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### Carbenes as versatile tools in polymer chemistry

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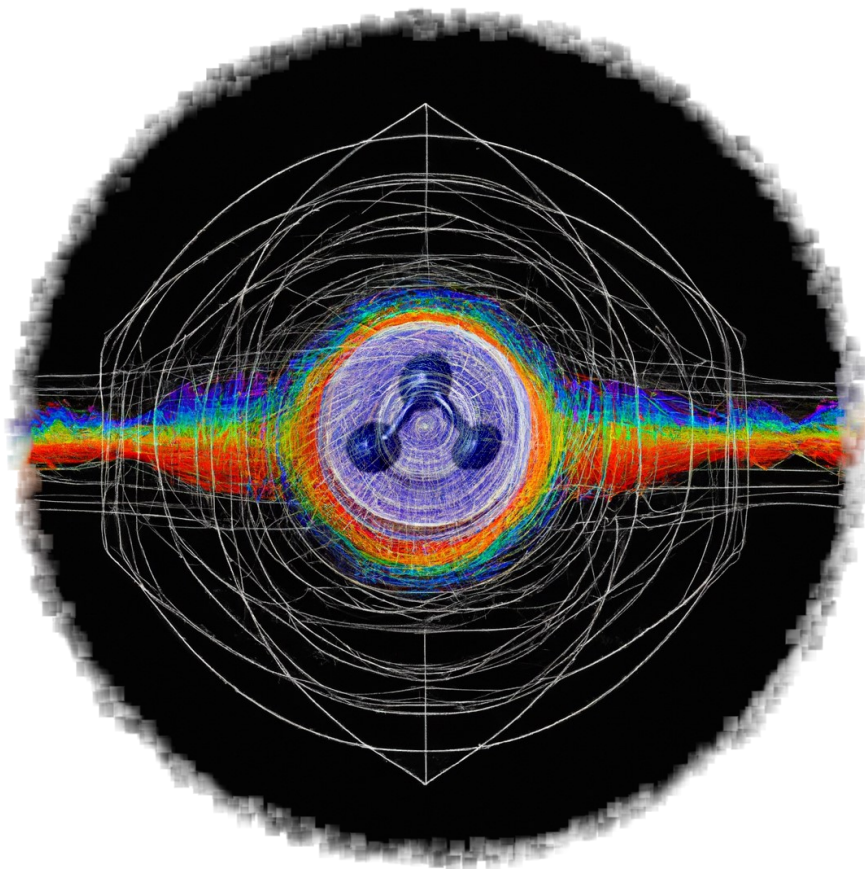
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# Chapter 1

## The Versatile Applications of Carbenes in Materials Chemistry



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## Introduction

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. Notably, the plastic market has witnessed a surge in interest for polyurethane (PU) materials. PlasticsEurope reports a global production of 21 million tons in 2021.<sup>1</sup> These specialty performance polymers possess a wide range of properties that are essential for applications in aerospace, medicine, adhesives, and textiles. Traditional PU synthesis involves chemicals that pose serious health hazards such as isocyanates and phosgene. Consequently, the exploration of alternative pathways for PU synthesis is gaining traction.<sup>2</sup>

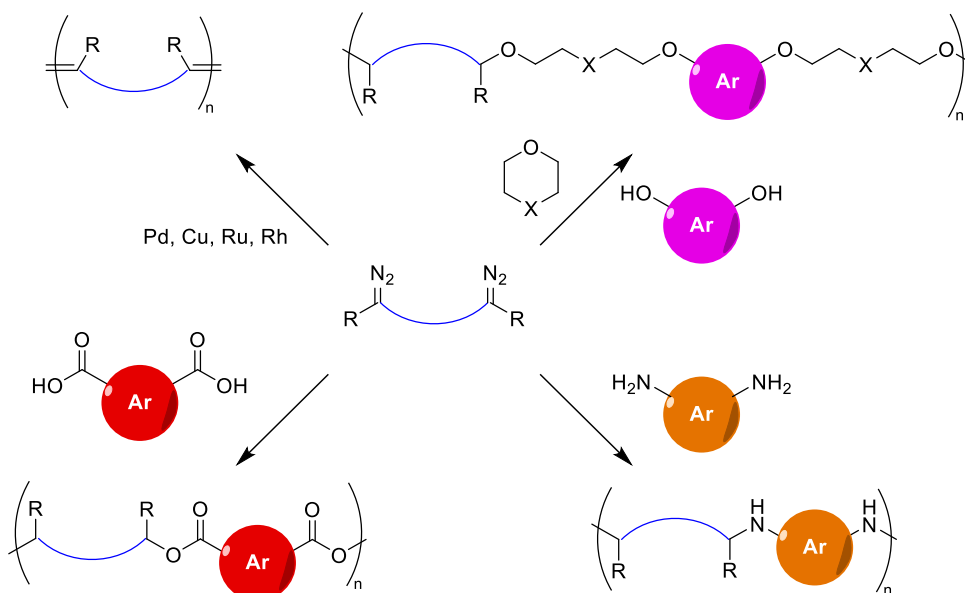
Coatings protect the materials they are applied on, for example wood or metal, thereby prolonging the lifetime of the coated object and thus reducing the need for replacement. There is a carbon footprint associated with the full coating lifecycle, however. This includes contributions from the production of raw materials, emission of VOC's, release of carbon originating from fossil source at the end of the coating lifetime, and energy requirement during the curing process. Many industrial coating processes incur a substantial energy consumption, primarily from the intrinsically high temperatures associated with thermal curing. Thermal curing processes are energy-intensive, because in such processes the coated object needs to be heated in full. High amounts of energy are therefore required in for example automotive, coil, and powder coating processes. An attractive strategy towards reducing this energy consumption would be photochemical curing, because then only the surface needs to be irradiated. Despite this advantage for the automotive industry, research towards light-induced paint curing has been underdeveloped.

Latent reaction techniques find their most advantageous application in the realm of polymer chemistry. The ability to precisely control the initiation of polymerization brings numerous benefits. It eliminates potential issues arising from incomplete mixing of highly reactive components and allows for the preparation of convenient, ready-to-use formulations. This simplifies experimental setups, enhances safety, and extends the available potlife times and processing windows. In the coatings industry this is already applied by use of latent catalysts for paint curing. Other modern technologies such as reaction injection molding, resin transfer molding, and photoresist preparation rely on the development of suitable latent catalytic systems. Precision triggering of polymerizations would broaden the chemistry available for use in all these manufacturing processes and in paint curing.

Carbenes can play a crucial role in the materials transition by serving as versatile intermediates and catalysts in various chemical reactions. Carbenes are highly reactive molecules containing a hypovalent carbon atom bearing two nonbonding electrons. They can exist in either a singlet state with spin-paired electrons or a triplet state with unpaired electrons. These unique electronic properties make carbenes valuable in the development of new materials and sustainable chemical processes. In the following sections we describe some key aspects wherein carbenes could play a major role in the materials transition.

