

Carbenes as Versatile Tools in Polymer Chemistry

Summary

This thesis explores the various uses of carbenes and the roles they can fulfill in the materials transition by attacking different problems with different carbenes. In the era of sustainable chemistry and evolving regulations, academic and industrial research is largely driven by the imperative to replace hazardous chemicals and harsh reaction conditions with eco-friendlier intermediates and processes.

In **Chapter 1**, we describe some of the areas where an impact can be made in terms of the ongoing materials transition. We highlight the ways carbenes have been used to develop novel polymers as both transition metal centered and free carbenes. Furthermore, we describe how carbenes have been used in the development of latent catalytic systems. To conclude this chapter, we describe what methods exist to characterize homogeneous catalytic systems and we lay out a vision of where new efforts towards developing characterization tools should be directed.

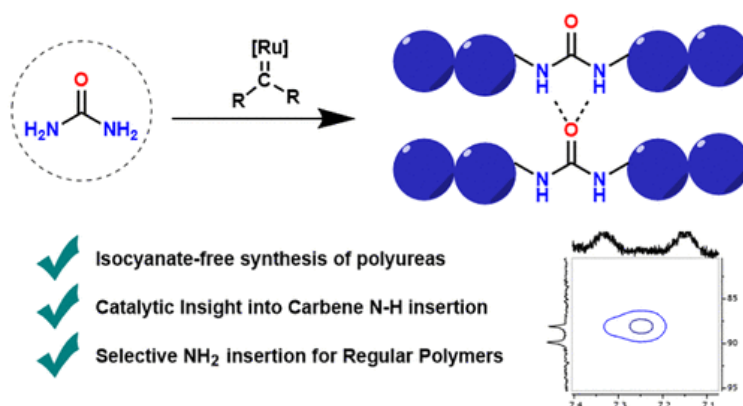


Figure 1. The reactions and insights presented in Chapter 2.

In **Chapter 2** we present a new isocyanate-free method to produce polyureas by Ru-catalyzed carbene insertion into the N–H bonds of urea itself in combination with a series of bis-diazo compounds as carbene precursors. We have demonstrated the capability to synthesize polyureas by ruthenium catalyzed N–H insertion reactions, wherein urea uniquely functions as nucleophile. With this protocol, polyurea moieties are accessible through a route completely free of isocyanate. The formed polymers were found to have material properties tunable through side chain or main chain substitution. The mechanistic investigations show nucleophilic attack of urea on the formed carbene to be rate

determining. This chapter shows the possibility of using diazo compounds in combination with transition metal catalysis to furnish novel routes towards isocyanate-free polyureas.



Figure 2. The acrylic crosslinking reaction presented in Chapter 3.

In **Chapter 3** we present a new set of diazo based crosslinkers that are shown to crosslink acrylic polymers through O–H insertion. Upon irradiation with blue light these molecules release dinitrogen and generate a carbene that reacts with the polymer binder around it. We show that depending on the molecular structure of the crosslinker the crosslinking efficiency changes, and the final material properties of the films can be tuned. Furthermore, we also show that the crosslinker structure has an influence on the side reactions that occur, with one crosslinker reacting partially with itself to form a β -lactone whereas another crosslinker does not. Thereafter, we showed that these diazo compounds can also be cured photochemically using blue light, without a difference in crosslinking efficiency when compared to thermal crosslinking. The best crosslinker was shown to provide a hardness similar to the currently utilized melamine curing systems, and films with excellent water resistance. This chapter paves the way for further usage of diazo functionalized crosslinkers in the curing of paints and coatings.

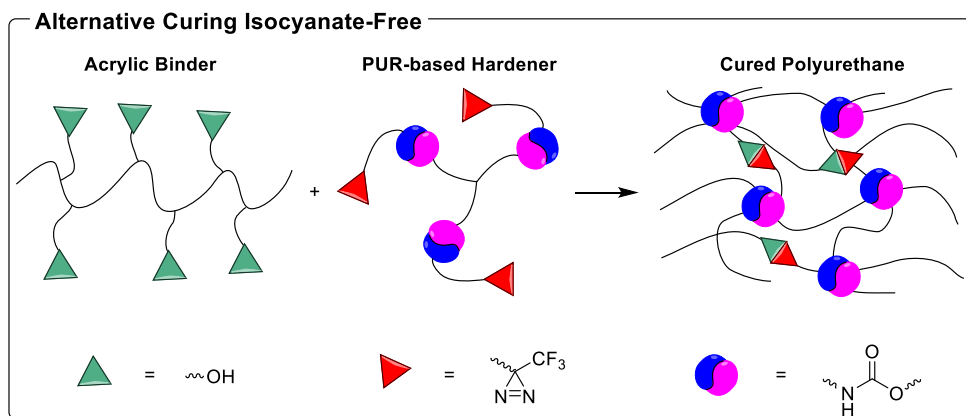


Figure 3. The PUR/diazirine-based crosslinking reaction presented in Chapter 4.

