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Articles

Synthesis, Characterization, and Polymerization Activity of [Bis(4,4′-bis(neophyldimethylsilylmethyl)-2,2′-bipyridyl)copper(I)]$^+$CuBr$_2^-$ and Implications for Copper(I) Catalyst Structures in Atom Transfer Radical Polymerization

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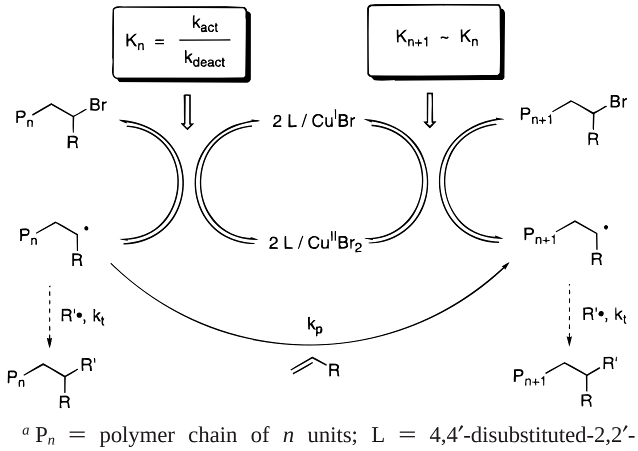
A series of 4,4′-disilyl-substituted-2,2′-bipyridine ligands were prepared using a metathesis reaction of the dianion of 4,4′-dimethyl-2,2′-bipyridine with several trialkylsilyl chlorides: 4,4′-bis(*tert*-butyldimethylsilylmethyl)-2,2′-bipyridine (dTBDMSbipy), 4,4′-bis(dimethylthexylsilylmethyl)-2,2′-bipyridine (dTHEXbipy), and 4,4′-bis-(neophyldimethylsilylmethyl)-2,2′-bipyridine (dNEObipy). It was observed that the side chain length correlated with the ability of the ligand to form hydrocarbon soluble complexes of copper(I) bromide, with dNEObipy forming the most soluble and easily crystallized complexes. The atom transfer radical polymerization (ATRP) of styrene using dNEObipy as the ligand displayed molecular weight control equivalent to other ATRP systems in which solubilizing ligands, such as 4,4′-di-5-nonyl-2,2′-bipyridine or 4,4′-di-*n*-heptyl-2,2′-bipyridine, were used. The one-to-one complex of dNEObipy with CuBr was prepared and its crystal structure was determined. The resulting complex had the ionic formulation [(dNEObipy)$_2$Cu]$^+$[CuBr$_2$]$^-$ and displayed similar activities in styrene ATRP as the standard 2 dNEObipy/CuBr catalyst system. These and other polymerization results in addition to NMR experiments suggest that the predominant copper(I) species formed in ATRP solutions is the 2-to-1 ligand-to-copper(I) cation, [(dNEObipy)$_2$Cu]$^+$, with either a dihalocuprate or halide counteranion, depending upon the conditions.

Introduction

Copper(I) bipyridine complexes have long been used in organic synthesis as catalysts for atom transfer reactions,[1−3] and recently, these complexes have acquired additional importance as catalysts for controlled/living radical polymerizations. Atom transfer radical polymerization (ATRP, Scheme 1) employs atom transfer from an organic halide polymer end group to a transition-metal complex to generate and deactivate propagating radicals. The controlled nature of these polymerizations is a result of the persistent radical effect.[4,5] Initially, a small amount of radical coupling serves to build up a concentration of deactivator (or copper(II) complex) until the rate at which the radicals are deactivated in an atom transfer step becomes faster than the rate at which the radicals can terminate through coupling and disproportionation.[6] As a result, polymers can be prepared using ATRP with a high degree of synthetic control over the final molecular weights, molecular weight distributions, and end group structures.[7] ATRP is applicable to a wide range of vinyl monomers and reaction conditions, and complexes of copper(I),[8−10] ruthenium(II),[11] iron(II),[12,13] and nickel(II)[14,15] with various ligands all demonstrate activity as ATRP catalysts.



Scheme 1. Simplest Working Mechanism of Copper(I)-Catalyzed ATRP Consistent with Known Experimental Facts, Consisting of the Atom Transfer Equilibrium ($k_{activation}/k_{deactivation}$), Propagation ($k_p$), and Termination ($k_t$)[a]

[a] P$_n$ = polymer chain of *n* units; L = 4,4′-disubstituted-2,2′-bipyridine; R = C$_6$H$_5$, CO$_2$R, CN, or CONR$_2$. References 16 and 17 contain extensive discussions regarding other possible species that may form in ATRP solutions, such as Cu(I)−alkene complexes or Cu−alkyl complexes.

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A good deal of spectroscopic and kinetic information is available on ATRP catalyzed by in situ catalyst combinations of 1 equiv of copper(I) halide to 2 equiv of 4,4′-disubstituted-2,2′-bipyridines.[16,17] However, the composition and structure of the copper center in these polymerizations are not known and usually are inferred from previous literature crystallographic studies of 2,2′-bipyridine (bipy) complexes. Haddleton et al.[18−20] have structurally characterized several copper(I) and copper-(II) complexes of bidentate 2-iminopyridines and have examined their activities in the ATRP of methyl methacrylate, which has provided much needed insight into that system. However, such structural information is lacking for the bipyridine ligand systems and, if known, would allow for deeper insights into the chemistry of copper(I) halide/2,2′-bipyridine ATRP systems. Furthermore, a number of outstanding issues in ATRP could be solved rationally through knowledge about the structure, solution dynamics, and chemistry of the copper centers involved in the atom transfer steps. These issues include effecting the polymerization of less active monomers (i.e., vinyl esters and dienes), extension of polymerization control to even higher molar mass polymers, and development of more active catalysts that can be used in smaller concentrations.