## 1 Carbenes as a Building Block in Polymerization

Carbenes have been employed in polymer chemistry for the synthesis of advanced materials with tailored properties. They can participate in polymerization reactions, leading to the formation of new polymers or functionalization of existing polymers. Carbenes enable the synthesis of well-defined macromolecules, including block copolymers,<sup>3</sup> graft copolymers,<sup>4</sup> and other complex architectures, which can exhibit enhanced mechanical, electrical, or optical properties.

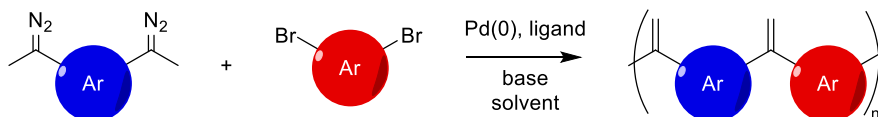


**Figure 1.** Various polycondensation reactions using bisdiazo compounds.

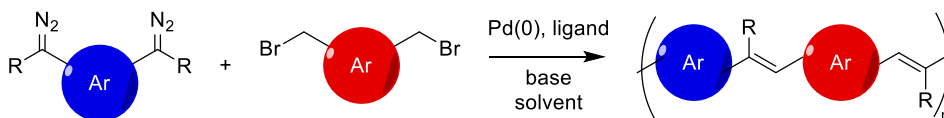
Using carbenes as monomer for polymerization has mainly been focused on C1 polymerization, wherein controlled decomposition of diazo compounds results in C–C bond formation.<sup>5</sup> Generally catalyzed by strong Lewis acids, or transition metals such as rhodium or palladium, this results in polymers bearing polar substituents on every main-chain carbon atom, which are difficult to synthesize by traditional vinyl addition polymerizations.<sup>3</sup> Carbenes have also been used as C1 building block in copolymerization to form polyynes

with a copper catalyst.<sup>6</sup> While using bisdiazo compounds as monomers has been known since 1961, all these reports focus on using carbene dimerization to form a C=C double bond (Figure 1).<sup>7-12</sup> The first report of a polymerization reaction wherein a bisdiazo compound is copolymerized with a polar X-H bond was the rhodium-catalyzed synthesis of polyethers in 2010.<sup>13</sup> In this work, the group of Inoue copolymerized a bisdiazo with an aromatic diol to form ether linkages through O-H insertion which unexpectedly resulted in incorporation of the solvent (tetrahydrofuran (THF), tetrahydropyran (THP) or 1,4-dioxane) into the main chain. Importantly, even though the polymers were acquired in low yields (up to 45%), this study showed that bisdiazo compounds can be used in reactions other than dimerization opening the possibility for using the versatile reactivity of carbenes for polymerization. Indeed, in a subsequent study the same group reported a similar O-H insertion reaction with bisdiazos and diacids to form polyesters.<sup>14</sup> Using a rhodium catalyst, polyesters with glass transition temperatures ( $T_g$ ) ranging from  $-50$  °C to  $24$  °C were synthesized. When using THF as a solvent, ether linkages are selectively incorporated in an ABC copolymer fashion whereas THP as a solvent competes for insertion, leading to alternating ether incorporation. This was later expanded to bis(1,3-diketones) which provides polyethers that can be cleaved under mildly acidic conditions.<sup>15</sup> These reports are rare examples of three-component polycondensation which was enabled by the multipronged reactivity of metal carbenes. It was later also shown that by using different bisdiazo monomers, the O-H insertion with diacids can be performed selectively without ether incorporation.<sup>16</sup> The applicability of bisdiazo compounds in polycondensation was expanded to the ruthenium catalyzed synthesis of polyamines.<sup>17</sup> When using dianilines as coupling partner, the formed ruthenium carbenes undergo N-H insertion to provide polyamines. The resulting  $T_g$  of the polyamines can be controlled in the range of  $88$  to  $173$  °C by tuning the dianiline linker.

### Pd-catalyzed synthesis of cross-conjugated polymers



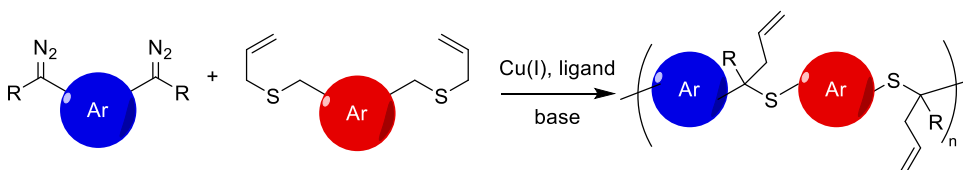
### Pd-catalyzed synthesis of poly(arylenevinylene)s



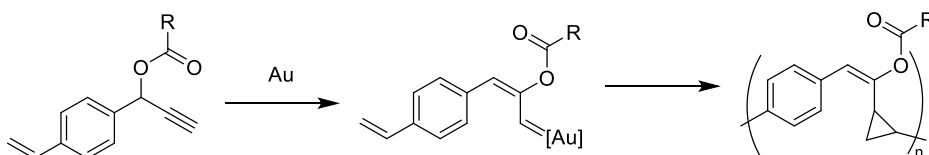
**Figure 2.** Palladium catalyzed carbene cross-coupling reactions to form polyenes.

Recently, carbene cross-coupling reactions have also been applied in polymerization, which uses bisdiazo compounds with arylbromides to form C=C double bonds in the presence of a low-valent palladium catalyst and base (Figure 2).<sup>18</sup> Concomitantly, the group of Wang and the group of Chen reported on using this methodology to form cross-conjugated polymers using a similar palladium-catalyzed procedure.<sup>19,20</sup> These polymers show unique optical properties that can be tuned by varying the monomer (e.g. fluorene or thiophene) or even the aggregation state of the polymer when using tetraphenylethylene units in the backbone. Furthermore, a ferrocene derivative of these polymers was later shown to be also an effective catalyst for the decomposition of ammonium perchlorate.<sup>21</sup> This methodology was extended towards poly(arylene vinylene)s, which are an important class of polymers that have been widely explored in optoelectronic devices.<sup>22</sup>

### Cu-catalyzed Doyle-Kirmse Polymerization



### Au-catalyzed polycyclopropanation



**Figure 3.** Copper- and gold-catalyzed polymerizations using metal carbenes as intermediate.

Another report that uses bisdiazido compounds comes from the group of Wang wherein allylsulfanes were used to generate sulfur containing polymers through a Doyle-Kirmse reaction (Figure 3).<sup>23</sup> This provided polymers with sulfur in the main chain which have good thermal stability ( $T_d$  265–309 °C). Interestingly, the authors also showed the possibility of using UV-light to degrade the polymers into low molecular components. Under UV irradiation (365 nm, 30 W) a sample of the polymer was degraded from a molecular weight ( $M_n$ ) of 26.3 kD to oligomers of 2.5 kD within 24 hours. The thermal stability combined with the light sensitivity of these materials provides an opportunity for selective degradation when combined into polymer mixtures.

In 2014 the group of Stoffelbach reported on the use of cationic gold(I) complexes to form polycyclopropanes.<sup>24</sup> Remarkably, carbenes were first postulated in the cyclopropanation of alkenes using ethyl diazoacetate by Buchner in 1903,<sup>25</sup> which means that it took more than 100 years to develop the first cyclopropanation-based polymerization! In this procedure, a carbene is generated through 1,2-migration of a pendant ester group to form a terminal gold carbene (Figure 3). Using this procedure, polymers with molecular weights ( $M_w$ ) up to 123 kD were generated in moderate yields. Furthermore, it was also shown that the polymers could be postfunctionalized by saponification of the ester to generate a unique  $\alpha$ -cyclopropylketone unit.