In **Chapter 4** we show the development of a polyurethane based crosslinker that can be used to formulate a one-component polyurethane coating with material properties similar to isocyanate-based polyurethane coatings. To achieve this, we synthesized a new

diazirine-based crosslinker that contains urethane groups within the structure. Upon heating, this generates free carbenes that can insert into the O-H bonds of acrylic polyols. We show that by combining this crosslinker with a polyol, an isocyanate-free one-component coating can be formulated that retains material properties of a traditional PUR coating such as a high storage modulus. A higher crosslink density of the final coating can be obtained by formulating an excess of the PUR crosslinker. This chapter shows the usage of free carbenes as an alternative curing method for isocyanate-free polyurethanes.

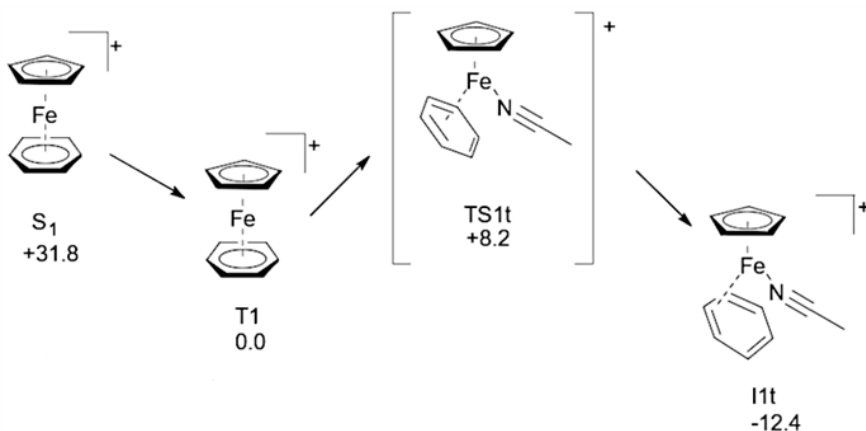


Figure 4. The crucial photodissociation step described in Chapter 5.

In **Chapter 5** we show that introducing mixed sandwich iron complexes as electron transfer mediators in aerobic oxidative esterification induces some degree of photolatility in this dual catalysis using Fe-based transition metal catalysts and N-heterocyclic carbenes. The oxidative esterification is applied in the crosslinking of formyl functionalized polystyrene as a model system, improving the material properties of the polymer. The mechanism was studied by DFT calculations, and we show that this photolatility is explained by the lower barrier for ligand dissociation from the Fe catalyst in the triplet state. Furthermore, we show through *in silico* studies that substituting the arene ring with electron deficient substituents such as nitro and trifluoromethyl aids in the photodissociation and could therefore lead to faster activating co-catalysts. This chapter opens new avenues to introduce latency by using mixed sandwich iron complexes in oxidative transformations.

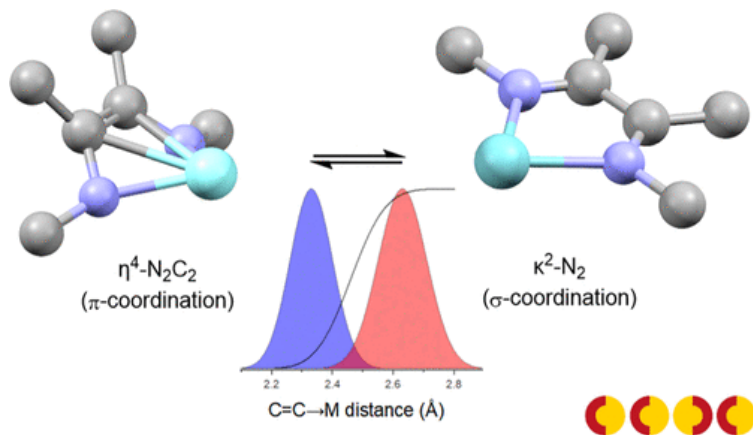


Figure 5. The coordination mode equilibrium that proved important in chapter 6.

In **Chapter 6** we present a metrical oxidation state model for 1,4-diazabutadiene (DAD) ligands, correlating the intra-ligand bond lengths with the oxidation state using information from X-ray structures. This model accounts for the difference in bond length distances between the different coordination modes of the fully reduced ligand. Several descriptors were evaluated to describe the labile coordination of the C=C backbone, and the bond centroid to metal distance was found to be more accurate and precise than the bond angles within the DAD ligand. As a small backbone interaction can already cause a large bending of the ligand, the more continuous nature of the C=C to metal distance better describes the highly flexible interaction. By analysis of a large dataset of structures available in the CSD, this coordination-fluxionality was described in a way that would not be possible by analysis of just a select few DAD complexes, contributing to a better understanding of the DAD coordination modes and their influence on the metal- or ligand-centered reactivity. The combination of FOD calculations and MOS analysis provides insight into complexes with strong π -backdonation and/or open-shell electronic structures. Furthermore, these studies underline the general value of comparing intra-ligand bond metrics of newly acquired structures to those available in large datasets of known complexes with redox-active ligands, which can help tremendously in assigning (ligand) oxidation states.

Overall, the findings acquired in the research presented in this thesis provide valuable insight into the role carbenes can fulfill in various places in materials chemistry. Thereby, the obtained knowledge opens up new avenues for the development of new catalysts, new monomers and new crosslinkers based on carbenes.