Experimental Section

Materials. Dimethylthexylchlorosilane (Aldrich) and neophyldimethylchlorosilane (Huls chemical) were distilled under vacuum before use. Styrene was distilled under vacuum before use. THF was stirred over Na/benzophenone and vacuum transferred before use. Acetonitrile (CH_3CN) was purified by stirring over anhydrous $CuSO_4$ for 24 h and then distillation from P_2O_5 before use. Diisopropylamine was stirred over CaH_2 and vacuum distilled before use. CuBr (Acros) was purified until colorless by grinding into a fine powder using a mortar and pestle, stirring in glacial acetic acid, consecutive washing with absolute ethanol and diethyl ether, and removing of volatile materials under vacuum. $[Cu(CH_3CN)_4]^+BF_4^-$ was prepared according to the procedure of Hathaway et al.[21] All syntheses and polymerizations were performed under nitrogen atmospheres using standard Schlenk techniques. Unless stated otherwise, all other materials were purchased from commercial sources and used without further purification.

Characterizations. Number-averaged molecular weights (M_n), weight-averaged molecular weights (M_w), and molecular weight distributions (M_w/M_n) were determined using gel-permeation chromatography in THF at 30 °C. Three Polymer Standards Services columns (100 Å, 1000 Å, and linear) were connected in series to a Thermoseparation Products P-1000 isocratic pump, autosampler, column oven, and Knauer refractive index detector. Calibration was performed using polystyrene samples (Polymer Standard Services; $M_p = 400-1\,000\,000$; $M_w/M_n < 1.10$). ^{1}H NMR spectra (300 MHz) and ^{13}C {^{1}H} spectra (75 MHz) were recorded using General Electric QE-300 NMR spectrometers. Chemical shifts, δ (ppm), were referenced to the residual proton signal or ^{13}C signal of the specified solvent. Significant ^{1}H NMR data are tabulated in order: multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant(s) in Hertz, and number of protons. Elemental analyses were performed by Desert Analytics, Inc., and Midwest Microlab.

Synthesis of 4,4′-Bis(*tert*-butyldimethylsilylmethyl)-2,2′-bipyridine, dTBDMSbipy. To 50 mL of THF was added diisopropylamine (3.05 mL, 21.8 mmol) and *n*-BuLi (8.60 mL, 21.7 mmol), and the solution was stirred at −78 °C. A solution of THF (100 mL) and 4,4′-dimethyl-2,2′-bipyridine (2.00 g, 10.9 mmol) was prepared and added via a Schlenk addition funnel to the former solution stirring at −78 °C. After 20 min, a solution of THF (50 mL) and *tert*-butyldimethylchlorosilane (3.27 g, 21.7 mmol) was prepared and added via a Schlenk addition funnel to the solution stirring at −78 °C. The reaction was allowed to stir and to warm slowly to room temperature over 24 h. The solution was then transferred to a separatory funnel, 100 mL of H_2O was added, and the aqueous layer was extracted using 4 × 25 mL of ethyl acetate. The organic layers were combined and dried over anhydrous $MgSO_4$, and volatile materials were removed under vacuum. The residue was recrystallized from ethanol, and 3.32 g (74%) of colorless crystals was obtained. Mp = 160−161 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.45 (2H, d, $J = 5.1$), 8.06 (2H, d, $J = 1.8$), 6.94 (2H, dd, $J = 5.1, 1.8$), 2.21 (4H, s), 0.93 (18H, s), −0.06 (12H, s). ^{13}C NMR (300 MHz, $CDCl_3$): δ (ppm) 55.7, 151.5, 148.5, 123.6, 121.0, 26.5, 23.1, 16.8, −6.6. Anal. Calcd. for $C_{24}H_{40}N_2Si_2$: C, 69.8; H, 9.7; N, 6.8. Found: C, 69.9; H, 9.5; N, 6.9.

Synthesis of 4,4′-Bis(dimethylthexylsilylmethyl)-2,2′-bipyridine, dTHEXbipy. The synthesis of 4,4′-bis(dimethylthexylsilylmethyl)-2,2′-bipyridine was the same as above replacing *tert*-butyldimethylchlorosilane with dimethylthexylchlorosilane (4.30 mL, 21.9 mmol). Recrystallization was performed using ethyl acetate, and colorless crystals, 5.21 g (60% yield), were obtained. Mp = 138−139 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.45 (2H, d, $J = 5.1$), 8.06 (2H, d, $J = 1.5$), 6.94 (2H, dd, $J = 5.1, 1.5$), 2.25 (4H, s), 1.68 (2H, m), 0.91 (12H, d, $J = 6.3$), 0.89 (12H, s), −0.04 (12H, s). ^{13}C NMR (300 MHz, $CDCl_3$): δ (ppm) 155.7, 151.5, 148.4, 123.7, 121.1, 34.8, 24.4, 23.6, 20.9, 18.7, −4.2.

Synthesis of 4,4′′-Bis(neophyldimethylsilylmethyl)-2,2′-bipyridine, dNEObipy. The synthesis of 4,4′-bis(neophyldimethylsilylmethyl)-2,2′-bipyridine is the same as above replacing *tert*-butyldimethylchlorosilane with neophyldimethylchlorosilane (4.70 mL, 21.7 mmol). Recrystallization was performed using hexane/ethyl acetate, and colorless crystals, 3.34 g (55% yield), were obtained. Mp = 133−134 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.41 (2H, d, $J = 5.1$), 7.95 (2H, d, $J = 1.8$), 7.25 (10H, m), 6.82 (2H, dd, $J = 5.1, 1.8$), 1.94 (4H, s), 1.39 (12H, s), 1.21 (4H, s), −0.24 (12H, s).^{13}C NMR (300 MHz, $CDCl_3$): δ (ppm) 155.6, 151.4, 150.5, 148.4, 128.0, 125.4, 123.4, 120.8, 37.2, 33.1, 32.6, 27.4, −1.8. Anal. Calcd for $C_{36}H_{48}N_2Si_2$: C, 76.5; H, 8.6; N, 5.2. Found: C, 76.4; H, 8.6; N, 5.2.

