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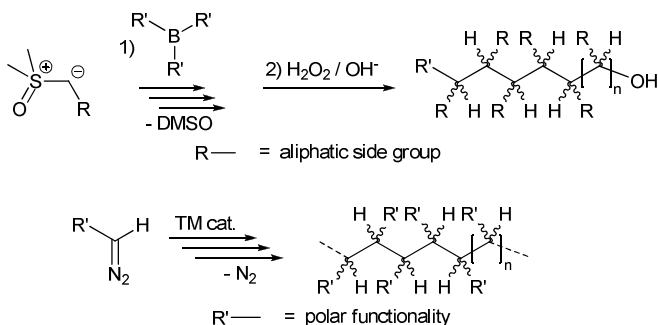
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Chapter 1

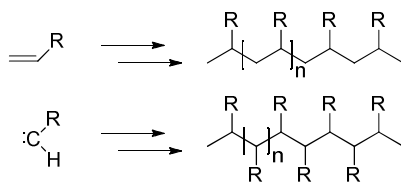
C1 polymerization and related C-C bond forming ‘carbene insertion’ reactions*



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1.1 Introduction

Polymerization of C=C bond containing substrates is currently the most important method to prepare polymeric materials, exemplified by the many large-scale industrial plants producing polyethylene, polypropylene, polystyrene, poly(vinyl chloride), poly(methyl methacrylate) and a variety of other polymers from vinylic substrates. In these ‘C2 polymerization’ reactions each monomer delivers two carbon atoms in each chain-growth step (Scheme 1). The required C=C bond containing monomers are mostly obtained from crude oil, and although these are currently cheap and abundant, their supply is finite and long-term strategies for the renewable production of olefins and other C2 monomers will become necessary for a sustainable supply of polymeric materials in the future. This will inevitably increase their price, which in turn creates opportunities for other materials from alternative monomer sources (which are currently more expensive, but may also have improved material properties).



Scheme 1. Polymerization of C2 and C1 monomers.

There are also important synthetic reasons to search for alternatives for ‘C2 polymerization’. For example, many polar functionalized C=C substrates (in particular highly substituted ones) do not polymerize, and their polymers are unknown. Many polar functional groups are not compatible with existing catalysts, causing severe problems in the preparation of *highly functionalized and stereoregular* polymers from C2 monomers. Most polymers derived from polar functionalized C2 monomers are obtained by (controlled) radical polymerization, which gives at best a poor control over the polymer stereo-properties. Only transition metal (TM) catalyzed processes would give access to highly isotactic or syndiotactic polymers, and such high stereoregularity is actually required to give the polymers their desirable material properties. However, preparing well-defined *stereoregular and high molecular mass* polymers *via TM catalyzed polymerization of polar functionalized C2 monomers* is extremely difficult. There are several reasons for this, such as catalyst poisoning by the polar substituents, weaker metal-substrate interactions with functionalized substrates, and poorly developed insights in the factors controlling catalytic stereoselective polymerization of polar

monomers. Nonetheless, such polymers would greatly expand the range of desirable polymer properties. Polar groups influence important material properties such as toughness, adhesion barrier properties, surface properties (paintability, printability, *etc.*), solvent resistance, miscibility with other polymers and rheological properties.¹ Thus the search for the ‘holy-grail’ in TM catalyzed polymerization continues, but it is questionable if general strategies for TM catalyzed stereospecific polymerization of polar functionalized C2 monomers can be developed.² The challenge becomes even larger if we try to polymerize C2 monomers with two or more polar substituents. For example, radical polymerization of dialkyl fumarates (*trans*-RO₂CCH=CHCO₂R) yields only relatively low molecular weight atactic polymers and dialkyl maleates (*cis*-RO₂CCH=CHCO₂R) do not polymerize at all.³ To the best of our knowledge, there are no TM catalysts that can polymerize C2 monomers with two or more polar substituents, not even to atactic materials.

If simple polar functionalities already cause such large problems, even bigger synthetic challenges are foreseen in trying to incorporate more complex functionalities such as fluorescent or phosphorescent dyes, stable organic radicals or energy and electron transporting functionalities. Such new polymers are desirable to prepare novel convenient and light-weight specialty materials and devices, such as polymeric organic LEDs, plastic batteries, conducting polymers and other plastic electronic components. Given the above synthetic problems, it is questionable if this will be possible at all using C2 polymerization techniques. As such we are facing important challenges in future polymer synthesis, which require us to develop new polymerization methods, that will allow us to prepare functional stereoregular (co)polymers containing a wide variety of functional groups in controllable amounts and at controllable positions. Novel strategies for their synthesis can also lead to useful non-petroleum based technologies for the production of commodity polymers. One such approach would be to grow our polymers from monomers delivering only one functionalized carbon unit (C1 monomers) in each chain-growth step (Scheme 1).

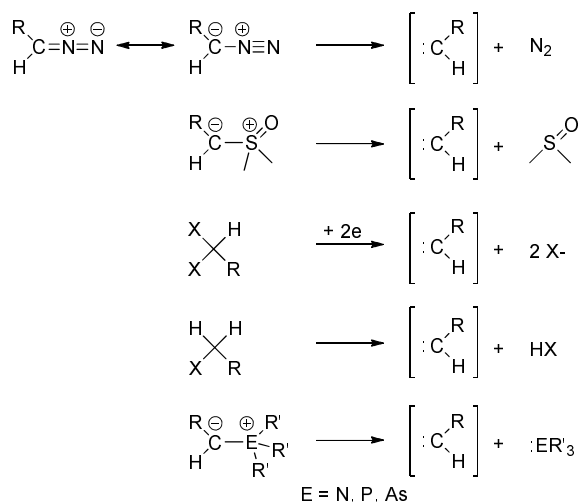
Polymerization of C1 monomers in principle allows the formation of (stereoregular) polymers which are functionalized at every carbon atom of the polymer backbone, thus providing great opportunities for the synthesis of new polymers with yet unknown properties. Some reported C1 polymerization techniques even allow a precise control over the nature of the polymer end-group functionalities. Polymerization of C1 monomers could thus open a world of completely new methods in polymer synthesis.