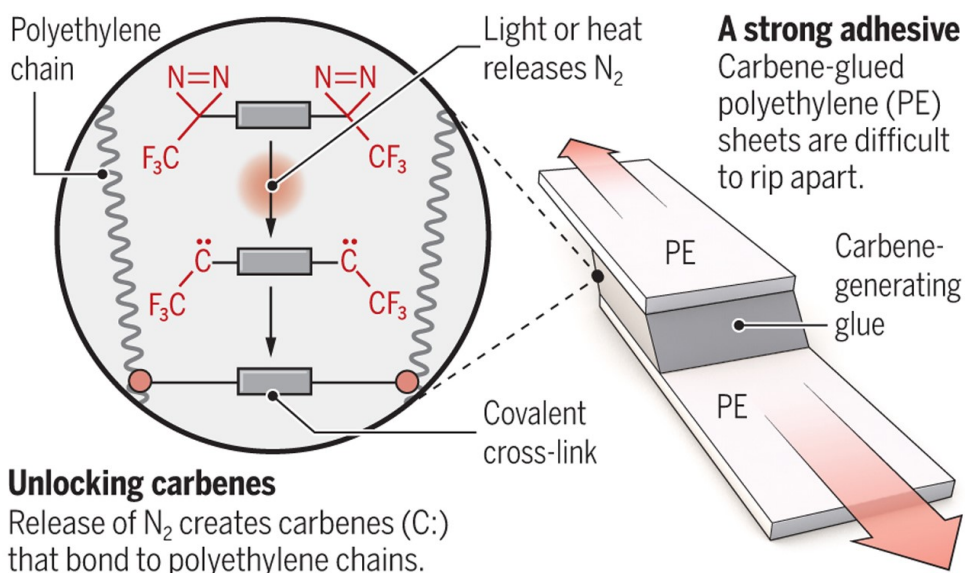
Many of the carbene based polymers discussed above have limited applications, however their unique macromolecular skeletons fundamentally show the possibility of using carbenes to access structures that are otherwise not accessible. Currently, the main factor limiting the applicability of carbene based monomer seems to be the requirement to generate them from high cost and dangerous starting materials such as diazoalkanes and geminal dihalides.<sup>26</sup> Recently, there has been an increasing amount of effort to access carbenes from more readily available starting materials such as aldehydes.<sup>27</sup> Another unique method for carbene generation that was recently explored is the usage of engineered enzymes to produce naturally occurring diazo compounds.<sup>28</sup> These methods could lower the cost associated with generating metal carbene intermediates, and thereby might push the above discussed procedures into commercial viability.

## 2 Free Carbenes in Polymer Chemistry

The development of universal methods for surface modification and cross-linking of polymeric materials is highly desirable. Mechanical properties of natural and synthetic materials strongly rely on the ability of the polymeric chains to form a three-dimensional (3D) network, for example, through cross-linking.<sup>29,30</sup> In natural macromolecules such as chitin and synthetic materials such as Kevlar, hydrogen-bond formation between amide groups form noncovalent cross-links. Many oil-based polymer coatings used in paints and

to protect wooden structures derive their 3D-structure and strength from covalent crosslinks formed in radical-based processes. Other examples of covalent cross-linking, such as vulcanization of rubber and the drying of glues, rely on reactive functional groups already present in the polymer.

Carbenes can be used to modify the surface or bulk properties of materials. Through carbene insertion reactions, functional groups or moieties can be introduced onto surfaces or incorporated within the bulk structure of materials.<sup>31,32,33,34</sup> This functionalization allows for improved adhesion, controlled wettability, enhanced biocompatibility, or the introduction of specific chemical functionalities in materials for targeted applications.<sup>35</sup>



**Figure 4.** Working mechanism behind bis-diazirine adhesives.

Free (singlet) carbenes and transition-metal carbene complexes can undergo direct C–H insertion instead of HAA to form covalent carbon-carbon bonds even from unactivated C–H bonds. Carbenes are used for polymer post-functionalization, as polymerization catalysts and as polymer backbone.<sup>36</sup> Tri- and tetravalent photoactivable azides and diazirines can cross-link polyethylene glycol, but efficient generic cross-linkers for the strengthening of unfunctionalized polyolefins have not been developed. In 2019, Lepage *et al.* reported a carbene cross-linker containing two diazirine motifs.<sup>37</sup> Free carbenes can be generated upon photochemically or thermally induced  $N_2$  loss. A drawback of molecules containing  $N_2$  expelling motifs (such as diazirines) is their explosion risk, and the authors abandoned known *bis*-diazirine compounds because of their volatile and explosive nature. They rationally designed a bis-diazirine cross-linker that finely balances risk and reactivity and



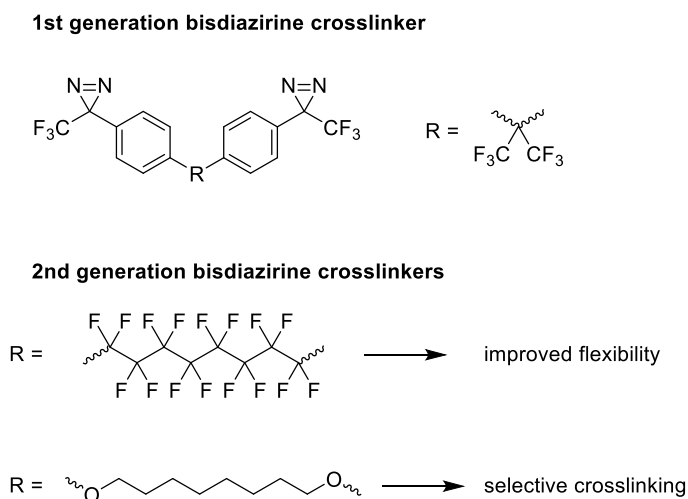
generates two free carbenes that insert into C–H bonds of the polymer. The tethered structure forms cross-links between different polymer chains, even those of PE and PP (Figure 4). The molecular weight of PP increased continuously with the amount of cross-linker added, corroborating successful cross-linking of the substrate. The bis-diazirine also cross-linked several other polymers, such as polyvinylalcohol (PVA). For PVA, whether carbene insertion occurred through C–H or O–H bonds was not investigated, but the latter seems most likely.<sup>38</sup> This cross-linking methodology could find applications in the upgrading of biopolymers in which O–H bonds are ubiquitous.

The authors also explored application of the cross-linker as an adhesive for high-density PE (HDPE). Adhesion to this low surface-energy material is difficult—it failed for a control sample with a commercial adhesive (SuperGlue). However, the bis-diazirine cross-linker showed high performance in adhesion tests, and analysis of ripped samples revealed a cohesive failure mechanism indicative of cross-linking to the HDPE surface. The adhesive properties were further improved upon in a later study, wherein second generation crosslinkers were synthesized with a longer perfluoro chain in between the reactive diazirine moieties (Figure 5).<sup>39</sup> As the first generation crosslinker can be considered to have a rigid structure, plastic deformation within the crosslinked polymer strands becomes quite difficult. When it is then used as an adhesive, this would lead to a lower mechanical toughness of the adhesive joint. Therefore, the second generation crosslinker included a flexible perfluoro chain which led to an improved compliance within the adhered samples.

