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Acrylonitrile Polymerization by Cy_3PCuMe and $(Bipy)_2FeEt_2$

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Abstract: Cy_3PCuMe (**1**) undergoes reversible ligand redistribution at low temperature in solution to form the tight ion pair $[Cu(PCy_3)_2][CuMe_2]$ (**3**). The structure of **3** was assigned on the basis of (i) the stoichiometry of the **1** = **3** equilibrium, (ii) the observation of a triplet for the PCy_3 C1 ^{13}C NMR resonance due to virtual coupling to two ^{31}P nuclei, and (iii) reverse synthesis of **1** by combining separately generated $Cu(PCy_3)_2^+$ and $CuMe_2^-$ ions. Complex **1** and $[Cu(PCy_3)_2][PF_6]$ (**5**) coordinate additional PCy_3 to form $(Cy_3P)_2CuMe$ and $[Cu(PCy_3)_3][PF_6]$, respectively, while **3** does not. Complex **1**, free PCy_3, and $(bipy)_2FeEt_2$ (**2**) each initiate the polymerization of acrylonitrile. In each case, the polyacrylonitrile contains branches that are characteristic of an anionic polymerization mechanism. The major initiator in acrylonitrile polymerization by **1** is PCy_3, which is liberated from **1**. A transient iron hydride complex is proposed to initiate acrylonitrile polymerization by **2**.

Introduction

The polymerization of olefins by insertion chemistry with Ziegler−Natta, Cr-based, or single-site metal catalysts provides a powerful approach to the synthesis of polyolefins, often with a high degree of control of polymer composition and structure.[1] A major current challenge in this area is to develop catalysts that are capable of polymerizing or copolymerizing polar olefins, particularly $CH_2{=}CHX$ monomers with functional groups directly bonded to the olefin unit, by insertion mechanisms.[2] While some success has been achieved in the copolymerization of acrylates and vinyl ketones with ethylene and propene,[3] a general solution to this problem is lacking. Here we report studies directed to the development of metal catalysts for the insertion polymerization/copolymerization of acrylonitrile (AN).

Polyacrylonitrile (PAN) and related copolymers are prepared commercially by radical polymerization of AN. Controlled/living radical AN polymerizations in the presence of LCuX (ATRP, L = substituted or unsubstituted 2,2′-bipyridine),[4] dithioesters (RAFT),[5] or N-oxides[6] have been reported. Radical PAN is normally completely linear. AN is also readily polymerized by anionic polymerization initiators, in which case lower molecular weight (vs typical radical PAN), branched PAN is formed. Branching arises by inter- or intramolecular abstraction of -$CH_2CH(CN)$- methine protons from the polymer backbone by the propagating carbanion.[7]

Numerous metal complexes have been reported to polymerize AN.[8−10] While many of these metal-initiated polymerizations are clearly anionic, the mechanism is less clear for others.[8g−j] In particular, Yamamoto and co-workers proposed that the neutral metal alkyl complexes Cy_3PCuMe (**1**)[9] and $(bipy)_2FeEt_2$

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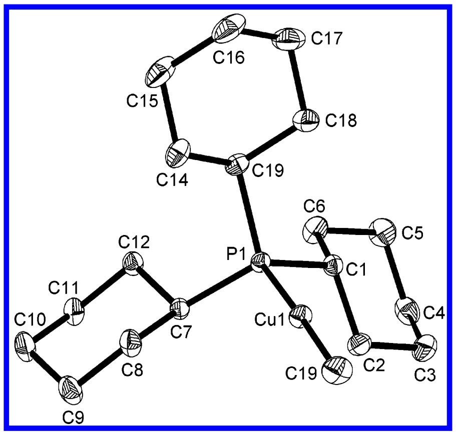

Figure 1. Molecular structure of **1**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

(**2**; bipy = 2,2′-bipyridine)[10] polymerize AN by insertion mechanisms. These reports, and the recent discovery of copper[3c,11] and iron[12] catalysts for ethylene polymerization, prompted us to investigate the structure and solution behavior of **1** and the reactions of **1** and **2** with AN in more detail, to determine the mechanisms by which these complexes polymerize AN.

Results and Discussion

Cy_3PCuMe (1). Complex **1** was synthesized by Yamamoto and co-workers[9] by reductive alkylation of $Cu(acac)_2$ with $Al(OEt)Me_2$ in the presence of PCy_3. This copper alkyl complex is quite stable, decomposing at 105 °C in the solid state with evolution of ethane.[9a,13] Complex **1** polymerizes acrylonitrile and copolymerizes acrylonitrile and acrylates.[9a] Complex **1** does not copolymerize AN and styrene, which the authors took as evidence for an insertion mechanism for AN homopolymerization.[9a]

We prepared **1** by the reaction of CuI with MeLi in Et_2O in the presence of PCy_3 at −35 °C. After evaporation of the solvent, the residue was extracted with a toluene/pentane mixture and crystallized at −40 °C, to afford **1** in 46% yield. While the overall yield is lower than in the original synthesis,[9a] isolation problems due to the presence of aluminum byproducts are avoided and crystalline material is obtained.

Table 1. Selected Bond Lengths and Angles for **1**[a]

Cu(1)−P(1)	2.1953(6)	P(1)−Cu(1)−C(19)	175.55(5)
Cu(1)−C(19)	1.916(2)	Cu(1)−P(1)−C(1)	109.24(5)
P(1)−C(1)	1.850(1)	Cu(1)−P(1)−C(7)	112.60(5)
P(1)−C(7)	1.855(2)	Cu(1)−P(1)−C(13)	116.05(5)
P(1)−C(13)	1.842(1)		

[a] Bond lengths are given in angstroms; bond angles are given in degrees.

Complex **1** is monomeric in the solid state with a linear coordination geometry at Cu (∠P(1)−Cu(1)−C(19) = 175.6(1)°; Figure 1, Table 1). No intermolecular contacts can be detected in the packing diagram, in accordance with the preference of Cu(I) for linear or tetrahedral geometries.[14] The Cu−Me distance in **1** [1.916(2) Å] is shorter than those in the tetrahedral complex $(Ph_3P)_3CuMe$ [2.04(1) Å][15] and the trigonal planar "pincer" complex $(Me_3SiC_5H_4)_2Ti(C_2SiMe_3)_2CuMe$ [1.966(2) Å][16] and is also shorter than Cu−C distances in monomeric anionic Cu alkyls (1.93−1.96 Å).[17,18]

Room-Temperature NMR Spectra of 1. Solutions of **1** in benzene-d_6, toluene-d_8, CD_2Cl_2, THF-d_8, or THF-d_8/CD_3CN mixtures display simple ^1H NMR spectra with multiplets for the cyclohexyl rings and a slightly broadened singlet for the Cu*Me* group.[19] The ^{31}P NMR spectra of **1** in these solvents contain one broad singlet in the region δ 14−17. The ^{13}C NMR spectrum of **1** at room temperature contains four PCy_3 signals, three of which show ^{31}P coupling with J_{CP} ranging from 6 to 18 Hz. The Cu*Me* ^{13}C resonance appears as a singlet at δ −7 to −9, depending on the solvent, and is significantly broadened by the $^{63,65}Cu$ quadrupole. No ^{63}Cu NMR signals are observed for **1**. With the exception of symmetrically substituted tetrahedral complexes, quadrupolar broadening usually prevents the observation of ^{63}Cu NMR spectra. In ^{63}Cu spectra of $[Cu(PR_3)_4][CuR'_2]$ ion pairs, for example, a signal was observed for the tetrahedral cation but not for the linear anion.[17b] No ^{63}Cu NMR signals were found for $(R_3P)_3CuR'$ complexes.[17b]

Variable-Temperature NMR Spectra of 1. When the temperature is lowered to below ca. 260 K, **1** is partially converted into a new species **3**. Equilibrium mixtures of **1** and **3** are observed in the temperature range 180−260 K. The transformation is reversible, and raising the temperature yields **1** quantitatively.

The ^1H and ^{31}P NMR spectra of **3** are similar to those of **1** (Figures 2 and 3).[20] The ^{13}C NMR spectrum of **3** contains four signals for the PCy_3 ligand, most of which are shifted slightly downfield from the signals of **1** (Figure 4). Significantly, the

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(19) The absence of ^{31}P coupling for the Cu−*Me* resonance may result from quadrupolar broadening by $^{63,65}Cu$ or from exchange of free and coordinated PCy_3. Since PCy_3 exchange in **1** is fast on the NMR time scale even at 190 K, even otherwise undetectably small amounts of free PCy_3 (from partial decomposition, hydrolysis, or impurities) would wash out the coupling.

(20) It was reported previously that the ^{31}P NMR resonance of **1** shifts upfield at lower temperatures; however, only one broadened signal was observed. These results are consistent with the **1** = **3** equilibrium described here; the lower field strength used in previous work did not enable resolution of the resonances for **1** and **3**. See Pasynkiewicz, S.; Poplawska, J. *J. Organomet. Chem.* **1986**, *302*, 269.

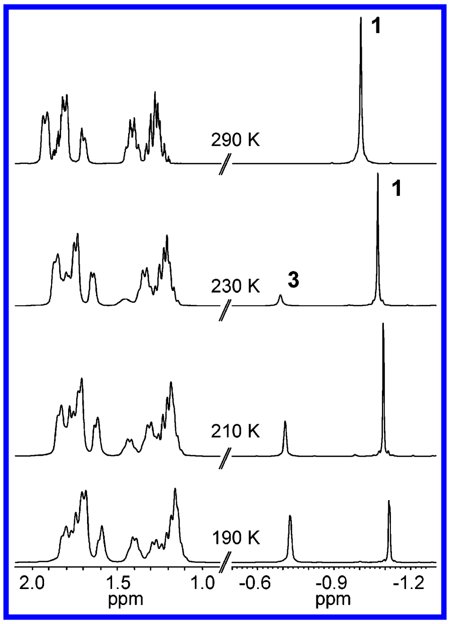

Figure 2. Variable-temperature ^{1}H NMR spectra of the **1** = **3** equilibrium in CD_2Cl_2.

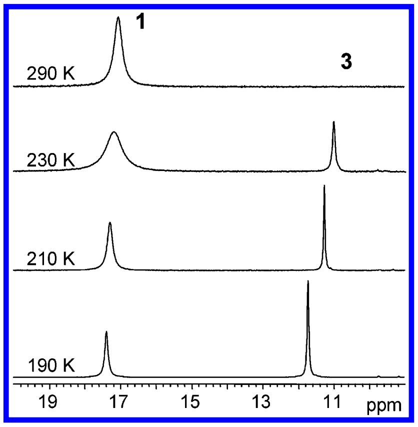

Figure 3. Variable-temperature $^{31}P\{^{1}H\}$ NMR spectra of the **1** = **3** equilibrium in CD_2Cl_2.