In this Chapter we focus on recently developed ‘C1 polymerization’ techniques as a valuable alternative for ‘C2 polymerization’. We will only discuss C1 monomer polymerization leading to main-chain saturated (sp³ hybridized) carbon-chain polymers and therefore polyisocyanides⁴ are excluded from this overview. Although

we use the general term ‘C1 polymerization’ to describe polymer growth from monomers delivering only one (functionalized) carbon unit in each chain-growth step, there are actually many different terminologies used in literature to describe different C1 polymerization techniques. These are ‘polyhomologation’ (mostly polymerization of ylides), ‘poly(substituted) methylene synthesis’, ‘polymerization of (substituted) diazo compounds’, and ‘carbene (insertion) polymerization’. We will use similar terminologies to discriminate between these different approaches in ‘C1 polymerization’.

Accessibility of C1 monomers

The synthesis of saturated carbon-chain polymers from C1 monomers implies the use of carbenoid monomers. So far, this has been dominated by the use of diazo compounds and ylides of sulfoxides, which can both be regarded as carbenoids, carbene precursors or synthetic equivalents of carbenes (Scheme 2).



Scheme 2. C1 monomer precursors.

A couple of papers report also the use of α,α -dihalocarbons as C1 monomer precursors. In principle carbenes are also accessible through deprotonation of halocarbons with strong bases, but this method has not yet been applied in C1 polymerization. A couple of recent papers describe that carbene ligands generated at early transition metals can be transferred to late transition metals,⁵ which may provide further yet unexplored opportunities in future C1 polymerization.

Aliphatic diazoalkanes are generally very unstable, and require low temperatures and dilute solutions to handle their reactivity.⁶ Although they are very reactive, flammable and explosive,⁷ they make excellent precursors for carbenes and have been applied in polymerization reactions. Although the thermal decomposition of diazomethane (reported already in 1898) is the first known route to

polymethylene,^{8,9} this potentially explosive process⁷ is not at all practical from a synthetic point of view. Also it does not provide any advantages over traditional transition metal catalyzed ethene polymerization to linear polyethylene (which was discovered more than half a century later).¹⁰⁻¹² Therefore, most reported C1 polymerization techniques involve the more practical use of a Lewis acid or transition metal (TM) catalyst to polymerize the diazo compounds.

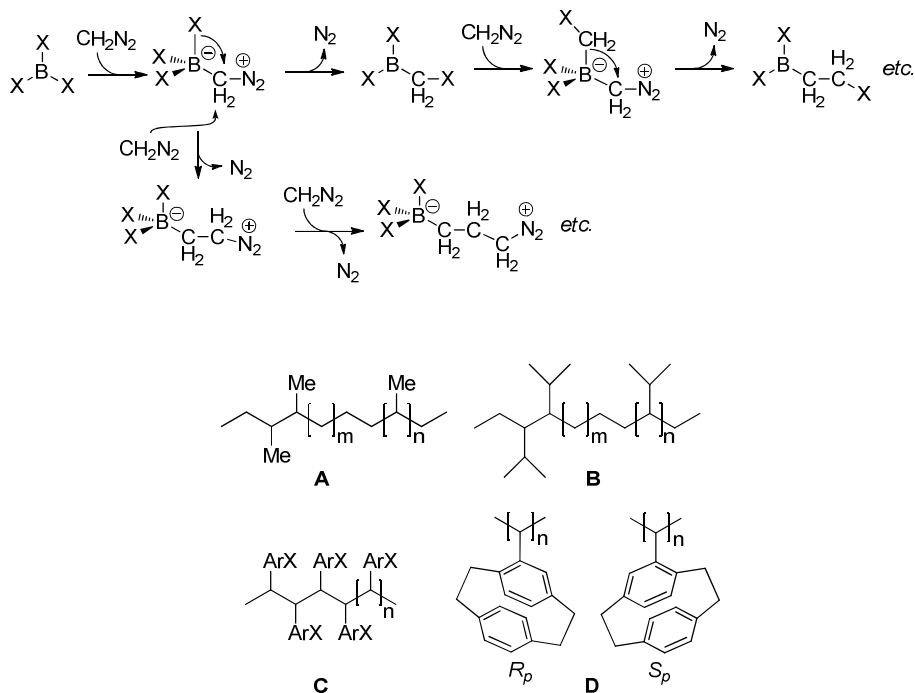
Unlike the inherently unstable diazoalkanes, diazocarbonyl compounds such as diazoacetates ($\text{N}_2\text{CHCO}_2\text{R}$) or diazoketones ($\text{N}_2\text{CH(CO)R}$) are reasonably stable, safe (even in large scale/industrial synthesis),¹³⁻¹⁶ easy to prepare, and extensively used as carbene precursors in organic synthesis. However, due to their increased stability only a few reports describe the *polymerization* (or oligomerization) of α -carbonyl stabilized 'carbenes' from diazocarbonyl compounds (*vide infra*).

Ylides of sulfoxides (*e.g.* ylides of DMSO) are also valuable synthetic precursors to carbenes. Elimination of a stable neutral fragment from either a diazo compound (N_2) or the ylide of dimethyl sulfoxide (DMSO) allows the generation of a carbene fragment amenable to polymerization reactions. Ylides of sulfoxides which are substituted on carbon are difficult to prepare, and often too instable to isolate.¹⁷ This somewhat limits their use in the preparation of (polar) substituted poly-carbenes.

A much larger variety of substituted diazo compounds is readily accessible,^{18,19} and thus currently allows for a much wider structural diversity in polymer synthesis. On the other hand, more structural variety might be possible with other ylides such as arsonium ylides.²⁰ Some polymerization reactions proceeding via boron catalyzed polymerization of allylic arsonium ylides (closely related to boron catalyzed polymerization of sulfur ylides) have been reported, but these result in C3 polymerization instead of C1 polymerization.^{21,22} However, with these monomers sometimes also C1 polymerization is observed, especially for the bulkier substituted allylic arsonium ylides.²³ This also makes one wonder if it would be possible to use other ylides in C1 polymerization, such as phosphonium based ylides.