The crosslinker was also an effective synthetic fabric strengthener. This was later expanded upon by applying the bis-diazirine molecule in topical crosslinking of ultra-high molecular weight polyethylene (UHMWPE) fabric.<sup>40</sup> This led to an increase in tear and perforation strength, even with small amounts of bis-diazirine (1 wt%). The improved performance was shown to be ascribable to intra- and interyarn cross-links in the fabric which leads to a strengthening in the bias direction. These structural changes cause the fabric to be able to absorb more energy which is beneficial to the ballistic performance of the fabric. This shows that using free carbenes to crosslink fabrics can be an interesting way to improve body armor.

Given that the group of Wulff observed relatively controlled reactivity toward cyclohexane, it can be assumed that singlet carbenes are formed that insert in a concerted manner into C–H bonds. However, formation of triplet carbenes that react through radical processes cannot be fully excluded. Radical-type pathways could potentially damage the polymer integrity, so investigation of the electronic structure of the formed carbenes is needed. Therefore, in 2021 an extensive structure–function study of aryl diazirines was published.<sup>41</sup> In this work, experimental techniques in the form of differential scanning calorimetry (DSC)

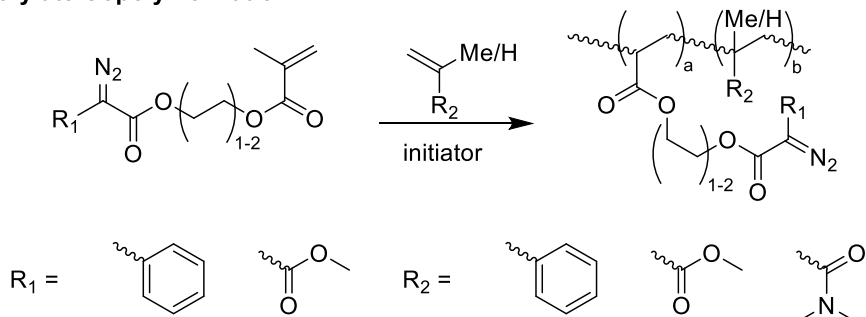
were combined with computational methods to study the properties and reactivity of diazirines and the thereafter resulting free carbenes. It was shown that a strong relationship exists between activation temperature for thermal decomposition and the  $\sigma^+$  Hammett parameter of the aryl diazirine, indicating a carbocation character in the transition state. Furthermore, it was shown that for  $\alpha$ -trifluoromethyl aryl carbenes, electron donating groups on the arene ring stabilize the singlet spin state. This is in line with previous work which indicates that for a methyl substituent, the singlet and triplet states of  $\alpha$ -trifluoromethyl aryl carbenes are magnetically bistable.<sup>42</sup> Whilst for all aryl substituents it was shown that the triplet barrier for C–H insertion always lies lower in energy, C–H insertion on the singlet surface should be kinetically viable as the barrier still remains lower than the barrier for carbene production. The knowledge from this article was applied in a later study where it was shown that an electronically optimized bis-diazirine outperformed the earlier generation crosslinkers in the crosslinking of polyethylene by >10-fold (Figure 5).<sup>43</sup>



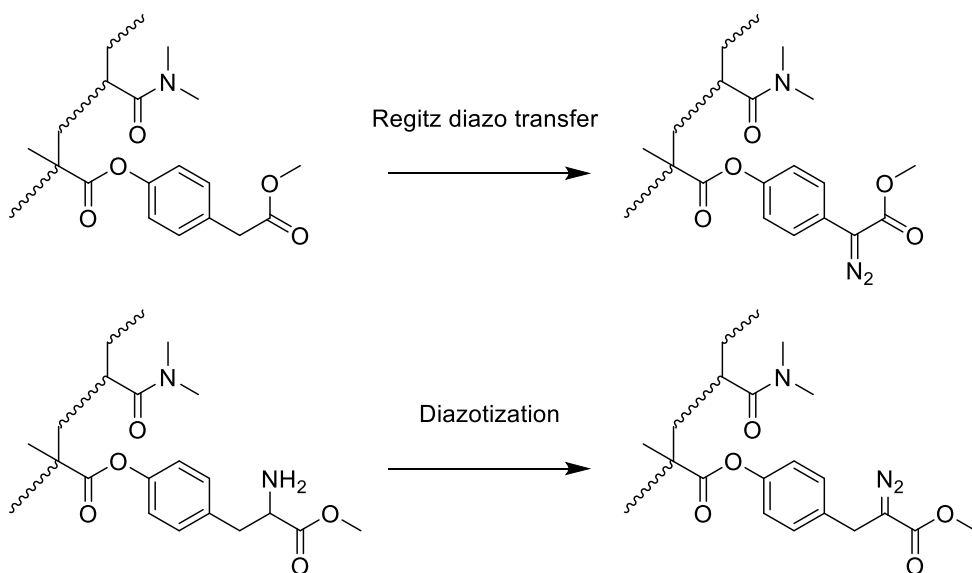
**Figure 5.** Structures of first and second generation bisdiazirine crosslinkers.

The bis-diazirine crosslinkers developed by the group of Wulff not only have potential applications as an adhesive and fabric strengthener, but similar reagents could be used in paints and coatings. Prospective biobased binders such as cellulose and lignin lack readily cross-linkable groups such as isocyanates, ketones, or alkenes. Indeed, preliminary studies show the efficacy of using diazirines to crosslink polysaccharides.<sup>44</sup> Thus, the cross-linking methodology presented here may help turn biomass-based macromolecules into functional materials.

### Acrylate Copolymerization



### Postfunctionalization



**Figure 6.** Methods to introduce diazo groups within polymers.

Diazo compounds, the linear isomer of diazirines, have thus far found less applications within materials chemistry, despite their ubiquitous use in organic photochemistry.<sup>45–48</sup> Malonic acid derived diazo compounds were successfully incorporated into styryl and acryl polymers by free radical polymerization (Figure 6).<sup>49</sup> Because this free radical polymerization can be initiated by AIBN at 60 °C, these diazo groups can be freely incorporated into these types of hydrophobic polymers as the peak decomposition temperature of the diazo moiety is around 170 °C. These polymers were shown to undergo crosslinking upon irradiation with UV-light or heating and have an enhanced surface attachment to hydrophobic surfaces when compared to acrylates without diazo functionalities. Furthermore, it was shown that biomolecules such as streptavidin can be incorporated covalently into these polymer matrices, indicating that the described system

could potentially be used for immunoassay experiments. These strongly hydrophobic polymers were also shown to be able to extend the lifetime of superhydrophobic surfaces by covalently linking impurities on the surface.<sup>50</sup> This type of chemistry was further expanded to poly(oxanorbornenes), from which hydrogel coatings were synthesized.<sup>51</sup> The diazo system was compared to a benzophenone-based system, which is another well-known UV-crosslinker, and was shown to lead to less chain scission events thereby crosslinking more selectively. Furthermore, the coatings were shown to enhance the microbial activity of the surface, killing 100% of applied *E. coli* bacteria within two hours. This opens the possibility to use diazo crosslinkers in coatings for biomedical applications. Another approach to make polymers containing diazo groups would be to postfunctionalize acrylate polymers with diazo groups, through either Regitz diazo transfer or through diazotization (Figure 6). For this approach it was shown that a push/pull type substitution with an arene on one side and an ester on the other is beneficial for the UV-induced activation kinetics of the diazo.<sup>52</sup> Aryl/ester substituted diazo compounds were also similarly applied in the covalent binding of protein-repellent thin films to the inner surface of (rubber) tubes.<sup>53</sup>