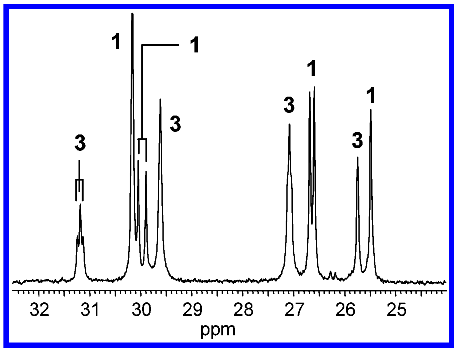

Figure 4. $^{13}C\{^{1}H\}$ NMR spectrum (PCy_3 region) of an equilibrium mixture of **1** and **3** in CD_2Cl_2 solution at 190 K.

PCy_3 C1 ^{13}C resonance of **3** in CD_2Cl_2 appears as triplet (δ 31.2) with J_{CP} = 7 Hz, in contrast to the doublet (δ 30.0) with J_{CP} = 19 Hz observed for **1**. The PCy_3 C2 and C3 ^{13}C resonances of **3** appear as broadened singlets, though the triplet structure can be seen qualitatively for the C2 resonance (δ 27.1).[21] Analogous results were obtained in toluene-d_8, THF-d_8, and THF-d_8/CD_3CN solution. The implications of this observation will be discussed below. No ^{63}Cu NMR signals are observed for **3** over the temperature range of 180−290 K, indicating that a symmetrical tetrahedral Cu species is not formed.

Table 2. Equilibrium Constants^{a} and Thermodynamic Parameters for the **1** = **3** Equilibrium (eq 1) in Different Solvents

solvent	K_1, 235 K (M^{-1})	$\Delta H°$ (kJ/mol)	$\Delta S°$ (J/(mol·K))	T range^{b} (K)
toluene-d_8	2.8(2)^{c}	−20.8(8)	−81(4)	180−260
CD_2Cl_2	0.73(3)	−20.5(2)	−90(1)	190−250
THF-d_8	2.0(2)	−21.7(3)	−87(2)	183−250
THF-d_8/CD_3CN^{d}	4.6(3)^{c}	−24.7(8)	−92(4)	210−230

^{a} Equilibrium constants were determined from ^{31}P NMR spectra for toluene-d_8 and from ^{1}H and ^{31}P NMR spectra for all other solvents. ^{b} Temperature range of K_1 measurements used to determine $\Delta H°$ and $\Delta S°$. ^{c} Standard deviation is estimated. ^{d} 41/59 ratio.

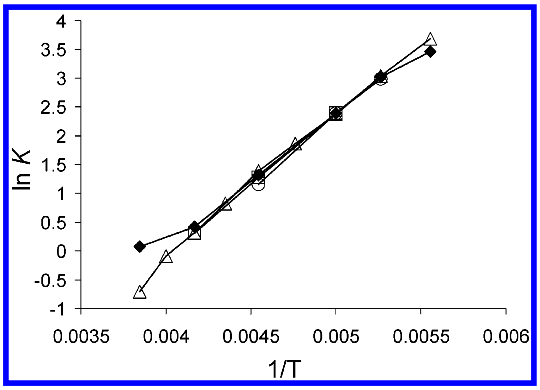

Figure 5. van't Hoff plots for the equilibrium constant K_1 = [**3**]/[**1**]^2 in toluene-d_8 solution with $[Cu]_{total}$ = 12 mM (○), 28 mM (□), 120 mM (◆), and 170 mM (△).

Determination of Equilibrium Constants and Molecular Formula of 3. The **1**:**3** ratio depends on the initial concentration of **1**, with higher concentrations favoring the formation of **3**. Measured values of the [**1**]/[**3**] ratio for solutions with $[\mathbf{1}]_{initial}$ = 12−170 mM, over the temperature range 180−260 K, are uniquely consistent with the equilibrium shown in eq 1 and show that **3** is formed from two molecules of **1**. Values for K_1 = [**3**]/[**1**]^2 are given in Table 2, and van't Hoff plots for different initial concentrations of **1** are shown in Figure 5. In accordance with the observed stoichiometry, reaction entropies of ca. −90 J/(mol·K) were obtained from these plots (Table 2). The equilibrium in eq 1 is rather insensitive to solvent polarity (Table 2).

$$\underset{\mathbf{1}}{2\ \mathrm{Cy_3PCuMe}} \rightleftharpoons \underset{\mathbf{3}}{(\mathrm{Cy_3PCuMe})_2} \qquad (1)$$

Solution Structures of 1 and 3. Since $Cy_3PCu^{i}Bu$[22] and $^{n}Bu_3PCuMe$[23] are monomeric in benzene and **1** is monomeric in the solid state, **1** is most likely monomeric in solution at room temperature. The key observations that provide information about the structure of **3** are (i) **3** has the molecular formula $(\mathbf{1})_2$ and (ii) the PCy_3 C1 ^{13}C NMR resonance of **3** is a triplet with J_{CP} = 7 Hz. The triplet structure is most likely due to virtual coupling to two phosphorus atoms.[24] To determine the influence

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[21] The C1−C4 ^{13}C NMR signals of the PCy_3 ligand were assigned in the order of decreasing ^{31}P coupling constants.

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Table 3. NMR Data of Neutral and Cationic Cu(I) Phosphine Complexes in CD_2Cl_2 Solution at 190 K

	^{31}P (δ)	^{13}C of C1 (δ)
Cy_3PCuMe (**1**)	17.4	30.0 (d, $J = 19$ Hz)
$[Cu(PCy_3)_2][CuMe_2]$ (**3**)	11.8	31.2 (t, $J = 7$ Hz)
$\{Cy_3PCu(\mu\text{-}I)\}_2$ (**4**)	10.6^a	32.4 (d, $J = 16$ Hz)^a
$[Cu(PCy_3)_2][PF_6]$ (**5**)	25.1	29.8 (t, $J = 11$ Hz)
$[Cu(PCy_3)_2][OTf]$ (**6**)	$15.6^{a,b}$	32.3 (t, $J = 9$ Hz)^{a,b}
$[Cu(PCy_3)_3][PF_6]$	3.8	not resolved
PCy_3	10.8	30.1 (d, $J = 15$ Hz)

[a] At 290 K; ^{13}C C1 chemical shifts at 190 K are usually 1−2 ppm downfield from the position at 290 K. [b] In $CDCl_3$; see ref 26.

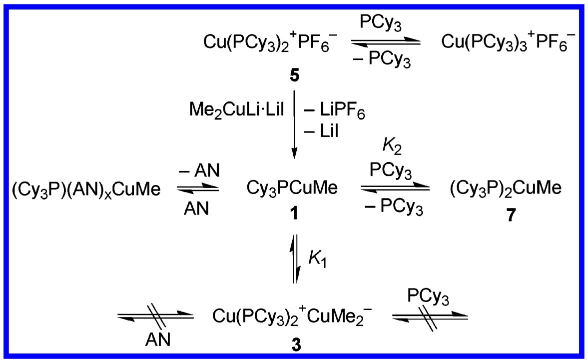
of coordination geometry on ^{31}P coupling in systems of this type, we recorded ^{13}C NMR spectra of the iodide-bridged dimer $\{Cy_3PCu(\mu\text{-}I)\}_2$ (**4**)[25] and the salt $[Cu(PCy_3)_2][PF_6]$ (**5**). The ^{13}C NMR spectrum of **4** in CD_2Cl_2 contains a doublet for C1 (Table 3). Apparently $^4J_{PP'}$ is smaller than $^1J_{PC}$ in this case and virtual coupling is not observed.[24] We thus exclude methyl-bridged dimers, e.g., $\{Cy_3PCu(\mu\text{-}Me)\}_2$, as possible structures for **3**. In contrast, the PCy_3 C1 ^{13}C resonance of **5** is a triplet with $J_{CP} = 11$ Hz, similar to that observed for **3**. Analogous results have been reported for $[Cu(PCy_3)_2][OTf]$ (**6**, Table 3).[26] The similarity of the ^{13}C NMR spectra of **3**, **5**, and **6** strongly implies that **3** contains a $Cu(PCy_3)_2^+$ unit, and therefore that **3** is the tight ion pair $[Cu(PCy_3)_2][CuMe_2]$.

To support the proposed structure of **3**, we investigated whether **1** can be obtained by combining separately generated $Cu(PCy_3)_2^+$ and $CuMe_2^-$ ions. Indeed, the methyl region of the ^1H NMR spectrum of a suspension of $CuMe_2Li{\cdot}LiI$ and an excess of **5** in THF-d_8 at 190 K contains only signals for **1** and **3**, in the ratio expected from the equilibrium constant K_1 determined in THF-d_8 at this temperature. The ^{31}P NMR spectrum also contains characteristic signals for **1** and **3**.[27]

Syntheses of copper phosphine alkyl compounds generally yield either monomeric $(R_3P)_3CuR'$ complexes or $[Cu(PR_3)_4][CuR'_2]$ ion pairs, depending on the size of the alkyl and phosphine ligands.[14,15,17b,28] Interconversion or ligand redistribution reactions have not been reported for these species. Complexes **1** and **3** thus represent a special case, where the neutral monomeric and ion-paired forms are of comparable energy.

Reaction of 1 with PCy_3. The ^{31}P spectra of mixtures of **1** and **3** in CD_2Cl_2 or toluene-d_8 that contain 0.5−3 equiv of excess PCy_3 do not exhibit a free *P*Cy_3 resonance between 180 and 290 K. Instead, the ^{31}P resonance of **1** is shifted upfield toward the free PCy_3 position. The ^1H Cu*Me* resonance of **1** also shifts slightly in the presence of PCy_3. In contrast, the ^{31}P and ^1H Cu*Me* resonances of **3** are unaffected by addition of PCy_3. However, the concentration of **3** is smaller than that in the absence of PCy_3 under otherwise identical conditions. These results indicate that **1** is in fast equilibrium with a species containing more than one phosphine ligand, most likely $(Cy_3P)_2CuMe$ (**7**), as shown in eq 2.[29] Trigonal planar $(Cy_3P)_2CuX$ complexes (X = Cl, Br, I) are known.[25,30]

Scheme 1



$$\underset{\mathbf{1}}{Cy_3PCuMe} + PCy_3 \rightleftharpoons \underset{\mathbf{7}}{(Cy_3P)_2CuMe} \qquad (2)$$

Reaction of 5 with PCy_3. The ^{31}P NMR spectrum of a solution of **5** and 0.5 equiv of PCy_3 in CD_2Cl_2 at room temperature contains only one *P*Cy_3 resonance, which is shifted upfield from that of **5** toward the free PCy_3 position. At 190 K, this signal is split into two sharp resonances at δ 25.1 (corresponding to **5**) and δ 3.8 in a ca. 2/3 intensity ratio. The ^{31}P NMR spectra of a mixture of **5** and 1 equiv of PCy_3 at 190 K contains only the δ 3.8 resonance. Accordingly, the δ 3.8 resonance is assigned to the trisphosphine species $Cu(PCy_3)_3^+$, and we conclude that **5** coordinates one additional PCy_3 ligand.