Synthesis of [Bis(4,4′-bis(neophyldimethylsilylmethyl)-2,2′-bipyridyl)copper(I)]$^+$CuBr$_2^-$. In a Schlenk flask, 5.0 mL of CH_3CN was degassed, and then copper(I) bromide (0.124 g, 0.862 mmol) and dNEObipy (0.504 g, 0.894 mmol) were added. The solution was stirred and heated at reflux under nitrogen until all solids had dissolved. The solution was cooled to 0 °C using an ice bath, and crystals slowly formed. The supernatant was removed via cannula, and volatile materials were removed under vacuum. Reddish/brown crystals were obtained in 0.460 g (72%) yield. Mp = 107−108 °C. The product was recrystallized from CH_3CN. ^{1}H NMR (300 MHz, CD_2Cl_2): δ (ppm) 8.35 (2H, d, $J = 5.1$), 7.58 (2H, d, $J = 1.8$), 7.13 (10H, m), 7.02 (2H, dd, $J = 5.1, 1.8$), 2.05 (4H, s), 1.40 (12H, s), 1.25 (4H, s), −0.22 (12H, s). ^{13}C NMR (300 MHz, CD_2Cl_2): δ (ppm) 154.0, 152.2, 150.7, 148.6, 128.4, 125.9, 120.8, 37.5, 32.8, 32.8, 28.6, −1.8. Anal. Calcd for $C_{36}H_{48}N_2Si_2CuBr$: C, 61.0; H, 6.8; N, 4.0; Br, 11.3. Found: C, 57.9; H, 7.0; N, 3.7; Br, 10.4.

Synthesis of [Bis(4,4′-bis(neophyldimethylsilylmethyl)-2,2′-bipyridyl)copper(I)]$^+$BF$_4^-$. In a Schlenk flask, dNEObipy (0.711 g, 1.26

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Table 1. Crystal Data and Structure Refinement for dNEObipy and Complex **1**

compound	dNEObipy	complex **1**
formula	$C_{36}H_{48}N_2Si_2$	$C_{72}H_{96}Br_2Cu_2N_4Si_4$
fw	564.94	1416.79
space group	$P2_1/c$	$P\bar{1}$
a, Å	7.9701(9)	13.671(8)
b, Å	22.075(2)	15.468(7)
c, Å	9.3996(11)	19.184(9)
α, deg		100.68(4)
β, deg	98.420(9)	98.86(4)
γ, deg		111.53(4)
V, Å^3	1635.9(3)	3597(3)
T, K	130(2)	130(2)
Z	2	2
d_{calcd}, g cm^{-3}	1.147	1.308
μ(Cu Kα), mm^{-1}	1.168	2.983
range of transm factors	0.74−0.83	0.68−0.94
wR2[a]	0.0988 (all data)	0.2454 (all data)
R1[b]	0.0409 ($I > 2\sigma(I)$ data)	0.0828 ($I > 2\sigma(I)$ data)

[a] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[(wF_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$.

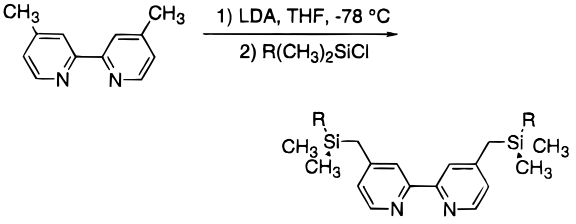
mmol) and $[Cu(CH_3CN)_4]^+BF_4^-$ (0.202 g, 0.643 mmol) were weighed, and then 20.0 mL of dry, degassed CH_3CN was added via cannula. The solution was stirred and heated at reflux under nitrogen until all solids had dissolved. The solution was cooled to room temperature and then to 0 °C using an ice bath, and crystals slowly formed. The supernatant was removed via cannula, and volatile materials were removed under vacuum. Reddish/brown crystals were obtained in 0.589 g (73%) yield. Mp = 150−151 °C. The product was recrystallized from CH_3CN. ^1H NMR (300 MHz, CD_2Cl_2): δ (ppm) 8.15 (2H, d, J = 5.1), 7.64 (2H, d, J = not resolved), 7.29 (10H, m), 6.98 (2H, dd, J = 5.1, not resolved), 2.05 (4H, s), 1.40 (12H, s), 1.25 (4H, s), −0.21 (12H, s). ^{13}C NMR (300 MHz, CD_2Cl_2): δ (ppm) 153.2, 151.9, 150.6, 147.9, 128.3, 125.8, 125.7, 120.8, 37.5, 33.2, 32.8, 28.5, −1.8. Anal. Calcd for $C_{72}H_{96}BN_4F_4Si_4Cu$: C, 67.55; H, 7.56; N, 4.38. Found: C, 67.48; H, 7.45; N, 4.42.

General Procedure for the Solution Polymerization of Styrene. A 25 mL Schlenk flask was charged with the amount of $[(dNEObipy)_2Cu]^+[CuBr_2]^-$, CuBr, and/or dNEObipy (see Table 2). Next, xylene, styrene, and 1-phenylethyl bromide were added, and the mixture was degassed by three cycles of freezing, evacuation, thawing, and backfilling with nitrogen. The flask was immersed in an oil bath at 105 ± 1 °C, and a time = 0 data point was taken immediately. At timed intervals, a 1.00 mL sample of the solution was withdrawn using a purged syringe and added to 5.00 mL of THF. The THF solutions were injected into the GC, and percent conversions were calculated relative to the time = 0 data points and using the xylene signal as an internal standard. The samples were then filtered through a small column of neutral alumina and a 0.2 μm filter and then injected into the GPC for analysis.