1.2 Lewis acid mediated polymerization of C1 monomers

Both diazoalkanes and ylides have resonance structures with a partial negative charge on their carbon atom (Scheme 2), as demonstrated by their nucleophilic behavior towards Lewis acids. The use of these reagents in polymer synthesis involves the insertion of their carbene fragments to a growing carbon-chain, which can be initiated and controlled with several Lewis acidic mediators. Boron, aluminum and silicon are all known to be active mediators for such 'carbene polymerization reactions',⁶ but boron has been most frequently used (Scheme 3).



Scheme 3. Boron mediated ionic and migration polymerization of diazomethane and polymers **A**, **B**, **C** and **D** obtained by boron mediated polymerization of other diazoalkanes.

Boron trifluorides and trialkyl boranes give the best yields and highest molecular weight polymers, but other boron halides, boron alkyls and boronic esters can also be used. A couple of reviews already deal with the polymerization of diazoalkanes with boron mediators,^{6,24,25} so here only the most important points will be briefly summarized here, while focusing on the new developments (such as the use of polar functionalized substrates). Lewis acid mediated polymerization of functionalized diazo compounds and ylides proved more difficult, but some recent examples are included.

1.2.1 Lewis acid mediated polymerization of diazo compounds

Polymerization of diazomethane mediated by a range of boron compounds (including boron compounds present in vacuum grease)²⁶ produces highly crystalline polymethylene. Molecular weights up to 3 million Da (Dalton, *i.e.* gram/mol) can be achieved with the BF_3 mediator (Table 1, entry 1).²⁷ The reaction is first order in diazomethane and boron.²⁸ It seems that different mechanisms are operative, possibly even depending on the nature of the boron mediator. An ionic mechanism involving nucleophilic attack of the partially negatively charged carbon atom of diazomethane onto the polarized carbon atom of growing chain $\text{X}_3\text{B}^--\{\text{CH}_2\}_n-\text{CH}_2-\text{N}_2^+$ intermediates has been proposed to be the dominant

polymerization mechanism by Davies *et al.*,²⁹ while Matthies favors repetitive intramolecular nucleophilic attack of the growing chain onto the diazomethane adduct (migration mechanism, see Scheme 3).³⁰ Only one chain grows from BF₃, presumably because the migration of an alkyl is favored over the migration of fluoride.³⁰ Of course three alkyl chains grow from trialkylboranes. It has later been suggested that both the ionic and the migration polymerization pathways occur simultaneously.^{6,31}

Table 1. Lewis acid mediated polymerization of diazo compounds (selected results).

Entry	Substrate	Lewis acid	molecular weight (Da)
1	diazomethane	BF ₃	3·10 ⁶
2	diazoethane	BF ₃	5000
3 ^a	diazoethane	BF ₃	20000
4	(2-diazo ethyl)benzene	BF ₃	3000
5	diazomethane + diazoethane	B(α-naphthyl) ₃	70000
6	diazomethane + diazo- <i>iso</i> -butane	B(α-naphthyl) ₃	1700
7	4-diazomethyl[2.2]paracyclophanes	BF ₃ ·Et ₂ O	~1200
8	ethyl diazoacetate	BH ₃	~500
9	diazoketones	Al(alkyl) ₃	~3000

^a Reaction performed at –115 °C

Higher diazoalkanes are polymerized to much lower molecular weight polymers in the presence of borane mediators. For example, BF₃ mediated polymerization of diazoethane and (2-diazo ethyl)benzene at room temperature yields molecular weights of only 5000 Da for polyethylidene and 3000 Da for polybenzylidene (Table 1, entries 2 and 4).³⁰ At lower temperatures (*ca.* –115 °C) higher molecular weight polyethylidene of 20,000 Da could be obtained (Table 1, entry 3), suggesting that thermal termination processes are the cause of the lower degree of polymerization at higher temperatures rather than the intrinsic steric hindrance between the side-groups. Hydride and alkyl group transfer to the electrophilic carbon fragments bound to boron have been proposed to explain the formation of lower weight polymers, which correlates with the observation of unsaturated end-groups in the polymers.³⁰

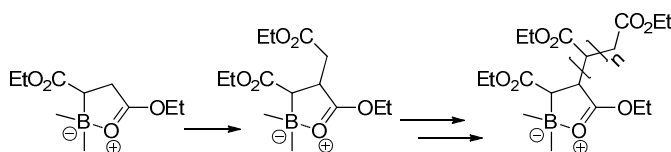
Co-polymerization of diazomethane and higher diazoalkanes mediated by tri-α-naphthylboron yields random copolymers of reasonable lengths for poly-co-methylene-ethylidene (**A**) (70,000 Da) but yields only short poly-co-methylene-isobutylidene chains (**B**) (1700 Da) (Scheme 3; Table 1, entries 5 and 6).²⁵ We are not aware of any papers reporting the formation of stereoregular polymers with boron or other Lewis acidic mediators, and likely all polymers formed by this method are atactic.

Thermal decomposition of a series of aryldiazoalkanes mediated by methanol was reported to yield linear carbon chains with aryl substituents as side-groups in reasonable yields, but fairly low molecular weight polymers (*M_n* in the range 700–11,000 Da) were obtained in this manner.³² BF₃ mediated polymerization of

aryldiazoalkanes also allows the formation of copolymers from different aryldiazoalkanes (**C**), but yields and molecular weights are still low (Scheme 3).³³

Recently, boron mediated polymerization of diazoalkanes was applied to construct polymeric structures based on paracyclophanes that give rise to enhanced π - π stacking (**D**).³⁴ Racemic as well as chiral 4-diazomethyl[2.2]paracyclophanes were polymerized with $\text{BF}_3 \cdot \text{Et}_2\text{O}$ resulting in low molecular weight polymers/oligomers in low yields (Table 1, entry 7; *rac*: $M_n = 1100$ Da, yield = 20%, R_p : $M_n = 1200$ Da, yield = 20%, S_p : $M_n = 1300$ Da, yield = 13%). Transannular π - π interactions were confirmed by UV-Vis spectroscopy. Quite remarkably, these interactions were not observed for poly(4-vinyl[2.2]paracyclophane), in which the polymer backbone contains only one paracyclophane per two backbone carbons ($-\text{[CH}_2\text{CHR]}_n-$ backbone). Circular dichroism profiles of the polymers containing planar chiral substituents (R_p and S_p) revealed optical activity.