In summary, coordination of additional PCy_3 takes place in the order **5** > **1** ≫ **3**. The resistance of **3** to reaction with PCy_3 reflects the strong interaction between the $Cu(PCy_3)_2^+$ and $CuMe_2^-$ units.

Coordination of Acrylonitrile to 1. Room-temperature ^1H NMR spectra of toluene-d_8 solutions of **1** (0.1 M) containing 0.8−5 equiv of acrylonitrile (AN) contain only signals for **1** and free AN. However, as the temperature is lowered, the AN signals broaden and shift slightly upfield, the shift being more pronounced at lower AN:**1** ratios. As the AN:**1** ratio is increased, the Cu*Me* ^1H resonance of **1** shifts slightly upfield and the ^{31}P NMR resonance of **1** shifts downfield (away from the position of free PCy_3). These changes are reversed by raising the temperature back to ambient. Also, the formation of **3** is reduced in the presence of AN. These observations indicate that AN reacts with **1** to form $(Cy_3P)(AN)_xCuMe$ in a fast equilibrium.

The reactivity of **1** in solution is summarized in Scheme 1.

Acrylonitrile Polymerization with 1. As originally reported by Yamamoto and co-workers,[9] solutions of **1** in toluene are

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(25) Bowmaker, G. A.; Boyd, S. E.; Hanna, J. V.; Hart, R. D.; Healy, P. C.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **2002**, 2722.

(26) Green, J.; Sinn, E.; Woodward, S. *Inorg. Chim. Acta* **1995**, *230*, 231.

(27) (a) An additional signal at δ 9.9 is observed in the ^{31}P NMR spectra of THF-d_8 solutions of $CuMe_2Li{\cdot}LiI$ and **5**. This signal is assigned to $[Cu(PCy_3)_2][PF_6]{\cdot}LiI$ (**5**·LiI) since the same chemical shift was observed for a 1:1 mixture of **5** and LiI in THF-d_8. At room temperature, only **1** and the putative **5**·LiI species were observed. The formation of $[Cu(PCy_3)_2][PF_6]{\cdot}LiI$ can be suppressed by use of excess $CuMe_2Li{\cdot}LiI$. In this case, signals assigned to $CuMe_2Li{\cdot}LiI$ (see ref 27b) can be detected at 190 K in addition to the methyl signals for **1** and **3**. At room temperature, fast methyl exchange occurs and only one broadened signal is observed in the methyl region of the ^1H spectrum. (b) Ashby, E. C.; Watkins, J. J. *J. Am. Chem. Soc.* **1977**, *99*, 5312.

(28) Leoni, P.; Pasquali, M.; Ghilardi, C. A. *Chem. Commun.* **1983**, 240.

(29) The equilibrium constant for eq 2, $K_2 = [\mathbf{7}]/([\mathbf{1}]{\cdot}[PCy_3])$, was determined as follows. Since **3** does not coordinate additional PCy_3, its concentration can be obtained from ^1H NMR spectra. This value, along with the independently determined equilibrium constant for the **1** = **3** equilibrium, enables determination of the concentrations of **1**, **7**, and PCy_3 (even though these species are in fast exchange with each other) and determination of K_2. In CD_2Cl_2, $K_2 = [\mathbf{7}]/([\mathbf{1}][PCy_3]) = 21(3)\ M^{-1}$ at 190 K, $\Delta H° = -22(1)$ kJ/mol, and $\Delta S° = -91(6)$ J/(mol·K). The $\Delta H°$ and $\Delta S°$ values were determined from K_2 values measured over the temperature range 190−230 K. The standard deviation for K_2 is a conservative estimate based on likely errors and observed standard deviations in similar systems. Standard deviations of $\Delta H°$ and $\Delta S°$ values are derived from the linear regression of the van't Hoff plot.

(30) Soloveichik, G. L.; Eisenstein, O.; Poulton, J. T.; Streib, W. E.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1992**, *31*, 3306.

Table 4. Acrylonitrile Polymerizations with Different Initiators in Toluene Solution

										% Et ends[a]	
entry	initiator	*T* (°C)	[AN] (M)	[AN]/[initiator]	time (min)	% conversion	activity[b]	*mm* (%)	branch number[c]	observed	theory
1	**1**	80	2.3	440	120	1	0.3				
2	**1**	23	2.3	440	355	5	0.5				
3	**1**	23	6.5	4400	3	26	1700	32	16	0.03	0.1
4[d]	**1**	0	3.9	1100	40	19	39 ± 18[e]	34	34	0.1	0.5
5	**1**	0[f]	3.4	1100	45	40	56	32	19	0.05	0.3
6	**1**	0	6.4	4100	60	20	60	32	26	0.04	0.1
7	**1**	−37	7.9	430	80	61	2	30			
8	**1**	−37	6.6	4500	135	17	25	31	15	0.05	0.1
9	**1**[g]	0	3.9	1000	40	11	15	35	44	0.2	1.0
10	none	0	3.9		45	0	0				
11[d]	PCy_3	0	3.9	1100	40	53	75 ± 15[e]	32	34	0	
12	PCy_3[h]	0	3.9	1100	45	54	86	33	31	0	
13	PCy_3[i]	0	3.9	1100	75	1	4				
14[d]	$Me_2CuLi{\cdot}LiI$	0	3.9	600	45	9	8	32	18	1.7	1.8
15	**5**	0	5.4	1000	120	0	0				
16[d]	**2**	23	15.2[j]	240	15	95	8	29	45	0.2	0.45
17[d]	**2**	23	8.9[k]	170	20	80	3	32	21	0.3	0.75

[a] The number of Et (Me in the case of **2**) end groups per 100 monomer units was determined from the ratio of the intensities of the ^1H $-CH_2CH_3$ resonance at δ 1.03 vs the main-chain $-CH_2-$ resonances at δ 2.0−2.6. For **2**, the ^1H $-CH(CN)CH_3$ resonance at δ 1.31 was used. The theoretical percentage of Et end groups (Me in the case of **2**) is the ratio that would be observed if exactly one Me group per **1** or Me_2CuLi (or one hydride per **2**) is utilized in initiation. [b] Defined as grams of PAN/([initiator][AN]hour). [c] The branch number is the number of branches per 500 monomer units and was determined from NMR spectra from the ratio of the intensities of the branch end $-CH_2CN$ resonances (δ 13.9 and 12.2 in ^{13}C, δ 2.7 in ^1H) to the main-chain $-CH_2-$ resonances (δ 32−39 in ^{13}C, δ 2.0−2.6 in ^1H). [d] Polymer molecular weights were determined for selected samples: entry 4, $M_w = 1.0 \times 10^4$ g/mol and $M_w/M_n = 1.9$; entry 11, $M_w = 1.2 \times 10^4$ g/mol and $M_w/M_n = 2.1$; entry 14, $M_w = 4.4 \times 10^3$ g/mol and $M_w/M_n = 1.4$; entry 16, $M_w = 7.3 \times 10^4$ g/mol and $M_w/M_n = 7.0$; entry 17, $M_w = 1.5 \times 10^4$ g/mol and $M_w/M_n = 3.8$. [e] Average of three experiments. [f] Toluene/AN mixture stirred with 10 mg of **1** at room temperature for 3 min and then vacuum-transferred to 10 mg of **1** at −196 °C and warmed to 0 °C (see ref 43). [g] Toluene partly replaced by 1-hexene; hexene:AN = 0.3. [h] 5 equiv of TEMPO added. [i] 0.6 equiv of $[Cu(NCMe)_4][PF_6]$ added. [j] Reaction conducted in neat AN. [k] Reaction conducted in a mixture of 1.5 g (28 mmol) of AN and 2.0 g (32 mmol) of vinyl chloride.

active for AN polymerization. As summarized in Table 4, AN (2−8 M in toluene) is polymerized by **1** to white PAN at temperatures ranging from −37 to 23 °C. The ^{13}C NMR spectrum of a representative PAN sample produced by **1** is shown in Figures 6a and 7a. The tacticity of PAN can be determined from the $-CH_2C(CN)H-$ methine resonance at δ 27 or the nitrile resonance at δ 120.[31] The PANs produced by **1** between −37 and 23 °C are all slightly isotactic (*mm* = 30−35%, Table 4). PAN obtained by radical polymerization is usually atactic,[32] while anionic polymerizations yield slightly to highly isotactic polymer.[32a,33] In previous work only small variations in tacticity were found in anionic polymerizations between −80 and 40 °C.[32a]

In addition to the main-chain $-CH_2C(CN)H-$ resonances, several other peaks are present in the ^{13}C NMR spectra of PAN produced by **1**, which are labeled with lowercase letters in Figure 6 or asterisks in Figure 7. These peaks are characteristic of branches formed in anionic polymerizations,[7b−d,32a,33a] and their assignments by Kamide and co-workers[7c] are shown in Figure 8. In contrast, signals for branched structures are absent from NMR spectra of PAN obtained by radical polymerization (Figures 6d and 7d).[4a−c,7c,32a,34] Approximately 30 branches per 500 monomer units (which includes monomer units in the branches) were found for AN:initiator ratios of ca. 1000 (Table 4).[35]

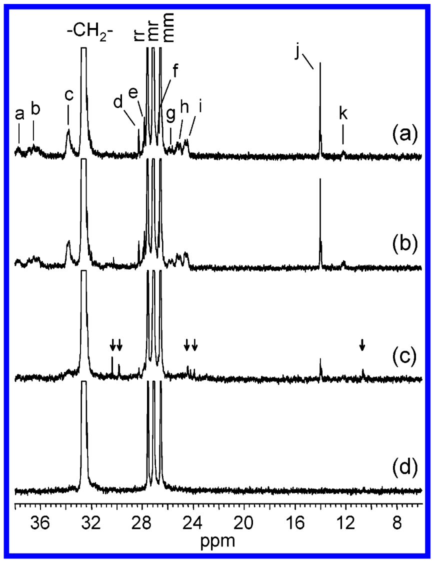

Figure 6. $^{13}C\{^1H\}$ NMR spectra (alkyl region) in DMSO-d_6 at 60 °C of PAN obtained with different initiators: (a) **1** (entry 4), (b) PCy_3 (entry 11), (c) $Me_2CuLi{\cdot}LiI$ (entry 14), (d) commercial PAN prepared by radical polymerization. Entry numbers refer to experiments in Table 4. The vertical scales are adjusted so that the intensity of the $-CH_2-$ resonance is normalized. Assignments are based on the labeling scheme shown in Figure 8. Small arrows indicate peaks that are only observed when $Me_2CuLi{\cdot}LiI$ is used as the initiator (see text).