The usage of multifunctional diazo compounds as low molecular weight crosslinkers was reported in 2022 by the group of Pan.<sup>54</sup> In this work, three different generations of crosslinkers were synthesized using a synthetically facile procedure. Upon heating, the diazo groups decomposed to generate active carbenes, which establish covalent bonds among polymer chains through C–H activation and insertion. The trifunctional crosslinker was found to be most efficient, albeit possibly explosive. Similar to the previous work on diazirine crosslinkers, this diazo based compound was also shown to improve the adhesion of UHMWPE and was furthermore applied in polymer co-crosslinking, as well as surface hydrophobicity modification.

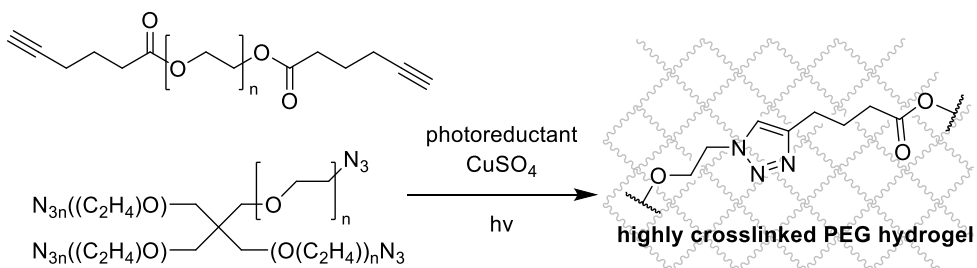
At this point, a distinction must be made between tailor-made polymers with crosslinking groups incorporated into the polymer chain and low molecular weight crosslinkers. Copolymerizing crosslinking groups into a polymer, or functionalizing existing polymers with crosslinking groups changes the material properties of the resulting composite, and therefore requires investigation on the degree of functionality on properties such as viscosity, glass transition temperature and film forming properties. When using already existing polymers and adding low molecular weight crosslinkers only the pre-existing polymer needs to be characterized and the effects of adding increasing amounts of crosslinker can be studied systematically without repeating the polymerization step. Therefore, for ease of application, low molecular weight crosslinkers are usually preferred. However, considerations such as solubility of the crosslinker within the polymer, which can

give rise to phase separation arising from excess crosslinker are problems that require special attention when using low molecular weight crosslinkers.<sup>55</sup>

### 3 Latency in Polymer Chemistry

The development of latent catalysts can offer several advantages and potential applications in various fields. Latent catalysts allow for precise control over the timing and location of catalyst activation. This feature is particularly valuable in scenarios where the catalytic reaction needs to be initiated at a specific time or location. By activating the catalyst when and where it is needed, efficiency can be improved, and unwanted side reactions minimized. Spatial and temporal control over chemistry is an aspect that is also found in fields other than material chemistry. For example, in nature, vitamin B<sub>12</sub> can act as a photolabile catalyst that regulates the production of carotenoids to act against oxidative stress, thereby providing temporal control.<sup>56</sup> In photodynamic therapy, photosensitizers can be locally activated to generate reactive oxygen species thereby providing spatial control over phototoxicity.<sup>57</sup>

Latent catalysts are inactive under normal conditions and can be stored and transported without significant degradation or loss of activity. They can be activated when needed, providing enhanced stability compared to traditional catalysts that may degrade over time or require specific storage conditions. For organic catalysts such as bases and acids, photogeneration is highly developed and thoroughly reviewed.<sup>58</sup> For transition metal catalysts there are two primary ways, stimuli-induced reduction or oxidation, for example by a photoreductant, or stimuli-induced ligand dissociation.

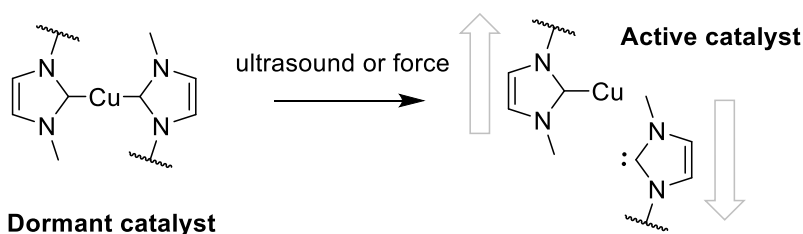


**Figure 7.** Photolabile copper click for the formation of triazole based hydrogels

One example of latent catalysis through stimuli-induced reduction comes from the group of Bowman and coworkers. In 2011, they reported on a photoinitiated catalyst for the copper-catalyzed alkyne-azide cycloaddition reaction (CuAAC).<sup>59</sup> While the CuAAC reaction has seen widespread application due to its simplicity and orthogonality with other chemical reactions, the spatial and temporal control of CuAAC is not easily achieved. The active Cu(I) catalyst is normally added as a Cu(I) salt, or generated *in situ* by addition of a reductant to a Cu(II) species. By using a latent reductant in combination with a Cu(II) source, temporal

control over the reaction can be achieved. By using cleavage-type photoinitiators Irgacure 819 and Irgacure 2959, temporal control over the CuAAC reaction was acquired in both aqueous and non-aqueous systems. Using standard photolithographic techniques, the latent CuAAC system was applied in hydrogel patterning (Figure 7). The spatial resolution achieved by this approach was expected to be in the 100  $\mu\text{m}$  range, based on the diffusivity of Cu(I), however patterning experiments readily produced 25  $\mu\text{m}$  features within 50 seconds of irradiation. This seminal work has led to the use of the photolabile CuAAC reaction for creation of functional materials such as shape memory materials and dental restoratives.<sup>60–64</sup>

Photoreduction to activate a latent catalyst can also be induced by a photoredox catalyst. This was used to achieve spatiotemporal latency in a poly[2+2]cycloaddition using a Co(II) precatalyst which can be reduced by a polypyridyl iridium photocatalyst to the active low-valent cobalt species. This provides control over the molecular weight and monomer conversion with visible light. Interestingly, the addition of a small-molecule initiator allows for a mechanism switch from step-growth to chain-growth. This was attributed to a change in the oxidation states operative in the cobalt catalytic cycle from Co(I)/Co(III) to Co(0)/Co(II). The chain-growth mechanism allowed for the synthesis of block copolymers.<sup>65</sup>