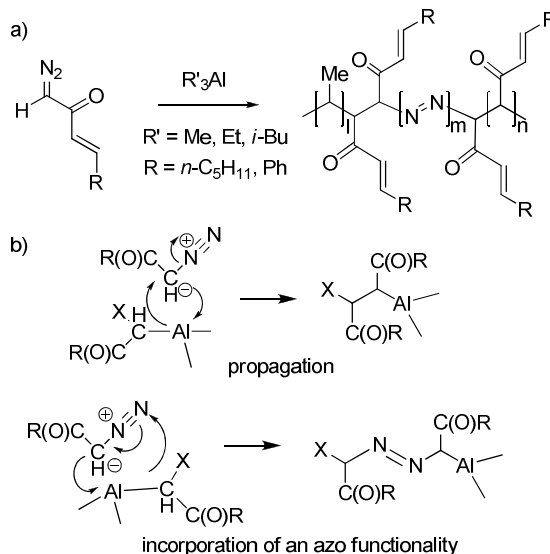
Lewis acid mediated polymerization of polar functionalized diazo compounds,¹⁸ such as diazo esters or diazoketones proved even more challenging. Trialkylboranes react with a variety of diazo esters, but generally only a single insertion is observed.^{35,36} The reaction of ethyl diazoacetate (EDA; $\text{N}_2\text{CHCO}_2\text{Et}$) with $\text{B}(\text{Pr})_3$ yields for example only ethyl ester $\text{Pr}-\text{CH}_2\text{CO}_2\text{Et}$ after aqueous work-up.³⁷ The lack of multiple insertions is probably the result of the relative stability of *O*-boron enolate intermediates generated after the first insertion. Remarkably, Shea and co-workers recently reported that BH_3 mediated decomposition of ethyl diazoacetate does lead to some more insertions. Not only the expected ethyl acetate was formed, but also dimer, trimer and a mixture of low molecular weight oligomers (400-500 Da, corresponding to tetramers, pentamers and hexamers, Table 1, entry 8) stemming from EDA were obtained.³⁸ The doubly homologated *C*-boron enolate is proposed to be the most stable intermediate in this reaction, and its further homologated analogs are the resting states in the oligomerization reaction of EDA (Scheme 4).



Scheme 4. C-boron enolates: intermediates in the homologation reaction of EDA.

Formation of slightly higher molecular weight polymers by organo-aluminum mediated polymerization of diazoketones was recently reported by Ihara and co-workers (Scheme 5).³⁹ The reaction produces low molecular weight oligomers (~3000 Da; Table 1, entry 9) with a rather low polydispersity (1.5). The obtained polymers are actually rather ill-defined random copolymers, because besides the

expected functionalized carbene units the polymer also contains substantial amounts of azo functionalities (~ 33 mol%) and ethylidene ($-\text{CH}(\text{Me})-$) units (~ 35 mol%, only observed in case of $\text{R} = \text{Ph}$, see Scheme 5a).

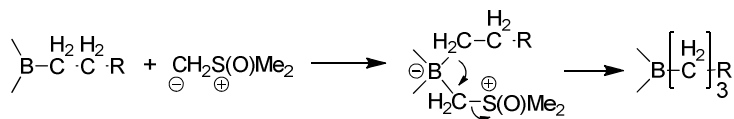


Scheme 5. a) Organo-aluminum mediated polymerization of diazoketones. b) Proposed mechanism of propagation and incorporation of azo functionalities.

The mechanism proposed for the 'carbene polymerization' by aluminum is similar to that proposed for the boron mediated reactions. Incorporation of azo functionalities was explained by attack of an Al-alkyl on the nitrogen fragment of the diazo compound (Scheme 5b), while formation of the ethylidene units was tentatively explained by reductive cleavage of the acyl group during polymerization.

1.2.2 'Polyhomologation': Borane mediated polymerization of sulfoxide ylides

In 1966, Tufariello and co-workers developed a method for the homologation of organoboranes.⁴⁰ In this reaction the carbon chains of an organoborane are elongated with one carbon atom fragment each. The carbon source for this reaction is an ylide of a sulfoxide moiety, which binds with its carbon atom to the electrophilic organoborane. This is followed by a 1,2-migration, perhaps better described as a nucleophilic attack of the *B*-alkyl fragment on the ylide carbon, with elimination of the sulfoxide (Scheme 6). After the chain-elongation the authors added nucleophilic reagents to displace the alkyl chains from boron. With OH^- as nucleophile, this leads to the formation of linear alcohols. Quite remarkably, the products obtained in this manner were actually mixtures containing mono- and bis-homologated alcohols. This means that in the absence of nucleophiles, multiple insertions of the ylide take place.

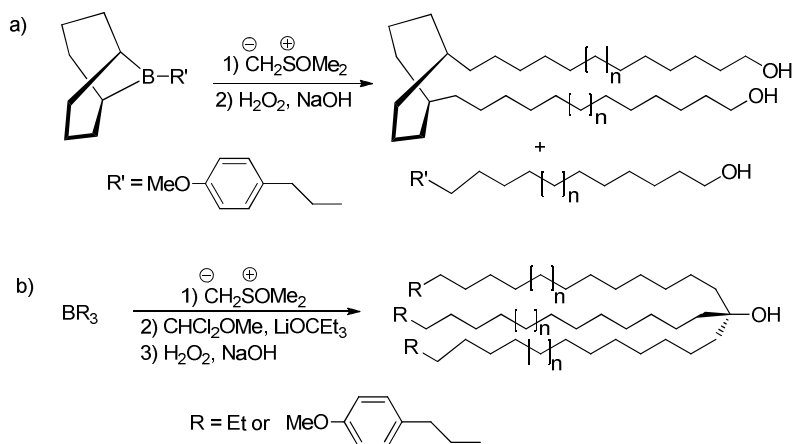


Scheme 6. Migration of the alkyl group to form homologated alkanes.