Compound **1** does not polymerize ethylene or hexene. When the polymerization of AN was carried out in the presence of hexene, no hexene incorporation in the PAN was observed and the microstructure of the PAN was nearly identical to that formed in the absence of hexene. The slight isotacticity, lack of temperature dependence of the tacticity, lack of activity in

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(31) (a) Balard, H.; Fritz, H.; Meybeck, J. *Makromol. Chem.* **1977**, *178*, 2393. (b) Kamide, K.; Yamazaki, H.; Okajima, K.; Hikichi, K. *Polym J. (Tokyo)* **1985**, *17*, 1233. (c) Kamide, K.; Yamazaki, H.; Okajima, K.; Hikichi, K. *Polym. J. (Tokyo)* **1985**, *17*, 1291. (d) Katsuraya, K.; Hatanaka, K.; Matsuzaki, K.; Minagawa, M. *Polymer* **2001**, *42*, 6323.

(32) (a) Kamide, K.; Ono, H.; Hisatani, K. *Polym. J. (Tokyo)* **1992**, *24*, 917. (b) Matsuzaki, K.; Uryu, T.; Okada, M.; Shiroki, H. *J. Polym. Sci., Part A* **1968**, *6*, 1475.

(33) (a) Opitz, G.; Heller, A.; Scheller, D.; Berger, W. *Acta Polym.* **1996**, *47*, 67. (b) Zheng, H.; Zhang, Y.; Shen, Z. *Polym. Int.* **2002**, *51*, 622. (c) Nakano, Y.; Hisatani, K.; Kamide, K. *Polym. Int.* **1994**, *35*, 207. (d) Nakano, Y.; Hisatani, K.; Kamide, K. *Polym. Int.* **1994**, *35*, 249.

(34) (a) Malsch, G.; Fritzsche, P.; Dautzenberg, H. *Acta Polym.* **1981**, *32*, 758. (b) Bajaj, P.; Sreekumar, T. V.; Sen, K.; Kumar, R.; Brar, A. S. *J. Appl. Polym. Sci.* **2003**, *88*, 1211. (c) Bajaj, P.; Sreekumar, T. V.; Sen, K. *J. Appl. Polym. Sci.* **2001**, *79*, 1640.

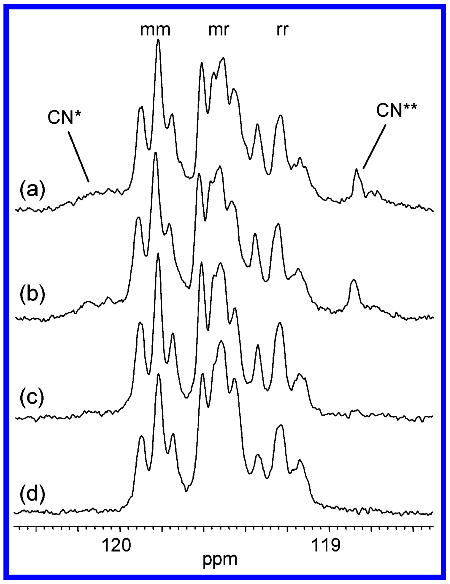


Figure 7. ^{13}C{^{1}H} NMR spectra (nitrile region) in DMSO-d_6 at 60 °C of PAN obtained with different initiators: (a) **1** (entry 4), (b) PCy$_3$ (entry 11), (c) Me$_2$CuLi·LiI (entry 14), and (d) commercial PAN prepared by radical polymerization. Entry numbers refer to experiments in Table 4. The vertical scales are adjusted so that the intensity of the -C*H*$_2$- resonance is normalized. Assignments are based on the labeling scheme shown in Figure 8.

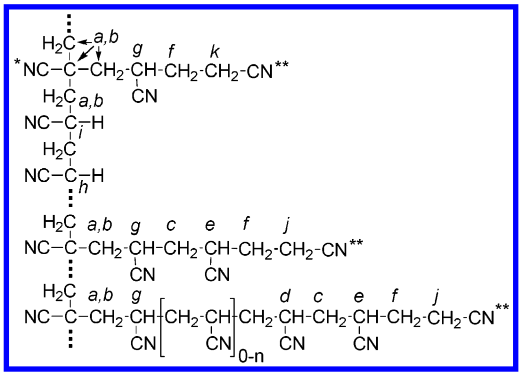
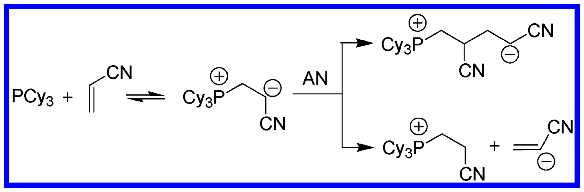


Figure 8. ^{13}C NMR assignments for branches in PAN. Letters and asterisks correspond to labeled peaks in Figures 6, 7, and 11. Assignments are based on ref 7c.

ethylene or hexene polymerizations, and most importantly, the presence of significant branching show that polymerization of AN by **1** proceeds by an anionic mechanism.

Identification of Initiating Species in AN Polymerizations by 1. Three possible scenarios for initiation of anionic polymerization of AN by **1** are (i) initiation by PCy$_3$ released from **1** or the minor species **3**,[36] (ii) initiation by the Cu-Me group of **1**, or (iii) initiation by the CuMe$_2^-$ anion of **3**. Initiation by PCy$_3$ would yield phosphonium cations, which are either covalently bound to the polymer chain or present as Cy$_3$PCH$_2$CH$_2$CN$^+$ cations (Scheme 2).[36d−f] The evidence discussed in this section strongly supports a significant role for PCy$_3$ initiation.

Scheme 2



Free PCy$_3$ is slightly more active than **1** for AN polymerization under identical conditions (Table 4, entry 11 vs entry 4). The presence of TEMPO does not influence activity or polymer microstructure in PCy$_3$-initiated AN polymerizations, in agreement with an anionic mechanism (Table 4, entry 12). In contrast, addition of 0.6 equiv of [Cu(NCMe)$_4$][PF$_6$] strongly inhibits polymerization, probably by trapping of PCy$_3$ to form **5** (Table 4, entry 13). Control experiments show that **5** is inactive for AN polymerization (Table 4, entry 15). The branching patterns are practically identical for PANs obtained with PCy$_3$ or **1**. Indeed, the ^{13}C NMR spectra of these PANs are virtually superimposable (Figures 6 and 7, compare spectra a and b in each figure).

To further probe the possible role of PCy$_3$ in AN polymerization initiated by **1**, we investigated the presence of Cy$_3$PR$^+$ cations in the PANs by ^{31}P NMR. ^{31}P spectra of PAN obtained with **1** at high initiator concentrations (AN/**1** = 40−50) and washed with HCl/H$_2$O and acetone contain three resonances between δ 34.1 and 34.4 (Figure 9a). These resonances are in the range expected for Cy$_3$P$^+$CH$_2$CR(CN)··· species (R = H or branch). For example, the ^{31}P resonance of [Cy$_3$*P*CH$_2$CH$_2$CN]Cl appears at δ 34.6 (Figure 9d), and chemical shifts of δ 28−33 were reported for [Cy$_3$*P*R]Br salts in CDCl$_3$ solution.[37,38] Repetitive (2×) dissolution of the PAN in DMF and reprecipitation in methanol, which was reported to remove noncovalently attached phosphonium species,[36d−f] does not significantly reduce the intensities of these resonances (Figure 9b). The ^{31}P spectrum of PAN produced with PCy$_3$ at low AN/PCy$_3$ ratios (and washed with HCl/H$_2$O and acetone) contains the same three δ 34.1−34.4 resonances and an additional resonance at δ 34.6 (Figure 9c). Reprecipitation of this PAN from DMF/MeOH removes the δ 34.6 resonance but not the δ 34.1−34.4 resonances. On the basis of these results, we assign the δ 34.1−34.4 resonances to Cy$_3$P$^+$CH$_2$CR(CN)··· species that are covalently attached to the polymer chain and the δ 34.6 resonance to the [Cy$_3$PCH$_2$CH$_2$CN]$^+$ cation, which is derived from the initial Cy$_3$P$^+$CH$_2$CH(CN)$^-$ zwitterion by proton abstraction from AN (Scheme 2) or by protonation during workup.[36] The small chemical shift difference ($\Delta\delta$ = 0.05) between the δ 34.6 resonance in PAN and the [Cy$_3$*P*CH$_2$CH$_2$CN]Cl resonance maybe due to the presence of PAN in the polymer solutions or to ion-pairing effects. These

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[35] The presence of branching is also indicated by the ^{1}H NMR spectra of the PAN samples. In addition to backbone C*H*$_2$ and C*H*(CN) signals at δ 2.06 and 3.15, a broad singlet at δ 2.7 is observed, which was assigned to the -C*H*$_2$CN units at branch or chain ends (ref 7c,d). We also observe a broad singlet at δ 2.4 with approximately the same intensity as the δ 2.7 resonance. The position and intensity suggest that this signal is also associated with branch or chain ends and probably corresponds to the penultimate methylene group (-C*H*$_2$CH(CN)CH$_2$CN).

[36] (a) Triaryl- and trialkylphosphines have been reported to initiate AN polymerization. (b) Horner, L.; Jurgeleit, W.; Klupfel, K. *Liebigs Ann. Chem.* **1955**, *591*, 108. (c) Morita, K.; Suzuki, Z.; Hirose, H. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 2815. (d) Jaacks, V.; Eisenbach, C. D.; Kern, W. *Makromol. Chem.* **1972**, *161*, 139. (e) Eisenbach, C. D.; Jaacks, V.; Schnecko, H.; Kern, W. *Makromol. Chem.* **1974**, *175*, 1329. (f) Eisenbach, C. D.; Franzmann, G.; Jaacks, V.; Schnecko, H.; Kern, W. *Makromol. Chem.* **1974**, *175*, 1789. (g) Markevich, M. A.; Kochetov, E. V.; Ranogajec, F.; Enikolopyan, N. S. *J. Macromol. Sci., Chem.* **1974**, *8*, 265. (h) Kuran, W.; Borycki, J. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 1251 (i) Heisenberg, E.; Jurgeleit, W. (Vereinigte Glanzstoff-Fabriken) US 2,921,-055, 1960.

