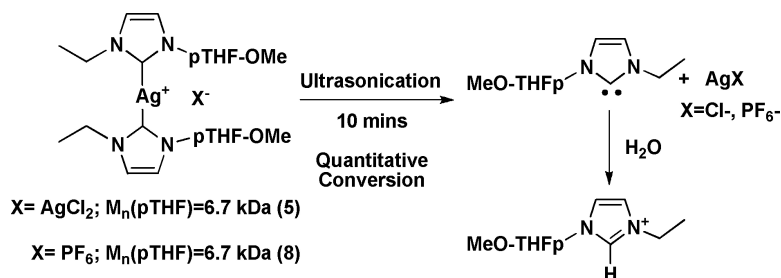


Highly Efficient Mechanochemical Scission of Silver-Carbene Coordination Polymers

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Highly Efficient Mechanochemical Scission of Silver-Carbene Coordination Polymers

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Promoting chemical reactions of molecules by mechanical activation of their bonds is a valuable enterprise, since it permits studying reactivity patterns that are fundamentally different from thermally activated reactions.¹ Recent evidence for the distinct pathways that mechanochemical and thermal reactions may take comes from experimental work on the ring opening of a polymer-functionalized benzocyclobutene,² and a theoretical study of decomposition of thiolate-metal interfaces.³

One of the most efficient ways to activate chemical bonds mechanically is by making use of ultrasound.⁴ When sonicating solutions, strong shear gradients arise around collapsing cavitation bubbles. In these gradients, polymers of sufficient length are stretched, and they eventually break midchain due to accumulation of stress.⁵ Ultrasonic chain scission of covalent polymers is site-specific for cleavage of weak peroxide⁶ and azo⁷ bonds. Scission is both completely selective and fully reversible for the weak coordinative palladium–phosphorus bond in palladium(II) coordination polymers.⁸ Furthermore, selectivity between coordinative bonds of different strengths has been observed in mixed Pd–Pt coordination polymers.⁹ Theoretical studies have predicted that mechanochemical scission of bonds in series is more selective than thermal decomposition.¹⁰

In contrast to its high selectivity, ultrasonic degradation of polymers is a relatively slow process that usually takes hours rather than minutes to complete. The rate of scission is chain-length dependent,^{4,11} and scission is characterized by a limiting molecular weight (M_{lim}),¹² below which scission does not occur. In covalent polymers, M_{lim} values are in the range of 21–120 kDa,^{13–15} depending on sonication conditions and the persistence length of the polymer.¹³

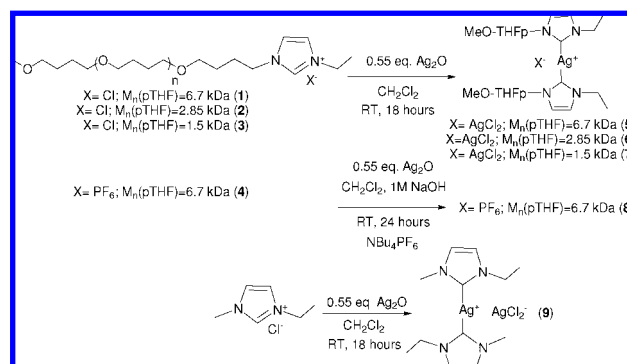
Higher rates of scission and lower limiting molecular weights would substantially simplify studying the mechanistic details of ultrasonic scission and mechanochemical reactivity. Decreasing M_{lim} would also provide a more atom efficient route to produce reactive species in a nonthermal fashion. The highly scissile polymers required for this should include a midchain bond that is relatively weak, yet inert in the absence of shear. Here, we present the remarkably efficient ultrasonic scission of silver complexes with polymeric N-heterocyclic carbene (NHC) ligands, which have molecular weights well below 10 kDa, yet are quantitatively broken in minutes to give highly reactive free carbenes.

Silver-NHC complexes with polymeric ligands (**5–8**, Scheme 1) were prepared from imidazolium terminated precursors **1–4**, which were obtained via a cationic ring opening polymerization of tetrahydrofuran initiated by methyl triflate¹⁶ and subsequent termination with N-ethyl imidazole, resulting in polymers with molecular weights of $M_n = 6.7$, 2.85, and 1.5 kDa, as analyzed by ¹H NMR. The polymers were anion exchanged to obtain chloride and PF₆. Subsequently, silver complexes **5–7** were formed by stirring the polymers with 0.55 equiv of silver oxide in dichlo-

romethane at room temperature for 18 h (Scheme 1).¹⁷ Analysis by ¹H NMR after filtration confirmed the quantitative complexation.

Silver-NHC complexes are known to exist either in a monocoordinated form, which can form a bridged dimer, or in a bis-coordinated form (Scheme 2).¹⁸ Scission of bridged complexes is not expected to result in the generation of free carbenes, because the weak Ag–Cl interaction will break preferentially. However, upon breaking a bis-coordinated complex, free carbene is produced. To favor the formation of bis-coordinated over bridged complex, a polar solvent (acetonitrile) was used for the sonication experiments, and a polymeric complex that is fixed in a bis-coordinated form (**8**) was included in the study.