The homologation experiments of Tufariello inspired the Shea group to investigate the possibilities of this reaction for polymer synthesis. In 1997 they reported ‘polyhomologation’ as a new reaction for the formation of linear polymethylene.⁴¹ This new method involves repetitive homologation in the presence of a large amount of ylide and yields long chain alkanes. Oxidative, basic aqueous work-up yields linear alkyl-chain polymers with a hydroxyl end-group. The reaction is a living polymerization, and thus the polymer length depends primarily on the initial feed ratio of the ylide with respect to the borane. Molecular weights up to 500 kDa have been achieved with this reaction.⁴² Polydispersities are generally in the range between 1.01 and 1.20. Because of the low solubility of higher alkanes at room temperature, the product has a broad distribution of oligomer chain lengths when the reaction is performed in THF. Performing the reaction in preheated toluene solutions or tetrachlorobenzene/toluene mixtures at 120°C, however, allows formation of high molecular weight polymers with low polydispersities (1.01–1.03).⁴² The reaction is first order in borane and zero order in the ylide substrate. Activation parameters (THF: $\Delta G^\ddagger = 19.5$ kcal/mol, $\Delta H^\ddagger = 23.2$ kcal/mol, $\Delta S^\ddagger = 12.6$ e.u.; toluene: $\Delta G^\ddagger = 20.1$ kcal/mol, $\Delta H^\ddagger = 26.5$ kcal/mol, $\Delta S^\ddagger = 21.5$ e.u.) are consistent with an addition-migration mechanism proposed already earlier by Tufariello for a single insertion (Scheme 6).⁴⁰

The polyhomologation reaction as introduced by Shea and co-workers makes it possible to introduce specific functional groups at both polymer ends, because one can choose the substituent on the starting organoboranes. A variety of different borane initiators BR_3 with different R groups are readily available *via* hydroboration of alkenes.⁴³ The nucleophile used for cleavage of the carbon-boron bond and termination of the living polymerization reaction determines the functionality on the other polymer end. Although chain termination through oxidative cleavage has been mostly applied to yield hydroxyl groups, the rich chemistry of the boron functional group in principle allows the introduction of a wide number of other functional groups like amines, halogens, hydrogen (alkanes) and carbon metal bonds.⁴⁴ A variety of functional telechelics and terminal functionalized polymethylenes have been prepared in this manner, which would be very difficult to obtain by ethene polymerization.

For example, the use of bridged organoboranes leads to hydroxyl-polymethylene substituted cyclooctanes⁴⁵ or adamantanes (Scheme 7a).⁴⁶ Trivinylboranes can be used to make α -vinyl end-functionalized polymethylenes.⁴⁷ Polyhomologation in combination with known organoborane transformations is a way to form new polymethylene structures like tris(polymethylene) substituted alcohols (Scheme 7b).⁴⁵

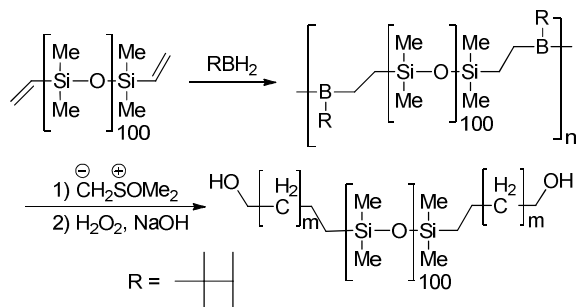


Scheme 7. Synthesis of hydroxyl-polymethylene substituted cyclooctane (a) and tris(polymethylene) alcohol (b).

Shea and co-workers transformed the polyhomologation reaction into a general method to prepare various telechelic polymethylenes, terminated with hydroxyl, aryl, organosilane, organotin, methyl sulfoxide, carbohydrate groups, biotin and fluorescent groups with quantitative incorporation of the functional end-groups.⁴⁸ The method also allows the preparation of cyclic organo-boranes, which can be transformed into cyclic ketones.⁴⁹ Such control over chain end functionalities could never be achieved with traditional olefin polymerization.

1.2.2.1 Block copolymers via polyhomologation

Block copolymers of poly-methylene and poly-ethyleneglycol were made by end-capping commercially available poly-ethyleneglycol with allylbromide, allowing hydroboration of the resulting allyl substituent. Subsequent polyhomologation with thus obtained tris-poly-ethyleneglycol-borane resulted in a well defined A-B block copolymer with controllable molecular weights of the two blocks. A-B-A triblock copolymers were obtained by hydroboration of divinylpoly(dimethylsiloxane) at both ends, followed by polyhomologation with the $H_2C^--^+SOMe_2$ ylide, thus leading to polymethylene-polydimethylsiloxane-polymethylene (Scheme 8).⁵⁰



Scheme 8. Formation of a triblock copolymer.

Such block copolymers are of interest because of expected special properties like their ability to micro separate and their potential applications in detergents, paints and blending agents. Triblock copolymers of the type shown in Scheme 8, form for example ‘nanodonut’ aggregates.⁵¹

1.2.2.2 Functionalized sulphur ylides in polyhomologation

Polyhomologation as described above uses unsubstituted sulfoxide ylide **1** (Fig. 1) for the synthesis of linear hydrocarbon polymers. For preparation of substituted carbon backbones, substituted ylides are required. The applied method for preparing ylides, *i.e.* *S*-methylation of dimethylsulfoxide followed by deprotonation of the *S*-Me fragment, is however not a general reaction and is not suitable to prepare substituted ylides. The Shea group reported that (dimethylamino)aryloxosulfonium ylide **2**,⁵² ylide **3**⁵² and ylide **4**⁵³ (Figure 1) can be prepared from sulfoxides which are easier to alkylate, and thus offer a somewhat wider variety of substituted substrates.