X-ray Crystallography. Crystals of the compounds studied were all handled in a similar manner. Suitable crystals of dTBDMSbipy and dTHEXbipy were mounted in the LT-1 cold stream of a Syntex P2$_1$ diffractometer equipped with a sealed Cu tube and graphite monochromator. Those of dNEObipy and $[dNEObipy)_2Cu]^+[CuBr_2]^-$ were mounted in the cold stream of a Siemens P4 diffractometer equipped with a LT-2 low-temperature apparatus. The radiation for the P4 diffractometer was Ni-filtered Cu Kα from a Siemens rotating anode source operating at 15 kW. In each case the temperature at the crystal was 130(2) K. Data on the P2$_1$ diffractometer were collected to a maximum 2θ of 134°, and data on the P4 diffractometer were collected to a maximum 2θ of 114°. Less than 0.1% fluctuation in the intensities of two standard reflections was observed during the data collection for all except dNEObipy for which a 5% decay was observed. The structures were solved using direct methods. Refinement was by full-matrix least-squares methods, based on F^2, using all data. Hydrogen atoms were located on a difference map and freely refined in dTBDMSbipy. In the other structures the hydrogen atoms were placed at geometrically reasonable positions and refined using a riding model. In the structure of dTHEXbipy there was a 50/50 disorder in the carbon atoms of the thexyl group. In the structure of $[dNEObipy)_2Cu]^+[CuBr_2]^-$ there was a 50/50 disorder of carbon atoms 63−66. Structural drawings of these two compounds showing the disordered atoms are contained in the Supporting Information. A relatively high R value (R1(obs data) = 0.083) was obtained in the refinement of $[dNEObipy)_2Cu]^+[CuBr_2]^-$ which is primarily due to poor counting statistics that resulted from the small crystal size (0.02 × 0.06 × 0.14 mm). No chemically significant peaks were present in the final difference maps of any of the four structures. Crystallographic programs were those of SHELXTL 5.1, G. Sheldrick (1997), distributed by Bruker-AXS, Madison, WI. Tables of neutral atom scattering factors, f' and f'', and absorption coefficients are from the following: *International Tables for Crystallography*, Volume C Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, Tables 6.1.1.3 (pp 500−502), 4.2.6.8 (pp 219−222), and 4.2.4.2 (pp 193−199), respectively. Empirical absorption corrections were applied using the program XABS2.[22]

Results and Discussion

The first step toward studying the structure and chemistry of the copper centers in ATRP was to develop bipyridine ligands that could form catalytically active complexes with copper(I) halides that were both soluble in the nonpolar media of the polymerizations and sufficiently crystalline for crystallographic studies. Reported ligands that satisfied the solubility criteria (i.e. 4,4′-di-5-nonyl-2,2′-bipyridine (dNbipy)[6,23] or 4,4′-di-*n*-heptyl-2,2′-bipyridine) (dHbipy))[6,23,24] formed complexes with copper(I) halides that were difficult for growing quality single crystals. Disubstituted 2,2′-bipyridines are readily available via metathesis reactions with the dianion of 4,4′-dimethyl-2,2′-bipyridine (dMbipy),[25,26] so we prepared several new ligands in which the substituents were derived from trialkylsilyl chlorides (eq 1). Because a wide range of trialkylsilyl chlorides are commercially available, we were able to vary the structure of the product in order to find a ligand system that met the aforementioned specifications.



(1)

R = *tert*-butyl, 1,1,2-dimethylpropyl, neophyl

The dianion of dMbipy was formed via the addition of a THF solution of dMbipy to 2 equiv of lithium diisopropylamide in THF at −78 °C (eq 1). To this dark red/brown solution was added 2 equiv of the appropriate trialkylsilyl chloride, and the solution was allowed to warm slowly to room temperature overnight. After workup, each of the ligands was isolated in satisfactory yield. In all, three new 2,2′-bipyridine ligands were prepared and characterized using this procedure (Figure 1): 4,4′-bis(*tert*-butyldimethylsilylmethyl)-2,2′-bipyridine (dTBDMSbipy), 4,4′-bis(dimethylthexylsilylmethyl)-2,2′-bipyridine (dTHEXbipy), and 4,4′-bis(neophyldimethylsilylmethyl)-2,2′-bipyridine

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Table 2. Data for the ATRP of Styrene in *p*-Xylene Solvent Using Different Catalyst Systems

catalyst	[Cu(I)]$_0$,[a] mM	[1-PEBr]$_0$, mM	[styrene]$_0$, M	time (min)	% conversion	M_n(expected)	M_n(GPC)	M_w/M_n
CuBr/2 dNEObipy[b]	60.4	61.6	6.10 M	0	0	0		
				79	23	2400	2700	1.07
				184	41	4200	4500	1.05
				318	52	5400	5900	1.06
				465	61	6300	7200	1.05
				589	67	6900	8100	1.05
complex **1**	61.0	61.6	6.10	0	0	0		
				89	25	2600	3300	1.06
				181	38	3900	5000	1.04
				342	51	5300	7000	1.05
				478	58	6000	8000	1.05
				595	60	6200	8300	1.05
complex **1** + 1 equiv of dNEObipy[c]	61.0	61.6	6.10	0	0	0		
				63	23	2300	2900	1.07
				135	36	3700	4500	1.05
				263	50	5200	6500	1.05
				377	58	6000	7500	1.05
				535	67	6900	8700	1.05
n-Bu$_4$N$^+$CuBr$_2$$^-$	61.0	61.6	6.10	0−600	NP			

[a] Based upon total copper(I) concentration (i.e., [Cu(I)]$_0$ = [(dNEObipy)$_2$Cu]$^+$ + [CuBr$_2$]$^-$ for complex **1**). [b] [CuBr]$_0$ = 60.4 mM and [dNEObipy]$_0$ = 121.6 mM. [c] One equiv of ligand based upon total initial copper(I) concentration; NP = no polymerization conversion observed.