[37] Bestmann, H. J.; Dötzer, R. *Synthesis* **1989**, *3*, 204.

[38] (a) In contrast, the ^{31}P resonance for Cy$_3$P=O appears at δ 50. Davies, J. A.; Dutremez, S.; Pinkerton, A. A. *Inorg. Chem.* **1991**, *30*, 2380. (b) Control experiments show that the δ 34.1−34.4 resonances are not derived from [Cy$_3$PH]Cl.

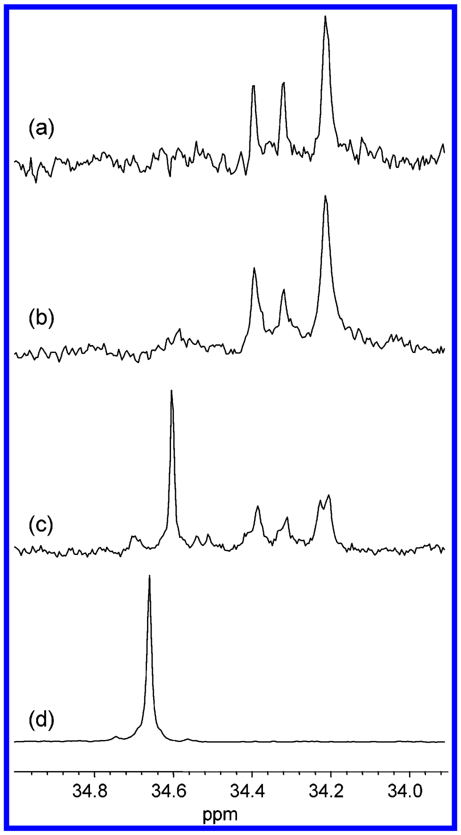

Figure 9. Cy_3PR^+ region of $^{31}P\{^1H\}$ NMR spectra (60 °C in DMSO-d_6): (a) PAN obtained with **1**, (b) PAN obtained with **1** and reprecipitated from DMF/MeOH, (c) PAN obtained with PCy_3, and (d) $[Cy_3PCH_2CH_2CN]Cl$.

results show that PCy_3 is a significant initiator in AN polymerizations by **1**. The initiating PCy_3 is most likely derived from **1** rather than **3**, since **5** is inactive for AN polymerization.

If **1** initiates AN polymerization by Me^- transfer to AN, CH_3-$CH_2CH(CN)$- end groups should be present in the PAN. The ^1H NMR spectra of PAN produced by **1** contain a signal at δ 1.03, which is not present in the spectra of PAN obtained with PCy_3 (Figure 10b,c). This signal appears as two overlapping triplets with a separation of $\Delta\delta = 0.004$ at 120 °C. The same triplet resonances are observed in much higher intensity if AN polymerization is initiated by $CuMe_2Li{\cdot}LiI$ (Table 4, entry 14; Figure 10a). We assign these resonances to $CH_3CH_2CH(CN)$-$CH_2CH(CN)$- chain ends with different tacticity, generated by initiation by Me^- addition to AN. For comparison, the CH_3-CH_2- resonances of *d,l*- and *meso*-3,5-heptanediol were observed at δ 0.93 and 0.94, and those for *d,l*- and *meso*-3,5-diiodoheptane appear at δ 0.76 and 0.78.[39] Several new, small peaks are present in the ^{13}C NMR spectrum of PAN produced by $CuMe_2Li{\cdot}LiI$ (arrows in Figure 6c), which probably also arise from the CH_3-$CH_2CH(CN)CH_2CH(CN)$- chain ends. The intensity of the ^1H δ 1.03 signal in PAN produced by **1**, compared to the CH_2 resonance at δ 2.1, indicates that ca. 20% of the methyl groups in **1** are transferred to the polymer chain (Table 4).[40] In contrast, when $CuMe_2Li{\cdot}LiI$ is used as the initiator, one methyl group per Me_2CuLi unit reacts with the monomer (Table 4, entry 14).

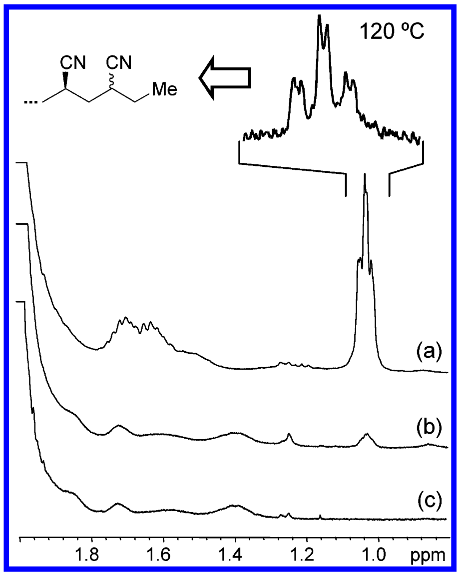

Figure 10. ^1H NMR spectra (alkyl region) in DMSO-d_6 at 60 °C of PAN obtained with different initiators: (a) $Me_2CuLi{\cdot}LiI$ (entry 14), (b) **1** (entry 4), and (c) PCy_3 (entry 11). Entry numbers refer to experiments in Table 4. The vertical scales are adjusted so that the intensity of the -CH_2- resonance is normalized.

Initiation of AN polymerization by Me^- transfer from **1** would generate an active propagating anion and a “$Cu(PCy_3)^+$” counterion. However, addition of “$Cu(PCy_3)^+$” (in form of an equimolar $[Cu(NCMe)_4][PF_6]/PCy_3$ mixture) to an active PCy_3-initiated AN polymerization (which was otherwise free of Cu) after $^1/_3$ of the polymerization time reduced the polymer yield to $^1/_3$ of that obtained in an otherwise identical polymerization. This result implies that “$Cu(PCy_3)^+$” strongly coordinates the active $RCH_2CH(CN)^-$ anions and quenches the polymerization (cf. the inhibition of AN polymerization by Li^+, vide infra). Thus, while Me^- transfer from **1** to AN clearly occurs, this process is not expected to lead to efficient PAN formation.

It is more difficult to assess the importance of initiation by Me^- transfer from the $CuMe_2^-$ unit in **3**, since this process would yield a more coordinatively saturated $Cu(PCy_3)_2^+$ cation. As mentioned above, $CuMe_2Li{\cdot}LiI$ does polymerize AN, but it is less active than **1** (Table 4, entry 14). Additionally, the PAN produced with $CuMe_2Li{\cdot}LiI$ is less branched than that from **1** or PCy_3 (Figures 6c and 7c, Table 4). The low activity and branching in $CuMe_2Li{\cdot}LiI$-initiated AN polymerization result from strong ion pairing involving the Li^+ cation.[7d,32a,41] Although it is clear from these experiments that $CuMe_2^-$ anions do initiate AN polymerization, the facts that (i) **3** is a very tight ion pair and (ii) **1** rapidly polymerizes AN under conditions where the concentration of **3** is vanishingly small (e.g., Table 4, entry 3)[42] are inconsistent with a significant role of **3** in AN polymerizations by **1**.

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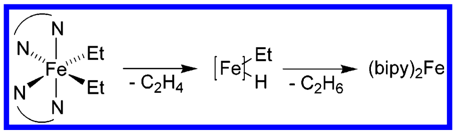
(39) (a) Yang, G. K.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 6045. (b) NMR data for 3,5-dicyanoheptane or 2,4-dicyanohexane have not been reported.

(40) Alternatively, the $CH_3CH_2CH(CN)$- chain ends may arise from the reaction of **1** with the $Cy_3P^+CH_2CH(CN)$- chain ends or the $Cy_3P^+CH_2CH(CN)^-$ zwitterion formed by PCy_3 initiation. Phosphonium cations with β-cyano alkyl substituents are known to react with nucleophiles, such as RO^-, by nucleophilic substitution (see ref 40b). In our hands, however, the reaction of $[Cy_3PCH_2CH_2CN]Br$ with **1** in CD_3CN produced CH_4 and AN, probably by deprotonation of the β-CH_2 group of $[Cy_3PCH_2CH_2CN]Br$ and subsequent dissociation of the regenerated zwitterion to AN and PCy_3. (b) Grayson, M.; Keough, P. T.; Johnson, G. A. *J. Am. Chem. Soc.* **1959**, *81*, 4803.

(41) Me^- transfer from $Me_2CuLi{\cdot}LiI$ yields CuMe (the fate of which is unknown) and a Li^+ cation. Retardation of polymerization rates by 1−2 orders of magnitude in the presence of Li^+ was reported for PPh_3-initiated AN polymerizations (see ref 36f). In our hands, the presence of 2 equiv of LiI completely quenches AN polymerization by **1** (under conditions otherwise identical to those of entry 4 in Table 4). LiI does not polymerize AN under the conditions used for $Me_2CuLi{\cdot}LiI$-initiated polymerization (entry 14, Table 4).

Scheme 3



The presence of both polymer-bound phosphonium species and CH_3CH$_2$CH(CN)- chain ends in PAN produced by **1** indicates that both initiation mechanisms, PCy_3 addition to AN and Me^- transfer, occur in AN polymerization by **1**. However, the identical microstructures of polymers obtained with **1** and PCy_3 and the efficient quenching of active AN polymerizations by "Cu(PCy_3)$^+$" imply that chain growth occurs mainly at polymer anions that have a phosphonium counterion. Therefore, we conclude that anionic AN polymerization by **1** primarily results from initiation by PCy_3, which is probably liberated from **1** by substitution by AN.[43]

(Bipy)$_2$FeEt$_2$ (2). The iron(II) complex (bipy)$_2$FeEt$_2$ (**2**) was synthesized by Yamamoto et al.[44] by reaction of Fe(acac)$_3$ with Al(OEt)Et$_2$ in the presence of bipy. Complex **2** slowly decomposes in solution at room temperature with evolution of ethane and ethylene (ca. 1/1).[10,45] The decomposition of **2** is inhibited by excess bipy but promoted by coordinating solvents (MeCN > DMF > acetone > THF) and was proposed to occur by partial or complete dissociation of a bipy ligand, β-hydride elimination to yield ethylene and a transient Fe−H species, and reductive elimination to yield ethane and (bipy)$_2$Fe (Scheme 3).[10a,45]

Compound **2** was reported to initiate AN polymerization.[10] The polymerization was proposed to proceed via π-coordination of the AN vinyl group to a vacant site created by partial dissociation of the bipy ligands, followed by insertion into the Fe−Et bond. Compound **2** also polymerizes methyl methacrylate and cyclodimerizes butadiene but is inactive for ethylene polymerization.[10]

AN Polymerization by 2. Dissolution of **2** in neat AN produces a deep blue solution. After a 15 min induction period, gas evolution followed by fast exothermic polymerization of AN to high molecular weight PAN is observed (Table 4, entry 16).[46] The evolved gas is mainly ethylene (ethylene/ethane = 10/1).