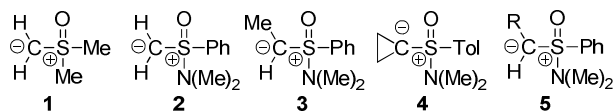


Figure 1. Different ylides for polyhomologation.

These sulfur ylides were successfully applied as monomers in the polyhomologation reaction. Unsubstituted ylide **2** could be polymerized to a high molecular weight polymer with low polydispersity. Like ylide **1**, ylide **2** is stable at higher temperatures. Substituted ylides **3** and **4** do not homopolymerize in the presence of organoboranes because of steric crowding at the boron center after insertion of one ethylidene or cyclopropylidene group, respectively. However, after slow addition of ylide **1** to a solution of ylide **3** containing B(Et)₃, random copolymers of **1** and **3** are formed with the same composition as ethylene propylene copolymers. Lower amounts of –CH(Me)– groups compared to methylene units are found in this polymer. The ratio of ylide **1** : ylide **3** can be varied to make a less substituted

polymer.⁵² Co-polyhomologation of ylide **1** and ylide **4** always led to polymers with lower incorporation of cyclopropyl groups (between 1:12 and 1:18, cyclopropyl:methyl) than expected by the feed ratio (between 1:3 and 1:5 for **4:1**).⁵³ According to the authors, the main cause is decomposition of ylide **4** under the reaction conditions, but it might also be explained by the higher activation energy for migration of the growing chain fragment to the bulkier cyclopropyl containing monomer **4** as compared to monomer **1** (Scheme 6, section 1.2.2). The incorporation of cyclopropylidene could be increased by adding ylide **4** in portions to the reaction mixture.

The authors speculate that it could be possible to prepare ylides with heteroatom containing functionalities (ylide **5**) to introduce functionality on the main chain carbons.⁵² Till today, this has not been demonstrated. This is remarkable, since Tufariello already showed in 1967 that it is possible to homologate organoboranes with one substituted methylene unit using either sulfur ylide $\text{Me}_2\text{S}^+-\text{CHCO}_2\text{Et}$ or arsonium based ylide $\text{Ph}_3\text{As}^+-\text{CHPh}$.²⁰

The Shea group further demonstrated that it is possible to prepare random copolymers of methylene units ($-\text{CH}_2-$) and trimethylsilyl substituted methylene units ($-\text{CHSiMe}_3-$) from reaction of ylide **1** and trimethylsilyl diazomethane with boranes.⁵⁴ Only rather low incorporation of $-\text{CHSiMe}_3-$ units is possible. With a higher feed ratio of trimethylsilyl diazomethane the polymer yield is low and the polydispersity increases substantially. Homopolymerization of trimethylsilyl diazomethane proved not possible. Copolymerization of ylide **1** with other substituted diazo compounds, such as ethyl diazoacetate, has not (yet) been reported to our best knowledge. This further demonstrates that it is probably not so easy to introduce polar functionalities to the main-chain using the boron mediated polyhomologation reaction.

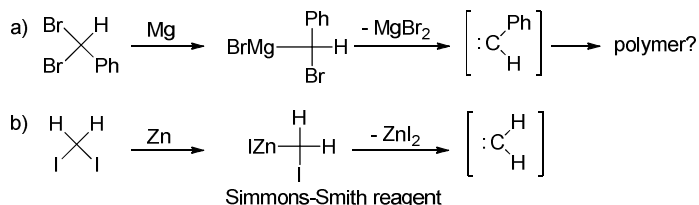
1.3 Miscellaneous polymerization reactions of other C1 monomers

1.3.1 Mg mediated polymerization of α,α -dihalogenated carbons

Besides diazo compounds and ylides, only a few attempts to use other C1 monomers have been reported thus far. Recently, Ihara and co-workers reported an interesting attempt to prepare benzylidene ($:\text{CHPh}$) carbene units by magnesium mediated reductive decomposition of α,α -dibromotoluene.^{55,56} The Simmons-Smith reductive decomposition of diiodomethane with metallic Zn, which allows carbene transfer to olefins in cyclopropanation reactions (Scheme 9), shows striking similarities.⁵⁷

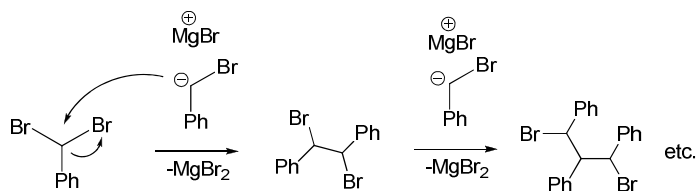
The intermediate α -bromo Grignard reagent was expected to decompose fast to benzylidene, and thus Ihara and co-workers attempted to use this carbene in subsequent carbene polymerization reactions. Reaction of α,α -dibromotoluene with excess magnesium indeed produces the desired carbon-chains with Ph side-chains. However, the material is not well-defined as the material contains, besides the

expected saturated $-\text{CHPh}-$ units, also substantial amounts of main-chain unsaturated $-\text{PhC}=\text{CPh}-$ fragments. In fact the polymer is a random copolymer of the type $\{-\text{CHPh}-\}_m\{-\text{PhC}=\text{CPh}-\}_n$. Only rather low molecular weight oligomers (< 1100 Da) were obtained, albeit with reasonably low polydispersities (1.30-1.50). These results led the authors to propose a very different mechanism for the polymerization than originally planned.



Scheme 9. Proposed polymerization of benzyldiene carbenes (a) and the similarity with the Simmons-Smith reaction (b).

The reaction apparently proceeds *via* multiple condensation steps of the intermediate α -bromo Grignard reagent with the α,α -dibromotoluene starting material (Scheme 10).