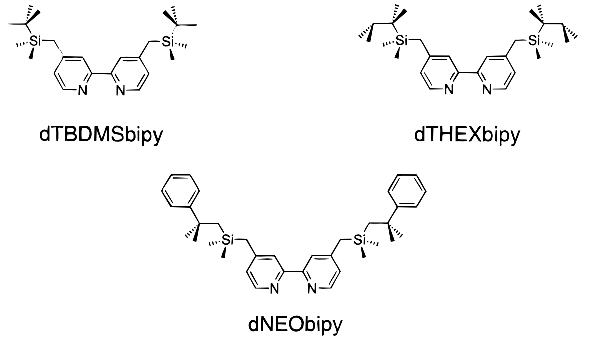


Figure 1. Three ligands prepared in this study: 4,4′-bis(*tert*-butyldimethylsilylmethyl)-2,2′-bipyridine, dTBDMSbipy; 4,4′-bis(dimethylthexylsilylmethyl)-2,2′-bipyridine, dTHEXbipy, and 4,4′-bis(neophyldimethylsilylmethyl)-2,2′-bipyridine, dNEObipy.

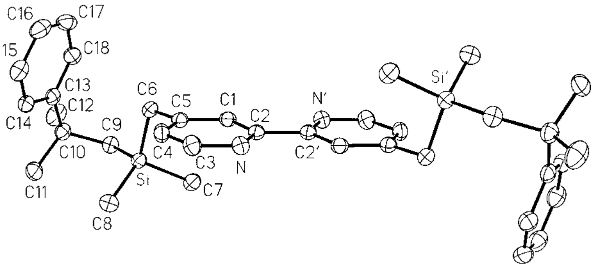


Figure 2. Crystal structure of 4,4′-bis(neophyldimethylsilylmethyl)-2,2′-bipyridine, dNEObipy.

(dNEObipy, Figure 2). We found that, under the conditions we used for these metathesis reactions, bulky trialkylsilyl chlorides with more than one nonmethyl substituent on the silicon center yielded very slow reactions and mixtures of mono- and disubstituted products, as determined from ^{1}H NMR spectra.

The crystal structures of the three ligands were determined, and the data for dNEObipy are shown in Figure 2 and Table 1, while corresponding data for dTHEXbipy and dTBDMSbipy are located in the Supporting Information. In the three structures, disorder is only present in the side chain of dTHEXbipy, which exists in a 50/50 population of two conformations. The bipyridine portions of the three ligands are structurally identical, crystallizing in a planar s-trans conformation and with inter-ring C−C bond lengths of 1.49−1.50 Å, ring C−C bond lengths of 1.35−1.40 Å, and C−N bond lengths of 1.34−1.35 Å. The core similarities of these ligands highlight the different shapes of the side chains attached to the 4,4′-positions. The extension of the chain away from the bipyridine portion of the ligand increases in the following order: dTBDMSbipy < dTHEXbipy < dNEObipy. This trend correlates well with our observations that dTBDMSbipy is unsatisfactory at forming complexes with CuBr that are soluble in nonpolar solvents and polymerization media, whereas both dTHEXbipy (good) and dNEObipy (best) form soluble complexes of CuBr during ATRP experiments. Using the latter ligand, dNEObipy, we were able to grow crystals of its complexes with copper(I) halides, and for these reasons we performed the rest of our work using dNEObipy.

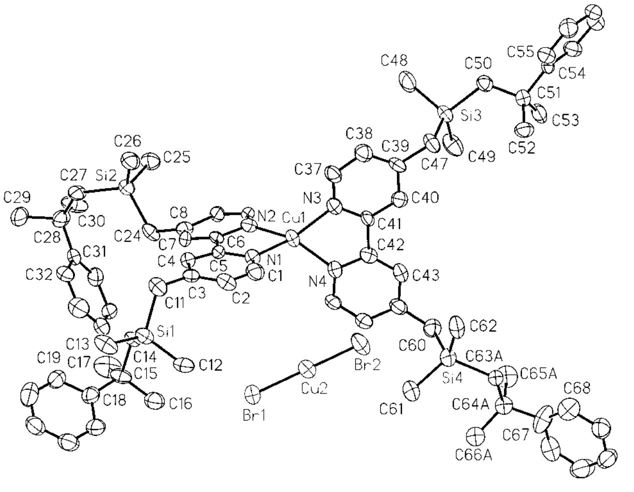
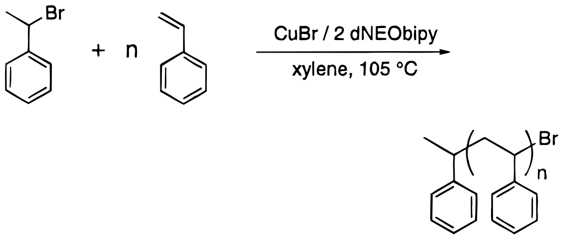


Figure 3. Crystal structure of [bis(4,4′-bis(neophyldimethylsilylmethyl)-2,2′-bipyridyl)copper(I)]$^+$CuBr$_2$$^-$, complex **1**.