The ^{13}C NMR spectra of PAN produced by **2** display resonances characteristic of branch units that are identical to those observed in PAN produced by **1** or PCy_3 (Figure 11). The branch number and tacticity are similar to the corresponding values for PAN obtained with **1** or PCy_3. These results provide strong evidence that **2** polymerizes AN by an anionic mechanism.

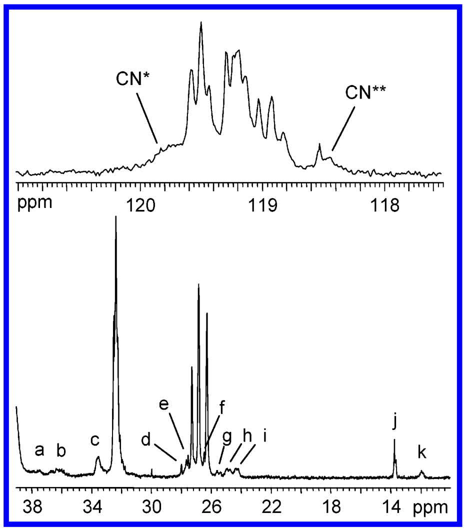


Figure 11. ^{13}C{^{1}H} NMR spectrum in DMSO-d_6 at 60 °C of PAN (top, nitrile region; bottom, alkyl region) produced with **2** (entry 16, Table 4). Assignments are based on the labeling scheme in Figure 8.

To confirm that AN polymerization by **2** does not occur by a radical mechanism, AN/vinyl chloride copolymerization by **2** was investigated. Vinyl chloride is readily incorporated in radical AN polymerizations.[47] However, the reaction of **2** with an AN/vinyl chloride mixture produced PAN with no vinyl chloride incorporation (Table 4, entry 17).[48] The branch patterns and tacticity of this material are very similar to those of PAN produced by **2** in the absence of vinyl chloride. Additionally, **2** does not homopolymerize vinyl chloride. These observations rule out a radical mechanism for AN polymerization by **2**.

Possible Initiators in AN Polymerization by 2. Free bipy does not react with AN over 24 h at ambient temperatures and therefore is not the initiator in AN polymerization by **2**.

The ^{1}H NMR spectrum of PAN generated by **2** contains a signal at δ 1.31 that splits into two doublets at δ 1.33 and 1.35 at 120 °C (Figure 12). These resonances are not observed in the spectra of PANs produced by either **1** or PCy_3. We assign these resonances to CH_3CH(CN)CH$_2$CH(CN)- chain ends generated by initiation by hydride addition to AN. For comparison, the ^{1}H NMR spectrum of PAN obtained by Li[Et$_3$BH] initiation contains the same signal (see Supporting Information), and the CH_3CH(CN)- resonances of 2,4-dicyanopentanes in DMSO-d_6 at 140 °C occur at δ 1.31 (*meso*) and 1.33 (*d,l*).[32b,49]

The most likely source of the initiating hydride species in AN polymerization by **2** is an Fe−H intermediate formed by decomposition of **2**. As noted above, coordinating solvents such as MeCN accelerate the decomposition of **2**, probably by stabilizing unsaturated intermediates formed by bipy dissociation.[10a,45] Analogously, substitution of a bipy ligand by AN

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(42) By use of the ΔH° and ΔS° values for the **1** = **3** equilibrium in Table 2, the concentrations of **1** and **3** under the conditions of entry 3 in Table 4 are calculated to be 1.5×10^{-3} M and 5.7×10^{-7} M, respectively. However, the actual concentration of **3** will be significantly lower than the latter value, since the formation of **3** is strongly inhibited by the presence of a large excess of AN (see text).

(43) To investigate whether the release of PCy_3 is due to impurities in the solvent or AN, a typical polymerization mixture (i.e., 2 mL of AN and 5.5 mL of toluene) was first stirred with 10 mg of **1** at 23 °C until polymerization started, as indicated by development of a yellow color and precipitation of PAN. The volatiles (toluene and AN) were then vacuum-transferred to another flask containing 10 mg of **1** at −196 °C. The flask was sealed and placed in an ice/water bath and polymerization was allowed to proceed. As shown in entry 5 of Table 4, the percent conversion, tacticity, branching, and end groups are similar to those for AN polymerization by **1** under standard conditions at 0 °C (entry 4). The differences are ascribed to the slow warming from −196 to 0 °C during polymerization. We thus conclude that PCy_3 is not liberated from **1** due to the presence of impurities in the solvent or monomer.

(44) Yamamoto, A.; Morifuji, K.; Ikeda, S.; Saito, T.; Uchida, Y.; Misono, A. *J. Am. Chem. Soc.* **1968**, *90*, 1878.

(45) Lau, W.; Huffman, J. C.; Kochi, J. K. *Organometallics* **1982**, *1*, 155.

(46) The resulting PAN is pale red, presumably due to residual Fe species.

(47) (a) Koenig, J.; Sueling, C. (Bayer AG) US 4118556, 1978. (b) Koenig, J.; Sueling, C.; Boehmke, G. (Bayer AG), DE 76-2604630, 1977. (c) Guillot, J.; Vialle, J.; Guyot, A. *J. Macromol. Sci., Chem.* **1971**, *5*, 735. (d) Koenig, J.; Wendisch, D. *Angew. Makromol. Chem.* **1980**, *92*, 191.

(48) For a radical batch copolymerization with AN and vinyl chloride present in equal starting concentrations (Table 4, entry 17), at least 20% vinyl chloride incorporation into the polymer is expected on the basis of the monomer reactivity ratios. See Odian, G. *Principles of Polymerization*, 3rd ed.; Wiley-Interscience: New York, 1991; p 479.

(49) Matsuzaki, K.; Uryu, T.; Okada, M.; Ishigure, K.; Oki, T.; Takeuchi, M. *J. Polym. Sci., Part B* **1966**, *4*, 487.

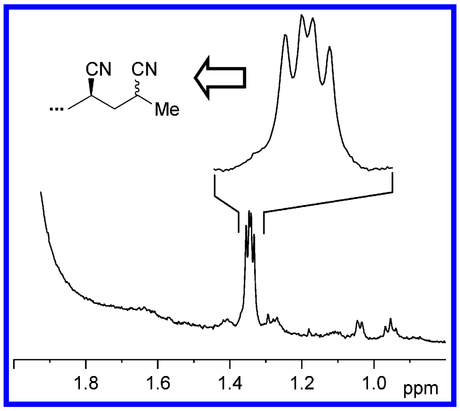
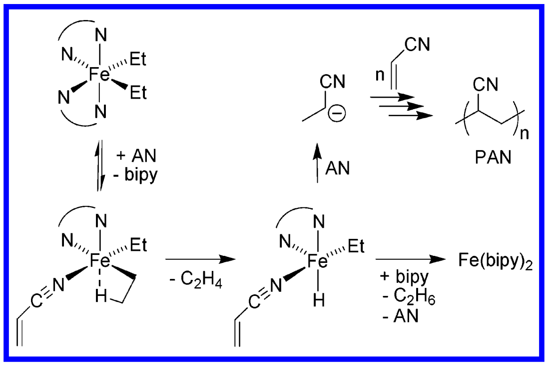


Figure 12. ^{1}H NMR spectrum (DMSO-d_6 at 120 °C) of PAN produced by **2** (entry 16, Table 4).

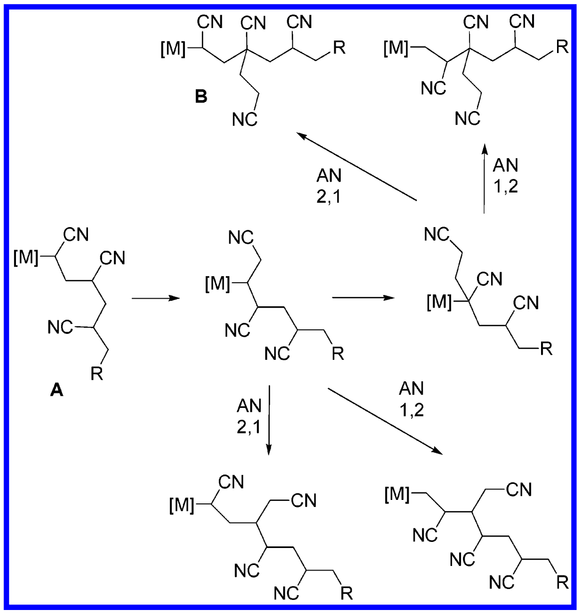
Scheme 4



should promote β-H elimination of **2** and formation of an Fe−H species. We propose that the Fe−H intermediate undergoes net hydride transfer to AN to initiate anionic polymerization, as shown in Scheme 4. The details of the hydride transfer step are unknown at this time. The evolution of ethylene, but only traces of ethane, during the polymerization is consistent with efficient trapping of the Fe−H intermediate by AN. In contrast, under identical conditions, the decomposition of **2** in MeCN in the absence of AN yields a 1/1 mixture of ethylene and ethane in accordance with literature reports.[45]

Branching in Insertion Polymerization of AN. The conclusion that AN polymerizations by **1** and **2** occur by an anionic mechanism rests primarily on the observation of branch structures, i.e., -CH$_2$CN-ended branches on tertiary -*C*R$_2$(CN) carbon atoms, in the PANs. Therefore it is important to consider whether insertion mechanisms can yield PANs with such branches. Branching in insertion polymerization of ethylene with late transition metal catalysts arises by chain-walking (repeated β-H elimination and reinsertion), followed by monomer insertion into a secondary alkyl−metal bond.[50] As illustrated in Scheme 5, branches with -CH$_2$CN ends could form in an AN insertion polymerization by chain-walking of a MCH(CN)CH$_2${CH(CN)-CH$_2$}$_2$R species (**A**) formed by 2,1-insertion of AN into an alkyl−metal bond.[51] However, to form the branch on a tertiary carbon (see **B**), a 2,1-insertion of AN into a tertiary alkyl−metal bond would be required. To the best of our knowledge, there is no evidence in the literature for olefin insertion into tertiary alkyl−metal bonds in polymerization reactions. For palladium and nickel catalysts, which typically yield branched polymers, ethylene insertion does not occur into tertiary alkyl−metal bonds.[50b,52] We thus exclude the possibility that an insertion mechanism yields the branched PANs produced by **1** and **2**.