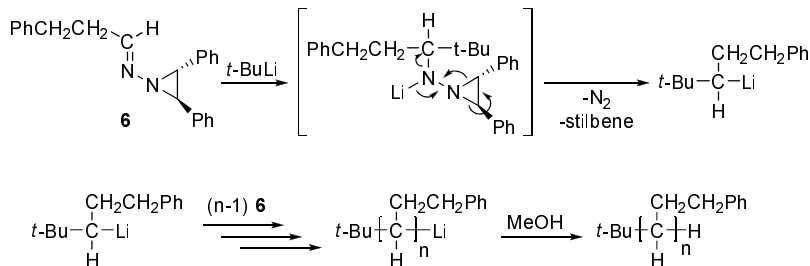
Scheme 10. Mg mediated polymerization of α,α -dihalogenated carbons.

Formation of main chain $-\text{PhC}=\text{CPh}-$ unsaturations was explained by deprotonation of $-\text{PhBrC}-\text{CHPh}-$ units expected to be formed within the proposed polycondensation mechanism. The method allows the copolymerization of α,α -dibromotoluene with other dihalogenated reagents, such as 1,6-dibromohexane, albeit to low molecular weight materials. Although the reaction takes a different course than expected, the idea is noteworthy, and in principle many other α,α -dihalocarbon sources could be applied in C1 polymerization reactions.

1.3.2 Anionic polymerization of C1 monomers

In 1996, Yamamoto reported an example of anionic C1 polymerization.⁵⁸ The reaction of arylaziridine hydrazone **6** with catalytic amounts of *t*-BuLi afforded, after addition of methanol, poly(phenylpropylidene) in 47% yield and with $M_n = 1786$ Da and $M_w/M_n = 1.20$ (Scheme 11). Also other initiators were used, such as *n*-BuLi and PhLi and these gave similar low molecular weight products.

The proposed mechanism involves initial attack by *t*-BuLi on the hydrazone to give the adduct shown in Scheme 11. A Shapiro type fragmentation yields a new organolithium compound, which can react further with **6** to form a carbon chain elongated organolithium compound.



Scheme 11. Anionic oligomerization of arylaziridine hydrazone **6**.

1.4 Transition metal catalyzed polymerization of C1 monomers

1.4.1 Polymerization of diazoalkanes (homogeneous processes)

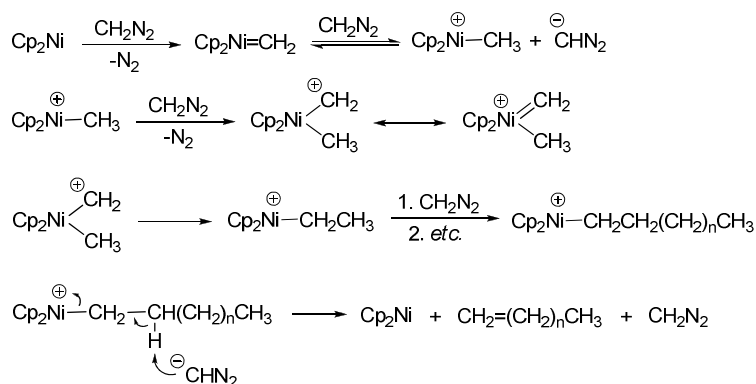
Most of the early reported studies on transition metal catalyzed polymerization of diazoalkanes were performed with copper and gold reagents and have been reviewed.^{6,25} The polymerization activity of other metals with diazoalkanes has been studied less extensively.²⁵ The most important older findings will be discussed shortly before we focus on the recent developments in more detail.

A broad range of copper reagents (copper metal, Cu^I and Cu^{II} salts) has been applied for polymerization of diazoalkanes, but the active catalysts are believed to be Cu^I species.⁶ However, Cu^{II} reagents, such as copper sulfate and copper stearate (which are *in situ* reduced to Cu^I) are usually applied for convenience.⁵⁹ In contrast to boron reagents, the use of copper stearate affords higher polymer yields in the polymerization of diazoethane and diazobutane (up to 92% for diazobutane) than obtained for diazomethane (9%).²⁸ With diazomethane, the reaction is first order in substrate and catalyst concentration.⁶⁰ The molecular weights of polymethylene obtained with copper reagents are up to 20,000 Da.²⁵ The mechanism of the Cu-mediated polymerization is not clear and several possibilities are mentioned: Step-growth *via* repetitive migratory insertion steps of carbene units (generated from the diazo compound) into a Cu^I-alkyl growing chain, rapid growth of a cationic chain, and radical polymerization by a stabilized Cu^I radical have all been proposed.⁶

In their search for better catalysts for polymerization of diazoalkanes, Nasini and co-workers decided to study AuCl₃ as an alternative to boron and copper. Upon addition of diazomethane, AuCl₃ is reduced immediately to colloidal gold particles and polymethylene is obtained in almost quantitative yield with molecular weights up to 50,000 Da.⁶¹ Gold metal was found to be the active material in this reaction; addition of diazomethane after complete reduction of AuCl₃, resulted in formation

Remarkably, analogous complexes such as ferrocene and dicyclopentadienylchromium do not affect polymerization of diazomethane. Nickelocene and dicyclopentadienylchromium are both paramagnetic, yet only nickelocene is active in the polymerization.

Based on their observations, the authors proposed a migratory insertion type mechanism (Scheme 12). A metal-carbene species (formed in the first step) is proposed to be protonated by diazomethane to form a rather unusual cationic Ni^{IV} -alkyl species. Reaction of diazomethane with this intermediate would then form a cationic Ni-alkyl-carbene species. Migration of the alkyl to the carbene is proposed as the carbon-carbon bond forming step. Repetition of these steps leads to chain growth. An E_2 -type deprotonation- β -elimination step is proposed as the termination step, thus liberating polymethylene with regeneration of nickelocene.



Scheme 12. Proposed mechanism of polymerization of diazomethane by nickelocene (Cp = cyclopentadienyl).