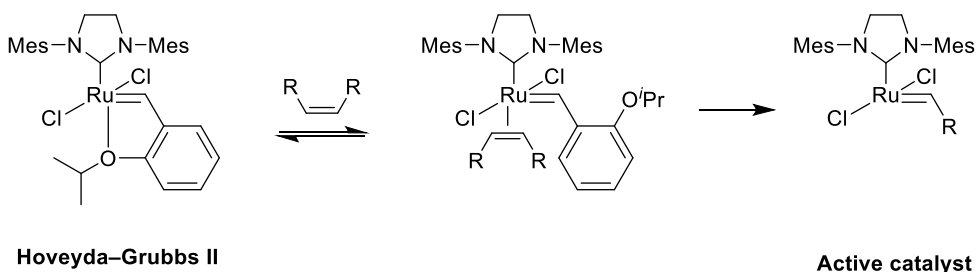


**Figure 8.** Mechanochemically responsive copper click reaction.

Another interesting method towards latency is the use of mechanochemistry. In 2015, Binder and coworkers reported on a pressure-sensitive Cu(I) click catalyst that can be activated through ultrasound or compression of a polymer.<sup>66</sup> Using either a telechelic polyisobutene or polystyrene binder functionalized with a N-heterocyclic carbene end group, Cu(I) biscarbene complexes which are dormant towards CuAAC were synthesized. In solution, dissociation of one of the NHC ligands can be induced by ultrasound which is generally the method to apply mechanical force in solution. In the solid phase, for efficient transfer of mechanical force the copper catalyst was embedded in a highly crystalline polytetrahydrofuran matrix containing starting materials for a fluorogenic click reaction. Compression with a hydraulic press indicated that the mechanochemically latent catalyst becomes active for CuAAC upon application of this stimulus. Spatial control is therefore

achieved by a mechanochemical trigger, which could have interesting applications such as in the self-healing of stress-reporting materials.

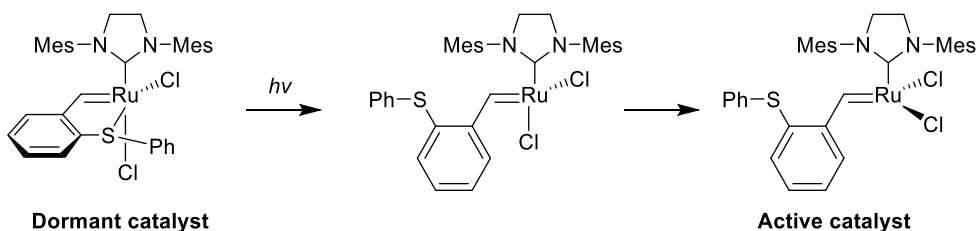
Ruthenium based olefin metathesis catalysts are by far the most well-developed class of latent catalysts. These catalysts find use in materials chemistry through ring-opening metathesis polymerization (ROMP) of strained alkenes such as norbornene. Interestingly, whilst the development of Grubbs catalyst from the 1<sup>st</sup> through the 3<sup>rd</sup> generation focused on developing fast-initiating systems, research into latent ROMP catalysts has focused on slowing down initiation in absence of an external stimulus.<sup>67</sup> Olefin metathesis catalysts have been studied in depth in the context of latency, as efficient ROMP reactions require mixing of the monomer and catalyst, molding and shaping to occur prior to polymerization.<sup>68</sup> These catalysts all contain a carbene ligand that reacts away in the first turnover of catalysis to generate the active species containing a carbene ligand that originates from the substrate (Figure 9). To do so, a *cis* vacant site is required for the substrate to bind. It was first recognized in 2000 that if the ruthenium center is coordinatively saturated, high temperatures can be required to induce dissociation of a ligand furnishing a latent catalyst.<sup>69</sup> If the carbene ligand is functionalized with a pendant ligand that chelates to the ruthenium center, latency can be induced in Grubbs type catalysts as well.<sup>70</sup> This remains the working principle behind all latent ruthenium catalysts thereafter.



**Figure 9.** Activation mechanism of Hoveyda-Grubbs type catalysts.

Simply exchanging the oxygen atom in the second generation Hoveyda-Grubbs catalyst for a sulfur atom produces a thermoswitchable catalyst due to the stronger ligation of sulfur to the ruthenium center.<sup>71</sup> Interestingly, the inclusion of a sulfur pendant group changed the most stable configuration of the chloro substituents to change to *cis* rather than *trans*.<sup>72</sup> This caused further stabilization of the complex, as the pendant S-donor is no longer *trans* to the NHC ligand.<sup>73</sup> This catalyst was thereafter applied in ROMP, where it remained dormant until a temperature of 100 °C.<sup>74</sup> Interestingly, the polydispersity indices (PDI) obtained by using this catalyst are considerably lower than expected from a slow-initiating catalyst. This can be explained by a turnover limited polymerization mechanism, wherein

the degree of polymerization is controlled by the turnover number of the active species rather than the more common ratio of monomer to initiator.



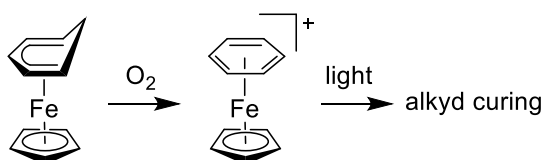
**Figure 10.** Mechanism of activation of photolabile olefin metathesis catalysts.

Introduction of a chromophore on the sulfur arm, by exchanging the alkyl aryl thioether for a diaryl thioether, increases the photosensitivity of the complex thereby creating a photolabile catalyst system.<sup>75</sup> Light induces the isomerization of the ligands from *cis* to *trans*, thereby activating the catalyst. Interestingly, this causes the system to be switchable, as heating the system isomerizes the active *trans* precatalyst back to the dormant *cis* form. Although this system operates well for substrates such as cyclooctene, highly activated ROMP monomers such as norbornene and dicyclopentadiene are also polymerized in the dark. Moreover, the complexes are not active enough for unactivated substrates, even at elevated temperatures. The difference between activity in dormant and activated states of a latent catalyst is what is described as the latency gap. The ideal “magic bullet” latent catalyst would be one with negligible activity towards even the most activated substrates in dormant form and high activity towards even the most unactivated substrates after stimulation. By introducing a trifluoromethyl group on the sulfur atom the catalyst becomes way more active whilst remaining dormant at room temperature.<sup>76</sup> The applications for these latent ruthenium catalysts keep growing. The photoswitching was shown to be able to guide reaction outcomes by selecting different wavelengths of light.<sup>77</sup> Commercially available catalysts were also shown to be photolabile under the right conditions.<sup>78</sup> Latent phosphite-ligated systems activate with visible light and have been shown to allow for 3D-printing of polydicyclopentadiene, which has been commercialized for additive manufacturing.<sup>79</sup> Using thermally latent ROMP catalyst in combination with plasmonic gold nanoparticles with a photothermal response allows for spatial control over ROMP using infrared light.<sup>80</sup>

Similar to the example of mechanochemical CuAAC discussed above, mechanochemically latent ROMP can also be achieved through the use of telechelic polymers. Synthesizing a ruthenium complex with two NHC ligands functionalized with a polytetrahydrofuran side chain provides a mechanochemically responsive complex.<sup>81</sup> Upon sonication one of the NHC ligands dissociates, providing an active precatalyst that can be used either in ring-



closing metathesis or ROMP. Attaching a polymer chain with a higher molecular weight leads to a more mechanoresponsive behavior, which is a clear support of a mechanical rather than a thermal mechanism. Spatial control is therefore achieved by a mechanochemical trigger, which could have interesting applications. For example, the latent ROMP catalyst could be embedded into a crosslinked material to achieve autonomous healing based on polymerization.