Scheme 5



Conclusions

This study provides new insights to the mechanism of AN polymerization by metal−alkyl complexes. Cy$_3$PCuMe (**1**) exists in a temperature-dependent equilibrium with the tight ion pair [Cu(PCy$_3$)$_2$][CuMe$_2$] (**3**) in solution. Compound **1** polymerizes acrylonitrile by an anionic mechanism. The major initiator in this reaction is PCy$_3$, which is released from **1**, probably by substitution by AN. Initiation by Cu−Me species also occurs, but chain growth occurs mainly at polymer anions that have a phosphonium counterion. (Bipy)$_2$FeEt$_2$ (**2**) also initiates anionic polymerization of AN. In this case, the initiating species is proposed to be a transient iron hydride produced by β-hydride elimination of **2**.

Experimental Section

All manipulations were performed with drybox or Schlenk techniques under a nitrogen atmosphere or on a high-vacuum line. Nitrogen was purified by passage through columns containing activated molecular sieves and Q-5 oxygen scavenger. Et$_2$O, THF, THF-d_8, and toluene-d_8 were distilled from sodium benzophenone; CH$_2$Cl$_2$ and CD$_2$Cl$_2$ were distilled from CaH$_2$. Acrylonitrile (AN) was distilled from CaCl$_2$, which was previously dried at 120 °C for 12 h on a high-vacuum line. NMR solvents and AN were deoxygenated by at least three freeze−pump−thaw cycles. Et$_2$O, THF, and CH$_2$Cl$_2$ were saturated with N$_2$ by repeated (>20 times) degassing/N$_2$ flush cycles. Pentane and toluene were purified by passage through columns of activated alumina and BASF R3-11 oxygen removal catalyst. (Bipy)$_2$FeEt$_2$ (**2**) was synthesized according to the literature.[10a] All other chemicals were purchased from Strem or Aldrich and used as received.

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(50) (a) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414. (b) Ittel, S. D.; Johnson, L. K., Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169.

(51) Chain-walking after 1,2-insertion of AN would yield *Me*CH(CN)- ended branches. The methyl end groups observed in the PAN produced by **2** or Li[Et$_3$BH] are present at much lower levels than the -CH$_2$CN ends and are ascribed to chain initiation by hydride transfer.

(52) Shultz, L. H.; Tempel, D. J.; Brookhart, M. *J. Am. Chem. Soc.* **2001**, *123*, 11539.

Elemental analyses were performed by Midwest Microlab. GPC measurements were performed on a Waters 150C high-temperature GPC. Samples were dissolved in DMF at 40 °C. Molecular weights were determined versus polystyrene standards and corrected by use of experimentally determined Mark−Houwink parameters. Details are given in the Supporting Information.

NMR spectra were recorded on Bruker DMX-500 or DRX-400 spectrometers. ^{1}H and ^{13}C chemical shifts are referenced to residual solvent signals: CD_2Cl_2, $\delta_{1H} = 5.32$ and $\delta_{13C} = 53.8$; toluene-d_8, $\delta_{1H} = 2.09$ and $\delta_{13C} = 20.4$; THF-d_8, $\delta_{1H} = 3.58$ and $\delta_{13C} = 67.4$; DMSO, $\delta_{1H} = 2.49$ and $\delta_{13C} = 39.5$. These values were used at all temperatures. ^{31}P and ^{19}F chemical shifts are reported relative to external H_3PO_4 (85%) and external neat $CFCl_3$, respectively, at room temperature. Coupling constants smaller than 5 Hz in ^{13}C spectra were determined by apodization with a Gaussian function. Polymer ^{13}C NMR spectra were recorded for 10 wt % DMSO solutions in sealed NMR tubes at 60 °C with an acquisition time of 2 s and without a relaxation delay. Using a relaxation delay of 6 s yielded the same values for tacticity and branching. An internal Ph_3PO standard was used to quantify signal intensities in ^{31}P NMR spectra. Temperatures in VT NMR experiments were calibrated by use of MeOH as a chemical thermometer.[53]

Electrospray mass spectra (ESI-MS) were recorded on freshly prepared samples (ca. 1 mg/mL in CH_2Cl_2) by use of an Agilent 1100 LC-MSD spectrometer incorporating a quadrupole mass filter with a m/z range of 0−3000. A 5 μL sample was injected by flow injection by use of an autosampler. Purified nitrogen was used as both the nebulizing and drying gas. Typical instrumental parameters were: drying gas temperature 350 °C, nebulizer pressure 35 psi, drying gas flow 12.0 L/min, and fragmentor voltage 0 or 70 V. In all cases where assignments are given, observed isotope patterns closely matched calculated isotope patterns. The listed m/z value corresponds to the most intense peak in the isotope pattern.

Cy_3PCuMe (1).[9a] A flask was charged with CuI (0.95 g, 5.0 mmol) and PCy_3 (1.5 g, 5.5 mmol), and Et_2O (20 mL) was added by cannula. The suspension was cooled to −35 °C and stirred for 15 min. A solution of MeLi in Et_2O (5.2 mL, 1.0 M, 5.2 mmol) was added by syringe and the suspension was stirred for 45 min at −35 °C. The solvent was evaporated while the temperature was kept below −10 °C to yield an off-white solid. The solid was dried for 1 h at room temperature under vacuum. The solid was extracted with toluene/pentane (1/1, 3 × 10 mL). The extracts were cooled to −40 °C for 1 week to yield colorless crystals (820 mg, 46%). In solution, **1** is in equilibrium with **3** below 260 K. ^{1}H NMR (190 K, CD_2Cl_2): δ 1.65−1.85 (m, **1** + **3**), 1.55−1.65 (m, **1**), 1.35−1.45 (m, **3**), 1.1−1.35 (m, **1** + **3**), −0.73 (s, 3H, **3**, Me), −1.11 (s, 3H, **1**, Me). ^{13}C{^{1}H} NMR (190 K, CD_2Cl_2): δ 31.2 (t, J = 7 Hz, **3**, C1), 30.2 (d, J = 3 Hz, **1**, C3), 30.0 (d, J = 19 Hz, **1**, C1), 29.6 (s, **3**, C3), 27.1 (t, J = 5 Hz, **3**, C2), 26.6 (d, J = 11 Hz, **1**, C2), 25.5 (s, **3**, C4), 25.5 (s, **1**, C4), −5.9 (br s, **3**, Me), −8.6 (br s, **1**, Me). ^{31}P{^{1}H} NMR (190 K, CD_2Cl_2): δ 17.4 (s, **1**), 11.8 (s, **3**). NMR data for other solvents and temperatures are given in the Supporting Information.

{$Cy_3PCu(\mu$-I)}$_2$ (4).[25] A suspension of CuI (20 mg, 0.11 mmol) and PCy_3 (29 mg, 0.10 mmol) in CD_2Cl_2 was heated in a sealed NMR tube to reflux for 10 min to yield a clear solution. ^{1}H NMR (290 K, CD_2Cl_2): δ 1.95 (m, 9H), 1.79 (m, 6H), 1.71 (m, 3H), 1.49 (m, 6H), 1.26 (m, 9H). ^{13}C{^{1}H} NMR (290 K, CD_2Cl_2): δ 32.4 (d, J = 16 Hz, C1), 30.5 (s, C3), 27.8 (d, J = 11 Hz, C2), 26.6 (s, C4).

$[Cu(PCy_3)_2][PF_6]$ (5). PCy_3 (250 mg, 0.89 mmol) and $[Cu(NCMe)_4][PF_6]$ (150 mg, 0.38 mmol) were dissolved in CH_2Cl_2 (5 mL) and the clear solution was stirred for 2 h at room temperature. The solvent was removed under vacuum, Et_2O (10 mL) was added, and the resulting slurry was stirred for 30 min at room temperature. The precipitate was collected by filtration, washed with Et_2O (2 × 10 mL), and dried under vacuum to yield 250 mg (0.32 mmol, 81%) of a colorless powder. ^{1}H NMR (290 K, CD_2Cl_2): δ 2.03 (m, 6H), 1.80−1.90 (m, 24H), 1.75−1.80 (m, 6H), 1.30−1.45 (m, 24H), 1.24 (m, 6H). ^{13}C{^{1}H} NMR (290 K, CD_2Cl_2): δ 31.8 (t, J = 11 Hz, C1), 31.8 (s, C3), 27.3 (t, J = 5 Hz, C2), 26.2 (s, C4). ^{31}P{^{1}H} NMR (290 K, CD_2Cl_2) δ: 24.9 (s, PCy_3), −144.2 (septet, J = 710 Hz, PF_6^-). ^{19}F NMR (290 K, CD_2Cl_2): δ 73.7 (d, J = 710 Hz). ^{1}H NMR (190 K, CD_2Cl_2): δ 1.93 (m, 6H), 1.78 (m, 24H), 1.67 (m, 6H), 1.27 (m, 24H), 1.12 (m, 6H). ^{13}C{^{1}H} NMR (190 K, CD_2Cl_2): δ 30.6 (s, C3), 29.8 (t, J = 11 Hz, C1), 26.3 (t, J = 6 Hz, C2), 25.2 (s, C4). ^{31}P{^{1}H} NMR (190 K, CD_2Cl_2): δ 25.1 (s, PCy_3), −144.5 (septet, J = 710 Hz, PF_6^-). Anal. Calcd for $C_{36}H_{66}CuF_6P_3$: C, 56.20; H, 8.65. Found: C, 56.07; H, 8.54.

