^+$/AIBN = 2.

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Me_6TREN and TPMA on one side and the bidentate BIPY system on the other one. The two systems with the tripodal ligands have greater aptitude than that with BIPY to bind both water and the cyanoisopropyl radical. While $[Cu^{I}(BIPY)_2]^+$ shows no thermodynamic gain for binding either a neutral molecule or the organic radical, the Me_6TREN and TPMA systems can be stabilized by addition of both a neutral donor molecule (acetonitrile, water) and the cyanoisopropyl radical. The stabilization provided by the radical is much greater and appears more favorable when binding occurs via the N atom to yield a less bulky Cu^{II}–N=C=CMe_2 moiety than via the C atom to yield an organometallic derivative. The experimental observation of a much greater impact of $[H_2O]$ and $[CH_3OH]$ on the product distribution for the Me_6TREN and TPMA system than for the BIPY system is thus consistent with both the OMRP and the IS-PCET pathways in RRT (Scheme 6).

3.g. Protonolysis with Triethylammonium Salts. In order to gain additional information on the RRT mechanism, we have finally opted for the use of a proton donor that is devoid of coordinating properties, namely a triethylammonium salt. This proton donor cannot operate via the IS-PCET pathway, whereas its greater acidity relative to water and methanol should enhance the OMRP pathway. Two different $[Et_3NH]^+$ salts, bromide and tetrafluoroborate, were used for the AIBN decomposition experiments, which were conducted only in CD_3CN for solubility reasons. The results are collected in Table 7. The blank experiment run in the absence of copper complex (entry 46) yields a very close iBN/dimer ratio to that of the decomposition without proton donor (Table 1, entry 1).

The results clearly show that the Et_3NH^+ salts enhance RRT relative to water and methanol. With Me_6TREN, an RRT/dimerization ratio of 5.11 was obtained when using only 2 equiv of $Et_3NH^+BF_4^-$ per AIBN (entry 47), whereas the equivalent amount of CH_3OH gives a ratio of 0.20 (Table 2, entry 14). This ratio further increased to 7.68 with 40 equiv (entry 48), vs 1.65 with the same amount of CH_3OH (Table 2, entry 15). These ratios are even greater than that obtained with 200 equiv of H_2O (4.28, Table 2, entry 12). Using $Et_3NH^+Br^-$ gave an essentially identical result (entry 49) to that of the BF_4^- salt, in agreement with the weak association of Br^- to $[Cu^{I}(Me_6TREN)]^+$ in acetonitrile.[67] For the TPMA complex, the RRT is equally enhanced (entries 50–51, *cf.* with the equivalent amounts of CH_3OH in Table 3, entries 28 and 29). Finally, even the BIPY system, for which a low impact of RRT was shown even in the presence of 200 equiv of CH_3OH (iBN/dimer = 0.11, Table 4, entry 40), exhibits an enhancement of RRT when using the Et_3NH^+ salt (entries 52 and 53), even though the impact of RRT remains largely inferior with respect to the use of the more reducing complexes with Me_6TREN and TPMA.

Thus, it clearly appears that RRT occurs primarily by what has been defined as the "OMRP route" in Scheme 6, although the DFT result rather support the formation of an N-bound Cu^{II} intermediate, rather than an organometallic complex. The acidic additive (water, methanol, or Et_3NH^+) can then provide a proton to cleave the Cu–N bond heterolytically and the extent of this process is highly dependent on the proton donor acidity. The observed isobutyronitrile product can result from either direct protonation of the conjugated C atom, or cleavage of the Cu^{II}–N bond with release of the ketenimine Me_2C=C=NH, which subsequently tautomerizes.[68]

The experimental results are actually rather consistent with the DFT predictions, because formation of the $[Cu^{I}(L)_n]^+$ adduct with $Me_2C^{\bullet}(CN)$ provides greater stability than coordination of water or acetonitrile. The stronger stabilization predicted for the Me_6TREN and TPMA system is in line with the greater fraction of RRT product obtained for those systems. Concerning the BIPY system, the DFT calculations show a slightly endoergic adduct formation with the radical via the N atom (e.g., the keteniminato form). However, the relative energy of this derivative makes it a thermally accessible intermediate for the RRT process. Therefore, it seems that the agreement between the calculations and the experimental result (for the RRT in the presence of Et_3NH^+) is good even at the semiquantitative level. As a final note, we can conclude that while the experiments run with Et_3NH^+ definitely prove the intervention of a pathway involving an adduct between the radical and the Cu^{I}/L complex, this does not exclude the contribution (or even the exclusive action) of an IS-PCET pathway in the presence of water or methanol.