**Figure 11.** Two-step latency in neutral iron cyclopentadienyl complexes.

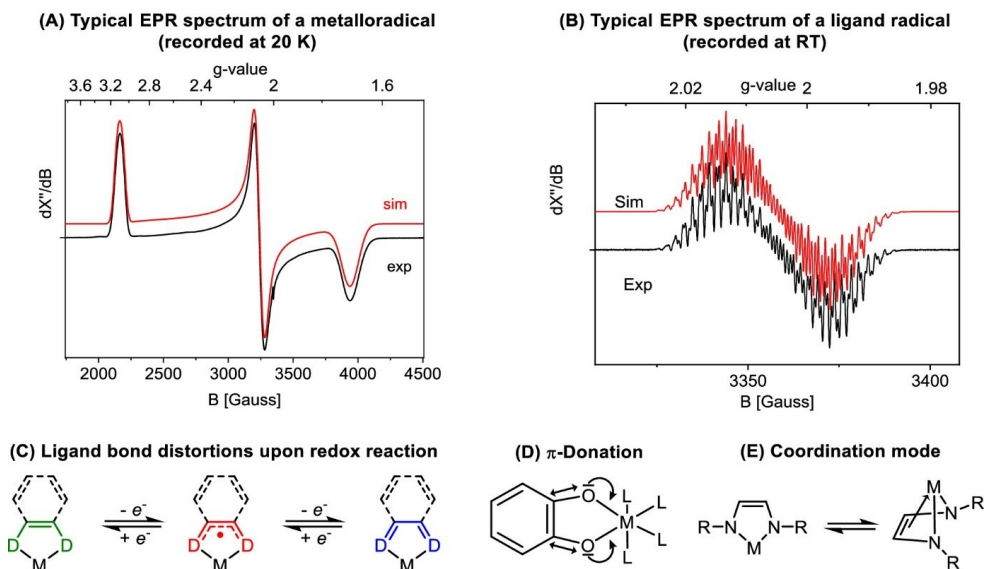
In oxidative curing of alkyd paints, latent transition metal catalysts are used to accelerate the drying process. Latency is of particular interest to the coatings industry as premature curing during storage of paint causes formation of a thick polymeric skin on the surface in old paint cans. Manganese complexes can be combined with a volatile ligand, 2-butanone oxime, that reversibly binds to the catalyst causing it to remain dormant whilst in a closed system.<sup>82</sup> For cobalt complexes, additives play a more complicated role in alkyd drying, the same 2-butanone oxime was shown to have a dual role as anti-oxidant.<sup>83,84</sup> Upon application of a coating containing these latent catalysts, the oxime ligand dissociates and evaporates thereby activating the catalyst. A drive to replace the cobalt oxime system with more benign one has spurred research into latent iron catalysts for alkyd curing.<sup>85</sup> Various iron arene organometallics act as cationic and free radical photoinitiators of epoxide and acrylate polymerization. In the catalytic cycles of polymerization, Fe(III) arenes are formed and involved.<sup>86</sup> Therefore, in 2022 the group of De Bruin applied these systems to the curing of alkyd paints.<sup>87</sup> When using [(Cp)Fe(arene)]<sup>+</sup> complexes, irradiation with ambient light induces dissociation of the arene ligand causing activation of the iron catalyst towards oxidative alkyd curing. Furthermore, reduction of the [(Cp)Fe(arene)]<sup>+</sup> complex to a neutral cyclohexadienyl derivative causes the complex to be *double latent*, requiring both oxidation and ligand dissociation prior to activation (Figure 11). It would be interesting to see if these types of arene complexes could also be used to induce latency in other oxidation reactions.

## 4 New tools to be developed in homogeneous catalysis

The development and mechanistic understanding of homogeneous catalysts is of pivotal importance for the application of homogeneous catalysts in materials chemistry. Typically, the reactivity of a transition metal-based homogeneous catalyst is primarily determined by the redox reactions taking place at the metal center, which is indirectly influenced by the redox-innocent (redox-inactive) spectator ligands that control the steric and electronic properties of the metal.<sup>88</sup> However, while still less common, many catalytic reactions have also been disclosed over the past years in which the ligand plays a much more active role, which includes both cooperative<sup>89,90</sup> and redox-active ligands.<sup>91,92,93</sup> In particular, studies regarding the influence of reactive redox-active ligands on the reactivity of transition metals have gained momentum, and have led to significant advances in challenging homogeneously catalyzed reactions, such as CO<sub>2</sub> reduction, water oxidation and methanol dehydrogenation for H<sub>2</sub> production.<sup>94–99</sup>

The characterization of complexes bearing redox-active ligands, and measuring changes in the oxidation state of the ligand upon a (redox) reaction, is an endeavor that typically requires combined information from various techniques. Closed-shell complexes can be investigated routinely by nuclear magnetic resonance (NMR),<sup>100</sup> wherein especially the degree of ligand (de)aromatization is easily recognized in <sup>13</sup>C- and <sup>1</sup>H-NMR, and can be used as an identifier of the ligand oxidation state. Unpaired electron density can be probed with electron paramagnetic resonance (EPR) techniques,<sup>101,102,103</sup> and further information about the oxidation state and coordination geometry of the metal center can be obtained by X-ray absorption spectroscopy (XAS).<sup>104,105</sup> Noteworthy, the latter can also be applied to donor atoms in the ligand, although this is often accompanied with poor data quality. UV-Vis/NIR spectroscopy can be used to probe metal-to-ligand (or ligand-to-metal) charge-transfer and intra-ligand excitation processes, which are both sensitive to perturbation of the ligand bond lengths (IR) and  $\pi$ -conjugation (UV-vis) by a redox stimulus.<sup>106</sup>

Especially when coupled to electrochemical techniques such as cyclic voltammetry (CV) or differential pulse voltammetry (DPV) in spectro-electrochemical (SEC) studies, this can afford useful information about the redox potentials and locus of the redox events (i.e. metal- or ligand-centered).<sup>107,108</sup> Magnetic susceptibility data, and information about the spin state of a complex can be obtained in solution by virtue of e.g. Evans' method, or in the solid state by a superconducting quantum interference device (SQUID) that probes the temperature dependence of the magnetization.<sup>109,110</sup>



**Figure 12.** Illustrative Examples of EPR Spectra ( $S = 1/2$  Systems) Characteristic for a Metalloradical (A) and Ligand-Radical Complex (B), Distortion of Ligand Bond Lengths upon a Redox Reaction (C),  $\pi$ -Donation from a Redox-Active Catecholate Ligand to a Metal, Causing C–O Bond Distortions (D), and Various Coordination Modes for DAD-Type Ligands (E)