$Me_2CuLi{\cdot}LiI$.[17c] A suspension of CuI (500 mg, 2.63 mmol) in Et_2O (10 mL) was cooled to −60 °C. A solution of MeLi in Et_2O (2.9 mL, 1.7 M, 4.9 mmol) was added by syringe. The suspension was stirred for 4 h, while it warmed to −30 °C, yielding a slurry of yellow CuMe in a colorless supernatant (***ATTENTION: CuMe is explosive when dry***. See ref 16 for information concerning safe handling and disposal of this compound.) The slurry was filtered cold and hexane (10 mL) was added to the filtrate. The solvents were removed from the filtrate under vacuum and the remaining solid was dried for 3 h under vacuum to yield 512 mg of a yellow powder, which was stored at −40 °C and used without further purification. This material was contaminated with 0.25 equiv of CuMe. ^{1}H NMR spectra in THF-d_8 contained signals for Me_2CuLi and Me_3Cu_2Li, formed by the reaction of CuMe with Me_2CuLi.[27b]

Acrylonitrile Polymerizations with 1. Details are provided in Table 4. Method A: The desired amounts of initiator and toluene (typically 5.00 g) were placed in a 100 mL Schlenk flask equipped with a stirring bar and a rubber septum. The solution was stirred for 5−15 min at the desired temperature, and acrylonitrile (typically 2.0 mL) was added by syringe with exclusion of light. The mixture was stirred for the desired time (typically 40 min) to yield in most cases highly viscous polymer suspensions. The polymerization was quenched by adding HCl/EtOH (10 mL of a 1 M solution), followed by EtOH (80 mL). The polymer was separated by filtration, washed repeatedly with acetone, 1 M HCl/H_2O, boiling water, and acetone, and then dried for at least 12 h under vacuum. Method B: The desired amounts of initiator and toluene were placed in a 50 mL reaction tube equipped with a Teflon stopcock. The solution was cooled to −196 °C and the desired amount of acrylonitrile was added by vacuum transfer. The reaction tube was sealed and placed into a bath at the desired temperature. The mixture was stirred for the desired amount of time, and the polymer was isolated by the procedure described in method A.

$[Cy_3PCH_2CH_2CN]Cl$.[54] A flask was charged with PCy_3 (100 mg, 0.356 mmol), $[Me_3NH]Cl$ (35.5 mg, 0.356 mmol), and MeCN (1 mL). AN (0.7 mmol) was added by vacuum transfer at −196 °C. The resulting slurry was heated to reflux for 10 min to give a clear solution. The solution was cooled to room temperature and layered with ethyl acetate (2 mL). After 12 h a crystalline precipitate was obtained. The precipitate was isolated by filtration, washed with ethyl acetate, and dried for 1 h under vacuum to yield a colorless powder (36 mg, 27%). ^{1}H NMR (330 K, DMSO-d_6): δ 3.00−3.05 (m, J_{PH} = 9 Hz, -CH_2CN, 2H), 2.77−2.81 (m, J_{PH} = 13 Hz, -C$H_2P^+Cy_3$ 2H), 2.59−2.63 (q, $^{2}J_{PH} = {}^{3}J_{HH}$ = 11 Hz, $P^+CH(CH_2$-$)_2$, 3H), 1.90−1.92 (m, 6H), 1.80−1.83 (m, 6H), 1.55−1.71 (m, 3H), 1.48−1.58 (m, 6H), 1.29−1.43 (m, 9H). ^{13}C{^{1}H} NMR (330 K, DMSO-d_6): δ 118.5 (CN), 28.8 (d, J = 40 Hz, C1), 25.7 (d, J = 4 Hz, C3), 25.6 (d, J = 12 Hz, C2), 24.4 (d, J = 2 Hz, C4), 10.8 (d, J = 44 Hz, PCH_2CH_2CN), 10.4 (d, J = 3 Hz, PCH_2CH_2CN). ^{31}P{^{1}H} NMR (330 K, DMSO-d_6): δ 34.6. Assignments and coupling constants are derived from selective ^{1}H and ^{31}P decoupling experiments. ESI-MS (MeOH) $[Cy_3PCH_2CH_2CN]^+$: Calcd m/z 334.3, found 334.2. Anal. Calcd for $C_{21}H_{37}PNCl{\cdot}(H_2O)_{0.5}$: C, 66.56; H, 10.11; N, 3.70. Found: C, 66.53; H, 10.09; N, 3.77. (^{1}H NMR analysis of the

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(53) Van Geet, A. L. *Anal. Chem.* **1970**, *42*, 679.

(54) Adapted from a synthesis of $[Ph_3PCH_2CH_2CN]Cl$: Teichmann, H.; Thierfelder, W.; Kochmann, W. DD 100960, 1972.

analyzed [$Cy_3PCH_2CH_2CN$]Cl sample in dry CD_3CN showed presence of 0.5 equiv of H_2O due to handling of the compound in air.)

[$Cy_3PCH_2CH_2CN$]Br. A flask was charged with PCy_3 (200 mg, 0.71 mmol), $BrCH_2CH_2CN$ (0.09 mL, 1 mmol), and benzene (5 mL). After 7 days a colorless crystalline precipitate was isolated by filtration and washed with benzene (5 × 2 mL) to give 45 mg (15% yield) of a colorless powder. ^1H NMR (290 K, CD_3CN): δ 2.90−2.95 (m, -CH_2-CN, 2H), 2.63−2.67 (m, -C$H_2P^+Cy_3$ 2H), 2.56 (qt, $^2J_{PH} = {}^3J_{HH} = 13$ Hz, $^3J_{HH} = 3$ Hz, $P^+CH(CH_2\text{-})_2$, 3H), 1.87−1.95 (m), 1.84−1.87 (m, 6H), 1.71−1.76 (m, 3H), 1.50−1.57 (m, 6H), 1.33−1.47 (m, 9H). ^{13}C-{^1H} NMR (290 K, CD_3CN): δ 30.2 (d, $J = 40$ Hz, C1), 27.2 (d, $J = 4$ Hz, C3), 26.9 (d, $J = 12$ Hz, C2), 25.7 (s, C4), 12.8 (d, $J = 45$ Hz, P$C$$H_2CH_2CN$), 12.4 (br s, PCH_2CH_2CN). The -CN resonance was not observed, probably due to overlap with the solvent signal. $^{31}P\{^1H\}$ NMR (290 K, CD_3CN): δ 34.5. ESI-MS (CH_3CN) [$Cy_3PCH_2CH_2CN$]$^+$: Calcd m/z 334.3, found 334.2. Anal. Calcd for $C_{21}H_{37}PNBr$: C, 60.87; H, 9.00; N, 3.38. Found: C, 60.86; H, 8.85; N, 3.35.

Acrylonitrile Polymerizations with (bipy)$_2$FeEt$_2$ (2). Details are provided in Table 4. A 100 mL Fisher-Porter bottle was charged with **2** (71 mg, 0.16 mmol). AN (2.0 g, 38 mmol) was added by vacuum transfer at −196 °C. The bottle was warmed to room temperature to afford a deep blue solution. After 15 min, gas evolution followed by rapid polymerization of AN was observed. After the desired reaction time, the bottle was vented and the resulting slurry was added to acidified MeOH (100 mL of a 1 M HCl solution). The solid precipitate was separated by filtration, washed with 1 M HCl, hot water, and finally acetone, and then dried under vacuum, yielding 1.9 g (95% conversion) of pale red PAN.

Analysis of Gases from the Reaction of 2 and AN. An NMR tube was charged with **2** (15 mg, 34 μmol). AN (0.21 g, 4.0 mmol) was added by vacuum transfer at −196 °C. The tube was warmed to room temperature to yield a deep blue solution. After 10 min, gas evolution followed by rapid polymerization of AN was observed. After 20 h, the volatiles were vacuum-transferred to another NMR tube that was cooled to −196 °C and then analyzed by ^1H NMR in CD_3CN, which showed that ethylene (20 μmol, 0.58 equiv, determined vs ferrocene as internal standard) and ethane were present in a ratio of 10/1.

Analysis of Gases from the Decomposition of 2 in CD_3CN. An NMR tube was charged with **2** (15 mg, 34 μmol), and CD_3CN (0.6 mL) was added by vacuum transfer at −196 °C. The tube was warmed to room temperature to afford a deep blue solution. After 20 h, the volatiles were vacuum-transferred to another NMR tube and analyzed by ^1H NMR, which showed that ethylene (25 μmol, 0.72 equiv, determined vs ferrocene as internal standard) and ethane were present in a ratio of 1/1.

Crystal Structure Determination of 1. Colorless crystals of **1** were obtained by cooling a toluene/pentane solution to −40 °C for 1 week. A colorless rhomb-shaped fragment (0.4 × 0.3 × 0.3 mm) was mounted on a Bruker SMART APEX system at 100 K. A "full sphere" data set was obtained by use of Mo Kα radiation ($\lambda = 0.710\,73$ Å), which samples approximately all reciprocal space to a resolution of 0.75 Å (θ range = 1.9−27.0°) by using 0.3° steps in ω and 30-s integration times for each frame. Integration of intensities and refinement of cell parameters were done with SAINT,[55] yielding 4111 independent reflections ($R_{int} = 1.8\%$). Absorption corrections were applied by SADABS based on redundant diffractions with maximum and minimum transmissions of 1.0 and 0.79, respectively.[55] The space group was determined as P1(bar) and final cell parameters were obtained from the full data set: $a = 9.163(2)$ Å, $b = 9.955(2)$ Å, $c = 10.825(2)$ Å, $\alpha = 88.81(3)°$, $\beta = 81.14(3)°$, $\gamma = 76.49(3)°$, $V = 948.4(3)$ Å^3, $Z = 2$, $d_{calc} = 1.257$ g/cm^3, $\mu = 1.230$ mm^{-1}, and $F_{000} = 388$. The structure was solved by direct methods.[55] All non-hydrogen atoms were refined anisotropically, and hydrogen atom positions were calculated and refined by riding model techniques.[55] Final agreement factors: R1 = 2.50%, wR2 = 6.72% for observed [$I > 2\sigma(I)$] and GOF = 1.070, R1 = 2.54%, wR2 = 6.75% for all reflections. The maximum residual electron density was 0.39 e Å^{-3}.

Acknowledgment. We thank Ian Steele for determination of the crystal structure, Antoni Jurkiewicz for technical support for NMR spectroscopy, and Bayer Polymers for GPC measurements. Funding by the Department of Energy (DE-FG02-00ER15036), Bayer Polymers, and Deutsche Forschungsgemeinschaft is gratefully acknowledged.

Note Added after ASAP: In the version published on the Web 1/23/2004, the structure in Scheme 3 and the TOC graphic was incorrect. The version published 1/27/2004 and the print version are correct.

Supporting Information Available: Additional NMR data, details of the crystal structure of **1**, details of polymer molecular weight determinations, and further experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

JA039018A

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(55) All software and sources of scattering factors are contained in the SHELXTL (version 5.1) program library (G. Sheldrick, Bruker Analytical X-ray Systems, Madison, WI).