4. CONCLUSION

We have analyzed the distribution of the cyanoisopropyl radical termination products in the presence of proton donors (water, methanol, and triethylammonium salts) and copper(I) complexes stabilized by three different ligand systems (Me_6TREN, TPMA, and BIPY) in two different solvents (CD_3CN, C_6D_6). The simultaneous presence of copper and proton donor provides access to a reductive radical termination (RRT) with formation of isobutyronitrile by stoichiometric transfer of an electron from the copper complex and by a proton from the acidic additive. The extent of RRT is affected by the nature of the Cu complex, of the proton donor and of the solvent in the orders BIPY ≪ Me_6TREN ∼ TPMA, CD_3OD < CH_3OH, D_2O < H_2O, $CH_3OH(D)$ < $H(D)_2O$ ≪ Et_3NH^+, and CD_3CN < C_6D_6.

The most surprising and unexpected result of this study, as suggested by the DFT calculations, is the tendency of the most reactive $[Cu(L)_n]^+$ complexes (i.e., those stabilized by the Me_6TREN and TPMA ligands, n = 1) to trap the cyanoisopropyl radical, a stabilized radical for which we considered trapping by a transition metal to be unlikely, and yield stabilized adducts that may be formally described as copper(II) complexes, though the spin density transfer from the organic radical to the metal is quite partial. No evidence for such an interaction was found for the less reactive system (L = BIPY, n = 2). It is also relevant to note that Cu^{I} is not known for forming stable organocopper(II) derivatives, even with strong radicals.[45] Even more surprising and unexpected is the indication by the DFT calculations that the N-bound keteniminato isomer is more stable than the C-bound cyanoisopropyl organometallic derivative, particularly for the more sterically demanding Me_6TREN system.

Coordination of donor molecules (acetonitrile, water) to the $[Cu(L)_n]^+$ complexes appears possible but is quite weak, according to the DFT calculations, for the two most reactive systems and not favorable at all for the BIPY system. An NMR investigation has not provided positive evidence for the presence of this interaction for water or methanol and the Me_6TREN system. Finally, the large extent of RRT for the Et_3NH^+ proton donor, which is at the same time the strongest acid of the series and has no coordinating properties, indicates that RRT proceeds via an intermediate Cu^{II} adduct, followed by protonolysis, rather than by an IS-PCET process. A potential alternative OS-PCET is excluded by the solvent effect and by the redox potentials trend. A possible contribution of

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IS-PCET to RRT, however, cannot be excluded for proton donors able to coordinate to the metal center.[31]

Overall, while this study is consistent with the proposition, made in a previous contribution,[28] that the saturated PMA−H made by reductive termination of PMA• chains in the presence of methanol in toluene solution may originate from the protonolysis of a PMA−Cu^{II}Br/Me_6TREN intermediate, the contribution (or dominance) of alternative PCET pathways cannot yet be totally excluded. In addition, we have shown in our study that, at least for the termination of the cyanoisopropyl radical, the C_6D_6 solvent does not contain sufficient amounts of water impurities to yield a significant impact of RRT, even for the most active Cu^{I}Br/Me_6TREN system. Yet, the PMA• termination in the absence of methanol was shown in the previous contribution[28] to yield dominant fraction of PMA−H product, not resulting from disproportionation. This puzzling result merits further studies, currently ongoing in our laboratories, which will be reported in a forthcoming contribution. Another puzzling result is that, although the occurrence of RRT (stoichiometrically oxidizing the ATRP activator complex L/Cu^{I} to an inactive L/Cu^{II}X complex) is promoted by water and other proton donors, the complexes investigated in the present study are quite robust ATRP catalysts even in water, to give well-controlled halogen-capped macromolecules with high chain-end fidelity.[69,70] A full understanding of how radicals interact with L/Cu^{I} complexes under polymerization conditions is paramount not only to rationalize the good performance of ATRP catalysts and possibly further improve them but also for implementing polymerizations successfully controlled by only OMRP, which presents certain advantages in particular for less activated monomers,[71−74] without interference of metal-catalyzed or -mediated terminations (CRT or RRT).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.9b00660.

Details of the NMR determination of the product distribution, on the NMR investigation of the interaction of proton donors and Cu^{I} complexes, and DFT results (Cartesian coordinates, energies, spin densities, and optimized geometrical parameters) (PDF)

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L.T. has carried out all the experimental work. R.P. has carried out the DFT calculations. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Notes

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■ ABBREVIATIONS

ATRP, atom transfer radical polymerization; CRT, catalytic radical termination; OMRP, organometallic-mediated radical polymerization; RRT, reductive radical termination; AIBN, azobis(isobutyronitrile); BIPY, 2,2′-bipyridine; Me_6TREN, tris[2-(dimethylamino)ethyl]amine; TPMA, tris(2-pyridylmethyl)amine

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