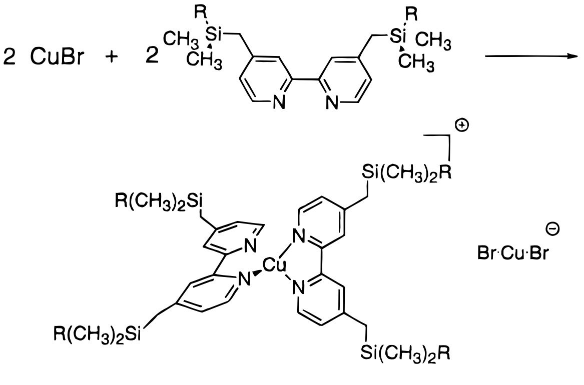
First we confirmed that ATRP using dNEObipy displays similar levels of control as those polymerizations using dNbipy or dHbipy. When a solution polymerization was conducted using CuBr (60.4 mM), dNEObipy (122 mM), 1-phenylethyl bromide (1-PEBr, 61.6 mM), styrene (6.10 M), and xylene solvent (eq 2), all the elements of a controlled/living radical polymerization were observed. As shown in Table 2, the number-averaged molecular weight (M_n) of the polystyrene increased with percent conversion and correlated well with the expected molecular weights on the basis of the ratio of converted monomer concentration to initial initiator concentration. Throughout the course of the polymerization, the molecular weight distributions



(2)

remained very narrow (1.05−1.07) and equaled the best reported for ATRP systems using dNbipy or dHbipy.

With this demonstration in hand, we proceeded to prepare and characterize copper(I) halide complexes using dNEObipy. When a solution of 1 equiv of dNEObipy and CuBr was heated at reflux in CH_3CN, a deep brown-red solution formed, and upon slow cooling of the solution, brown-red crystals of complex **1** formed in 72% yield (eq 3). Differences in ^1H and ^{13}C NMR chemical shifts for the pyridyl ring protons in the product versus those of the free ligand confirmed complex formation, and elemental analysis confirmed a ligand-to-metal stoichiometry of one-to-one. Crystals suitable for X-ray analysis were grown using a butyronitrile/hexane solvent system.



(3)

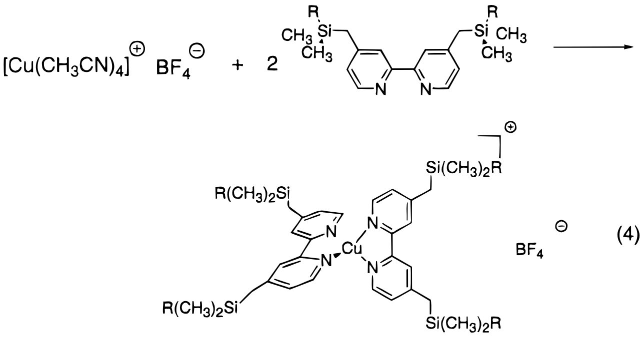
Complex-**1**

The structure of complex **1** is shown in Figure 3 and indicates an ionic formulation of $[(\mathrm{dNEObipy})_2\mathrm{Cu}]^+[\mathrm{CuBr}_2]^-$. The crystal and structure refinement data are located in Table 1. In the cation, the bipyridine ligands are coordinated to the copper in the s-cis conformation, and the average bond lengths and angles are unchanged from those of the free ligand: inter-ring C−C bond lengths of 1.48−1.51 Å, ring C−C bond lengths of 1.36−1.41 Å, and C−N bond lengths of 1.33−1.38 Å. The Cu−N bond lengths range from 2.02 to 2.05 Å, and the two N−Cu−N chelate angles are 82.0(4) and 80.8(4)°. These bond lengths and angles are consistent with reported values from other complexes containing $[(\mathrm{bipy})_2\mathrm{Cu}]^+$ cations.[27,28] The dihedral angles between the two planes containing the ligand pyridyl rings are 15.2° for the rings containing N(1) and N(2) and 2.5° for the rings containing N(3) and N(4). These angles and their differences most likely can be ascribed to the fact that the cation has no crystallographically imposed symmetry and to crystal packing forces. In the side chains there was a 50/50 disorder of two conformations for carbon atoms 63−66.

The dihedral angle, α, between the two planes formed by N(1), N(2), Cu(1) and N(3), N(4), Cu(1), respectively, is 89.0°. Coppper(I) bis(bipyridyl) and other $\mathrm{Cu(NN)}_2^+$ cations usually exhibit a flattening distortion in the solid state attributed to crystal packing forces that produces a range of dihedral angles from approximately $\alpha = 70$ to 80°.[29] That the dihedral angle for complex **1** is near 90° most likely is due to the large side chains occupying space between the bis(bipyridyl)copper(I) cores and reducing the crystal packing forces that contribute to this distortion. In the anion, the Cu−Br bond lengths are 2.22 and 2.23 Å, and the geometry is nearly linear with a Br−Cu−Br angle of 177.4(1)°. These values are consistent with those reported for other structurally characterized dibromocuprate anions.[30−32] The closest distance between the anion and the copper center of the cation is 4.825 Å between Br(1) and Cu-(1), which indicates no substantial interactions between these two ions.

Pallenberg et al.[32] examined both the solution and solid-state structures of a range of 1-to-1 complexes of 2,9-dialkyl-1,10-phenanthrolines with copper(I) halides. For those ligands that possessed small alkyl substituents, the authors found that while different types of solid structures could be observed, each of the complexes displayed solution structures comprised of a 2-to-1 ligand-to-copper(I) cation and a dihalocuprate anion. When preparations were conducted using two equivalents of ligand to copper(I) halide, the authors observed substantially similar NMR spectra and elemental analyses that were consistent with a 2-to-1 ligand-to-copper(I) cation and a halide anion. Because 2-to-1 ligand-to-copper(I) cations seem to be the preferred structure in solution for phenanthroline complexes, it was important to verify this possibility for the dNEObipy system.