For electronic doublet ( $S = 1/2$ ) systems, EPR spectroscopy is a particularly useful technique to locate the spin density in paramagnetic complexes, thereby aiding the elucidation of the electronic structure of open-shell complexes containing redox-active ligands.<sup>101–103</sup> In continuous wave EPR, the magnetic field is swept under a constant wavelength of microwave irradiation, detecting signals at different strengths of the magnetic field. The magnetic field at which a signal is detected can be converted to a  $g$ -value, which provides information on the local environment of an unpaired electron. Generally speaking, if the unpaired electron is primarily located on a light atom (e.g. carbon, nitrogen or oxygen), the  $g$ -value is close to that of a free electron ( $2.05 > g_e = 2.0032 > 1.95$ ), while for unpaired electrons located on heavier atoms (i.e. metal centers), spin-orbit coupling interactions in the molecule typically cause deviations from  $g = 2.0032$ . The  $g$ -value is therefore very useful to study the location of the unpaired electron, i.e. metal or ligand centered (Figure 12A-B). The presence and magnitude of coupling of a certain nuclear spin to the unpaired electron, the hyperfine coupling interactions, provides even more information about the location of the unpaired electron, especially when combined with (DFT) EPR property calculations. At low temperatures (i.e. in absence of molecular rotation during measurement), both the  $g$ -values and hyperfine interactions can be split into their  $x$ ,  $y$  and  $z$  components, providing information regarding the electronic symmetry of the paramagnetic compound.

These techniques are often used in combination with computational studies to obtain additional insight into the electronic structure of the complex bearing a redox-active ligand.

Whereas (time-dependent) single-reference density functional theory<sup>111–114</sup> (DFT) calculations are relatively cheap (computationally inexpensive), adequate and well-established, also the use of multireference post-Hartree-Fock methods such as complete active space self-consistent field<sup>115</sup> (CASSCF) is sometimes warranted for computational analysis of complexes bearing redox-active ligands. The possible involvement of multireference states can often be investigated routinely by an inexpensive fractional occupation density (FOD) analysis, clearly indicating whether additional (computationally expensive & elaborate) multireference calculations are necessary.<sup>116</sup>

Ligand bond distortions upon oxidation or reduction are characteristic of ligand-centered redox activity (Figure 12C), and can be readily measured by SC-XRD (single crystal X-ray diffraction), which is therefore a useful tool to study redox events taking place at redox-active ligands. Accompanied by technological advances, crystal structure determination has changed from a vocational to a routine measurement.<sup>117</sup> Consequently, SC-XRD derived structures were pivotal in solving many early redox non-innocence issues, such as in the description of metal-dithiolene complexes.<sup>118</sup> After acquiring and solving a crystal structure, the oxidation state of the ligand can be reliably deduced through comparison of the observed bond metrics to similar complexes in literature.

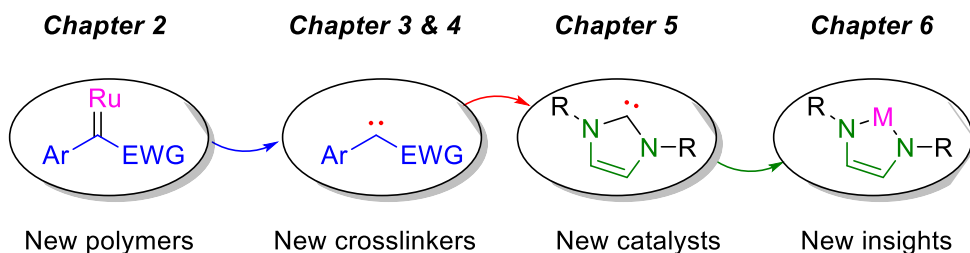
With the aid of structural databases (i.e. the Cambridge Structural database (CSD) and the Protein Databank (PDB)) the possibility arose to use a set of crystal structures for more subtle ligand distortion effects. This approach has been used in 2000 by Wieghardt *et al.*<sup>119</sup> to describe the redox non-innocence of the pyridine-2,6-diimine (PDI) ligand framework, for which the reduced forms had not been described up until that point. A larger literature study in 2019 on the same PDI ligand framework described the use of a single structural parameter ( $\Delta$ ) to study oxidation state dependent distortions.<sup>120</sup> Besides oxidation state dependent ligand bond distortions, it was reported that  $\pi$ -backdonation from second- and third-row transition metals to the PDI ligand also influences the ligand bond lengths.

In related work, Brown<sup>121</sup> described an empirical model to calculate a metrical oxidation state (MOS) of amidophenoxide and catecholate ligands, which is based on correlations between bond lengths and the ligand oxidation state. The model is based on crystallographic information from the CSD and through input of the intra-ligand bond distances the model provides a single numerical value which reflects the ligand oxidation state. By comparing various molybdenum and vanadium complexes, the  $\pi$ -donation capability of various amidophenoxide and catecholate ligands was investigated. Whereas intermediate bond distances in redox-active ligands are typically interpreted in terms of partial electron transfer from/to the ligand, this work showed that a  $\pi$ -bonding model can also provide a satisfactory description of redox-active ligands that seem to have a geometry in-between two integer ligand oxidation states. As such, caution is required in assigning

oxidation states to ligands in cases where strong  $\pi$ -bonding effects may be important (Figure 12D). Interestingly, for a similar set of redox-active ligands it is known that various coordination mode plays an important role on the reactivity of the complex (Scheme 2E), however it is unknown how this influences the assignment of the oxidation state based on intra-ligand distances.

## Outline of this thesis

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 **Chapter 2** we use metal-centered carbenes to make new biobased polymers, in **Chapter 3 and 4** we use free carbenes to crosslink acrylics and in **Chapter 5** we induce latency into dual-catalysis combining NHC-type carbenes with a transition metal catalyst. **Chapter 6** deviates a bit from the preceding chapters, and describes a new method to characterize homogeneous catalysts, specifically providing fundamental insight into complexes with redox noninnocent ligands.



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. The mechanism was investigated by kinetics and DFT studies, revealing the rate-determining step to be nucleophilic attack on a Ru–carbene moiety by urea. This study paves the way to use transition-metal-catalyzed reactions in alternative routes to polyureas.

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. The best crosslinker was shown to provide a hardness similar to the currently utilized melamine curing systems, and films with excellent water resistance.

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 used diazine functionalities that generate carbenes upon heating which react with alcohol functionalities in a polyol to generate a crosslinked network with a high storage modulus. These studies pave the way for further usage of diazo functionalized crosslinkers in the curing of paints and coatings.

In **Chapter 5** we show that introducing mixed sandwich iron complexes as electron transfer mediators in aerobic oxidative esterification induces some degree of photolateness in N-heterocyclic carbenes used in dual catalysis when combined with an Fe-based transition metal catalyst. 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 photolateness is explained by the lower barrier for ligand dissociation from the Fe catalyst in the triplet state. This chapter opens up new avenues to introduce latency by using mixed sandwich iron complexes in other oxidative transformations.

Assigning oxidation states to metals and ligands is an important tool for understanding and predicting the chemical reactivity. For complexes containing redox-noninnocent ligands, the oxidation state of the ligand can be ambiguous. 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. 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. 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.

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