Scheme 1. Synthesis of Silver(I)-Based Coordination Polymers (**5–9**)



To observe scission, recoordination of dissociated ligand to the metal must be suppressed. Sonication experiments¹⁹ were therefore performed in the presence of a small amount (0.1% v/v) of water that reacts with the carbene to give the imidazolium product, which was followed in time with ¹H NMR to determine the extent of scission (Figure 1, Table 1). Sonication of a 1.5 g/L solution of **5** in acetonitrile for 10 min resulted in 49% conversion of silver-NHC complex to polymeric imidazolium salt. We discovered that the addition of 1% (v/v) of carbon disulfide to the wet solution further enhanced the conversion rate to the level that sonication for 10 min resulted in complete (>99%) conversion, with 31% conversion after 1 min.²⁰ Several control experiments were performed with low molecular weight complex **9**. Sonication of this complex led to a modest 6% breakage after 10 min, with 32% conversion after 60 min. Without sonication, thermal conversion was 0% or 30% after 18 h at 27 °C (the internal temperature of the reaction vessel during sonication) or 60 °C, respectively.

The effect of ligand molecular weight on the rate of scission was studied further using complexes **6** and **7** ($M_n(pTHF) = 2.85$ and 1.5 kDa), which showed conversions of 57 and 34%, respectively, after sonication for 10 min. The molecular weight

dependence of the conversion rate confirms a dominant mechanical contribution to the reaction, since thermal scission of the Ag–C bonds is not expected to be molecular-weight dependent.

Table 1. Scission of Polymers 5–9 upon Sonication for 10 min

complex	MW (kDa) ^a	counterion	solvent	conversion
5	13.4	AgCl ₂ [−]	acetonitrile	>99%
6	5.7	AgCl ₂ [−]	acetonitrile	57%
7	3.0	AgCl ₂ [−]	acetonitrile	34%
9		AgCl ₂ [−]	acetonitrile	6%
5	13.4	AgCl ₂ [−]	toluene	35%
8	13.4	PF ₆ [−]	toluene	88%

^a Number average molecular weight of the combined p(THF) substituents.

When sonication was performed in the less polar solvent toluene, conversion after 10 min of sonication was markedly lower at 35%. The lower conversion probably reflects combined effects of shifting the equilibrium toward monocoordinated species, and higher strength of the coordinative Ag–C bonds in toluene, which have substantial ionic character.²¹ Fixing the complex in its dimeric form by replacing AgCl₂[−] in the toluene experiment with the weakly coordinating PF₆[−] counterion restored conversion to 88%. This indicates that the dominant reason for the lower breakage with the AgCl₂[−] counterion in toluene lies in a shift of the equilibrium to monocoordinated complexes. The lower rate of conversion in the less polar solvent also argues against ionic aggregation as the origin of the remarkable efficiency of scission.

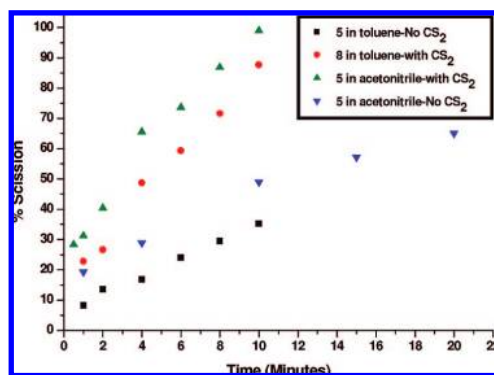
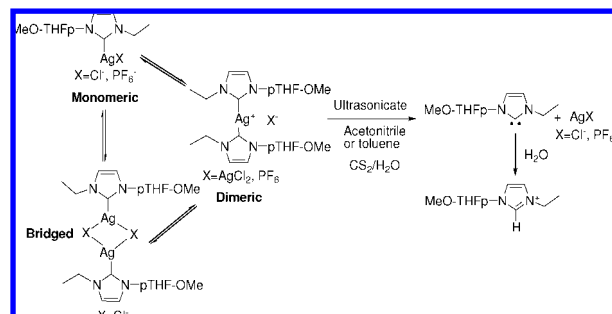


Figure 1. Time dependent ultrasonic scission of silver-NHC coordination polymers 5 and 8.

The net conversion plotted in Figure 1 is the outcome of competing hydration and recoordination reactions. The marked moderation of rate after 1 min may reflect increased recoordination with silver salts accumulating in solution, and points at an intrinsic scission rate that is higher than apparent after 10 min.

In conclusion, we have shown that polymeric Ag–NHC coordination complexes display exceptionally high scissability when sonicated. In the presence of water, scission is irreversible, and formation of the imidazolium product is easily quantified. The mechanical origin of scission is evident from the dependence on molecular weight. The mechanochemical process described here generates carbenes, which have been shown to catalyze organic transformations such as transesterification and polymerization of lactides.^{22,23} Current efforts are focused on the development of polymeric silver-NHC complexes for mechanocatalysis.

Scheme 2. Scission of Silver-NHC Coordination Polymer and Trapping of Carbene by H₂O



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Supporting Information Available: Synthetic procedures, characterization and ¹H NMR spectra for all compounds (1–9) and the ¹H NMR spectra of the sonicated solutions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (20) Whether CS₂ accelerates scission or enhances reaction of the carbene with water is presently not known. However, intermediacy of a NHC-CS₂ adduct can be excluded, since this adduct is stable under sonication conditions (see Supporting Information).
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