Shown in Table 3 are ^1H NMR chemical shifts for the pyridyl ring protons of dNEObipy in a series of copper(I) species. The chemical shifts for complex **1** closely match those of solutions containing a 1-to-1 mole ratio of CuBr and dNEObipy. These data might suggest a preference for the formation of 2-to-1 ligand-to-copper(I) cations. However, copper(I) has a d^{10} electronic configuration and will exhibit fast ligand exchange; therefore, solutions with the same stoichiometric composition will be identical and have identical NMR spectra independent of the manner of preparation. Thus, $[(\mathrm{dNEObipy})_2\mathrm{Cu}]^+\mathrm{BF}_4^-$, complex **2**, was prepared (eq 4). Because tetrafluoroborate is an inert, noncoordinating anion and cannot undergo conproportionation and other reactions with the bis-ligand cation to



(4)

Complex-**2**

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Table 3. ^{1}H NMR Data (300 MHz, CD_2Cl_2) for the Pyridyl Ring Protons for Complex **1**, Complex **2**, and in Situ Mixtures of CuBr and dNEObipy[a]

sample	chem shift (ppm) of pyridyl ring aromatic protons (CD_2Cl_2)		
dNEObipy	8.41	7.98	6.84
complex **1**	8.34	7.58	7.01
CuBr/1 equiv of dNEObipy[b]	8.31	7.62	7.01
complex **2**	8.15	7.64	6.98
CuBr/2 equiv of dNEObipy[b]	8.27	7.76	6.98

[a] Spectra were recorded after all components had dissolved. [b] 5.0 mg (0.035 mmol) of CuBr, 19.7 mg (0.035 mmol) of dNEObipy, 0.50 mL of CD_2Cl_2. [c] 5.3 mg (0.037 mmol) of CuBr, 41.4 mg (0.073 mmol) of dNEObipy, 0.50 mL of CD_2Cl_2.

form new copper(I) species, in solution complex **2** will remain a bis-ligand cation. The ^{1}H NMR spectrum of complex **2** thus provides a reasonable measure of the chemical shifts of $[(\text{dNEObipy})_2\text{Cu}]^+$, with small effects possible due to the nature of the counteranion. As seen in Table 3, the chemical shifts of complex **2** are similar to those of complex **1** and of solutions containing a 1-to-1 mole ratio of CuBr and dNEObipy. The chemical shift for one of the protons is approximately 0.15 ppm different from that of the latter species, but the small difference could be due to the effect of the different counterion. Thus, the data suggest that the preference for the formation of 2-to-1 ligand-to-copper(I) cations found for the aforementioned phenanthroline/copper(I) halide systems extends to the bipyridine systems as well.

In light of these NMR data it was of interest to compare the ATRP activity of complex **1** with that of 2-to-1 ligand-to-CuBr ATRP catalyst mixtures and to see if there were any differences. Table 2 shows the kinetic and molecular weight data for a series of analogous polymerizations of styrene using different copper(I) species as the catalyst, and a few important results were observed. First, for polymerizations using complex **1** as the catalyst, the active copper(I) species was not CuBr_2^-, because no polymerization conversion was observed when styrene ATRP was attempted using n-$\text{Bu}_4\text{N}^+\text{CuBr}_2^-$ [33] as the sole copper(I) species. Second, the observed rates of polymerization, molecular weights, and molecular weight distributions did not differ substantially when either CuBr/2 dNEObipy or complex **1** was used as the catalyst. Third, to mirror more closely the conditions found in the polymerizations using CuBr/2 dNEObipy, the addition of a second 1 equiv of ligand to polymerizations using complex **1** did not significantly affect the results.

As shown by Matyjaszewski et al.,[6] the rate of styrene ATRP using variable ratios of dNbipy to CuBr in in situ catalyst formulations reached a maximum for the ligand-to-metal stoichiometry of two-to-one. Considering that complex **1** was as effective a catalyst for styrene ATRP as CuBr/2 dNEObipy, we surmised that the additional 1 equiv of ligand necessary for the maximum rate when using in situ catalyst formulations may be a consequence of solubility. At the concentrations used in the in situ catalyst formulations, the initial concentration of free ligand is quite low, and the active copper(I) complex may not form either in sufficient quantity (an equilibrium effect) or sufficiently fast (a kinetic effect) for the maximum rate to be observed.

In light of these results, the ^{1}H NMR spectrum of a solution of 2-to-1 mole ratio of dNEObipy and CuBr was analyzed. In CD_2Cl_2, a single set of chemical shifts was observed for the pyridyl ring protons (Table 3), and the 2,4-disubstituted pyridine coupling patterns were observed as well. The chemical shifts of two out of three of the pyridyl ring protons correlated well with the corresponding chemical shifts found for other bis-ligand copper(I) cations. The chemical shift of the third proton was approximately 0.1 ppm outside the range of chemical shifts found for the other bis-ligand copper(I) cations, but the difference is sufficiently small that the data are still consistent with the structure being a bis-ligand copper(I) cation. The fact that the chemical shifts found for the 2-to-1 mole ratio of dNEObipy and CuBr solutions were not at the geometric mean of the 1-to-1 solution and the free ligand chemical shifts indicates that the majority of the solution species must be $(\text{dNEObipy})_2\text{Cu}^+\text{Br}^-$ and not complex **1** in dynamic equilibrium with free ligand (^{1}H NMR spectra of complex **2** in CD_2Cl_2 with an added 1 equiv of dNEObipy showed broadened signals at room temperature).

Table 4. ^{1}H NMR Data (300 MHz) for in Situ Mixtures of CuBr on n-$\text{Bu}_4\text{N}^+\text{CuBr}_2^-$ with dNEObipy[a]

sample	chem shift (ppm) of pyridyl ring aromatic protons		
dNEObipy (CD_2Cl_2)	8.41	7.98	6.84
dNEObipy (toluene-d_8)	8.47	8.52	6.55
n-$\text{Bu}_4\text{N}^+\text{CuBr}_2^-$/2 dNEObipy (toluene-$d_8$)	8.46	8.51	6.55
n-$\text{Bu}_4\text{N}^+\text{CuBr}_2$/2 dNEObipy ($CD_2Cl_2$)[c]	8.27	7.75	6.96
CuBr/2 equiv of dNEObipy (CD_2Cl_2)[d]	8.27	7.76	6.98

[a] Spectra were recorded after all components had dissolved. [b] 5.0 mg (0.011 mmol) of n-$\text{Bu}_4\text{N}^+\text{CuBr}_2^-$, 9.8 mg (0.017 mmol) of dNEObipy, 0.50 mL of toluene-d_8. [c] 10.1 mg (0.022 mmol) of n-$\text{Bu}_4\text{N}^+\text{CuBr}_2^-$, 22.9 mg (0.041 mmol) of dNEObipy, 0.50 mL of CD_2Cl_2. [d] 5.3 mg (0.037 mmol) of CuBr, 41.4 mg (0.073 mmol) of dNEObipy, 0.50 mL of CD_2Cl_2.

While the aforementioned result is consistent with the study by Pallenberg et al.,[32] who used $CDCl_3$ as the NMR solvent, it is inconsistent with the polymerization results. A possible explanation for the observed difference is that in nonpolar solvents (i.e., toluene, styrene) the complex formation equilibrium might be stopped at the bis-ligand copper(I) cation/dibromocuprate pair. In polar solvents (i.e., methylene chloride, methyl methacrylate), extra bipyridine ligand could displace the two bromide ligands of the dibromocuprate counteranion to form a bis-ligand cation and two bromide counteranions (eq 5). The

$$[(\text{dNEObipy})_2\text{Cu}]^{\oplus}\ \text{CuBr}_2^{\ominus} + 2\ \text{dNEObipy} \xrightleftharpoons{K_{eq}}$$

Favored in nonpolar solvents

$$[(\text{dNEObipy})_2\text{Cu}]^{\oplus}\ \text{Br}^{\ominus} + [(\text{dNEObipy})_2\text{Cu}]^{\oplus}\ \text{Br}^{\ominus} \quad (5)$$

Favored in polar solvents

lack of solvation of the bromide in nonpolar solvents would destabilize it. In the dibromocuprate anion, the charge is distributed over a larger amount of space, presumably requiring less solvation energy.

To test this hypothesis, two NMR spectra were acquired of a 2-to-1 ratio of dNEObipy to n-$\text{Bu}_4\text{N}^+\text{CuBr}_2^-$, one in CD_2Cl_2 and one in toluene-d_8 (Table 4). Immediately upon mixing of the two colorless reagents in CD_2Cl_2, a deep red-brown solution formed indicating coordination of dNEObipy to the copper(I) centers. The ^{1}H NMR spectrum of this solution showed the same pyridyl ring proton chemical shifts at that of the solution of 2-to-1 mole ratio of dNEObipy and CuBr. Upon mixing of the

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[33] Nilsson, M. *Acta Chem. Scand. B* **1982**, *36*, 125−126.

two reagents in toluene-d_8 no color change was observed and the ^{1}H NMR spectrum showed the same pyridyl ring proton chemical shifts as dNEObipy. Upon heating of this solution at 110 °C for 30 min, only a faint brown-red color developed, and no change in the chemical shifts of the pyridyl ring proton signals was observed. The data suggest, at the very least, that the predominant copper(I) species in solution during styrene ATRP using CuBr/2 dNEObipy in situ catalyst formulations is the 2-to-1 ligand-to-copper(I) cation. Additionally, the data suggest that the counteranion is prediminantly a dibromocuprate anion; however, the stoichiometry of dihalocuprate versus halide counteranion is not known presently.

In conclusion, it was shown that substituents at the 4,4′ positions of 2,2′-bypyridines could be varied in order to synthesize copper(I) ATRP catalysts that are both soluble in nonpolar bulk monomer and suitably crystalline for isolation and crystallographic analysis. A metathesis reaction of the dianion of 4,4′-dimethyl-2,2′-bipyridine with neophyldimethylsilyl chloride was used to prepare 4,4′-bis(neophyldimethylsilylmethyl)-2,2′-bipyridine (dNEObipy). The ATRP of styrene using dNEObipy as the ligand displayed molecular weight control equivalent to other ATRP systems in which solubilizing ligands, such as dNbipy or dHbipy, were used. The one-to-one complex of dNEObipy with CuBr was prepared, and its crystal structure was determined. The resulting complex had the ionic formulation $[(\text{dNEObipy})_2\text{Cu}]^+[\text{CuBr}_2]^-$ and displayed activities in styrene ATRP similar to those of the in situ 2 dNEObipy/CuBr catalyst system. These polymerization results in addition to NMR experiments suggest that the predominant copper(I) species formed in ATRP solutions is the 2-to-1 ligand-to-copper(I) cation, $[(\text{dNEObipy})_2\text{Cu}]^+$, with either a dihalocuprate or halide counteranion, depending upon the conditions. We are presently investigating the connection between such structures observed in solution and the catalytically active species in ATRP.

Acknowledgment. We acknowledge the UC Davis Committee on Research for financial support.

Supporting Information Available: ORTEP projections of 4,4′-bis(*tert*-butyldimethylsilylmethyl)-2,2′-bipyridine, dTBDMSbipy, and 4,4′-bis(dimethylthexylsilylmethyl)-2,2′-bipyridine, dTHEXbipy, structural drawings of dTHEXbipy and complex **1** showing the disordered atoms, ^{1}H NMR spectra for entries within Tables 3 and 4 and corresponding discussion within the text, and X-ray crystallographic files in CIF format for the structure determinations of dTBDMSbipy, dTHEXbipy, dNEObipy, and complex **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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