Polar functionalized diazo compounds, such as ethyl diazoacetate can not be polymerized by nickelocene; only dimerization products diethyl maleate and fumarate are formed and in the presence of cyclohexene, cyclopropanation takes place. The increased acidity of ester functionalized alkyl moieties (generated by the use of EDA) might make the E₂-type elimination reaction easier than with

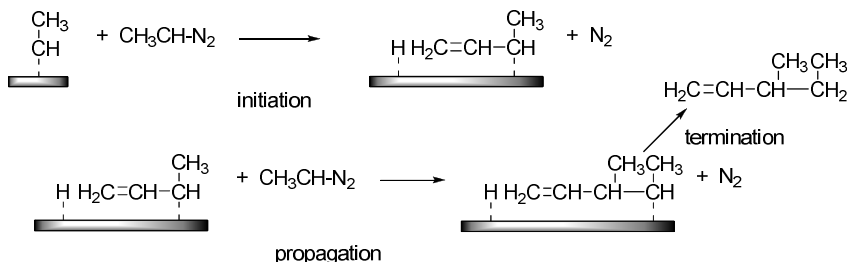
diazomethane (Scheme 12, last step). Reaction of nickelocene with diazofluorene and diphenyldiazomethane leads to little or no polymer, which was ascribed to steric hindrance. Another possible explanation is that these substrates do not contain an acidic proton required to generate the metal-alkyl species (Scheme 12, first and second step).

Recently, the polymerization of a sterically hindered substrate, phenyldiazomethane by $\text{Pd}_2(\text{dba})_3(\text{CHCl}_3)/\text{pyridine}$ was reported by Ihara *et al.*⁶⁵ Compared to polymers obtained by thermal decomposition of aryldiazomethane,³² the molecular weights and yields are low ($M_n = 1420$ Da, $M_w/M_n = 1.47$, <20% yield). Furthermore, substantial incorporation of azo groups was observed (~25%), similar to the polymers obtained by polymerization of diazocarbonyl compounds with organo-aluminum compounds (Scheme 5a, section 1.2.1).³⁹

1.4.2 Heterogeneous polymerization of diazoalkanes and polar functionalized diazo compounds on metal surfaces

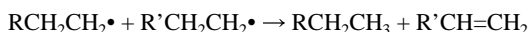
In 1961, Nasini *et al.* discovered the polymerization activity of gold metal and this prompted them to expose surfaces of a wide range of metals to diazoalkanes. In decreasing yield, the surfaces of the following metals produced polyethyldiene from diazoethane: Cu, Ti, Fe, Mg, W, Ni, V, Mn, Ta, Pt, Co, Zn, Cd, Au, Cr, Al and Mo. The use of Pd, Rh, Zr and Ag metal surfaces did not yield any polymer. Remarkably, small amounts of *stereoregular* polyethyldiene from diazoethane were formed on gold surfaces (actual tacticity unclear). This is the first reported example of stereoregular polyalkyldiene.⁶¹

No explanation was given for the stereoregulating activity of gold, but a general mechanism for the polymerization was proposed. The reaction can initiate by addition of a diazoethane molecule to an adsorbed carbene with liberation of dinitrogen and hydrogen transfer to the metal surface (Scheme 13). The polymer is formed by subsequent migratory insertion of a metal bound diazoethane into the metal surface bound alkyl unit until termination occurs through "reductive elimination" of the hydrogen and alkyl fragments formed in the initiation reaction (Scheme 13).



Scheme 13. Proposed mechanism of formation of polyethyldiene on a metallic surface.

Tao, Allara and co-workers used this surface initiated polymethylene synthesis as a strategy to prepare crystalline ultra-thin coatings on gold surfaces by simply exposing the gold surface to a solution of diazomethane in ether.⁶⁶ The polymerization initiates in the first stage of the reaction at defect sites of the gold-surface. In later stages, film growth is slower until the surface is almost completely covered with polymer. Because the authors observed a Me group with IR spectroscopy, they suggest a mechanism proceeding *via* radical intermediates. In this mechanism two adsorbed methyldene species combine to form a biradical ($2:\text{CH}_2^* \rightarrow \cdot^*\text{H}_2\text{C}-\text{CH}_2^*$, which is in fact an excited state of ethene adsorbed on the gold surface), and propagation with adsorbed CH_2 molecules can take place. Radical disproportionation as termination step would afford methyl and vinyl end-groups:



Since the polymerization initiates at high energy defect sites on the surface, the film does not form uniformly on the surface. To overcome this, Guo and Jennings modified the gold-surface with copper and silver.⁶⁷ Polymer growth on these modified surfaces is linear with time and with copper the polymerization is faster than on the unmodified gold surface. Increasing the amount of silver inhibits the polymerization, probably due to coverage of the gold active sites.

In a later study, ethyl diazoacetate (EDA) was employed to obtain ester-functionalized polymer coatings. Homo-polymerization of this substrate was not possible, but when a mixture of diazomethane and EDA was used, a random copolymer was formed (incorporation of ester groups: 1-4%).⁶⁸ The polymer film thickness could be tuned by the EDA concentration and was much larger for the copolymer (up to several hundreds of nanometers). In the presence of EDA, the polymer growth is almost linear with time and does not slow down. EDA seems to act as a co-catalyst; although it enhances polymer growth and growth rate, it is incorporated in only small amounts. The growth of the film takes place at the gold surface interface and not at the solution-polymer interface.

Moreover, addition of radical inhibitors does not influence the reaction and added alkenes were not built in. Primary amines inhibit copolymerization, but do not affect the growth of polymethylene. This shows, in contrast to a former study by Tao and Allara *et al.*,⁶⁶ that radical or cationic polymerization mechanisms can not play a dominant role. Probably, two different mechanisms are active here; one is the homopolymerization of diazomethane which initiates fast and grows linearly and then slows down. The other is proposed to involve insertion copolymerization of diazomethane and EDA. The mechanism involves an adsorbed ethyl ester carbene species ($\text{Au}=\text{CHCO}_2\text{Et}$), which removes electron density from the gold surface by the electronegative ester group (Figure 2).

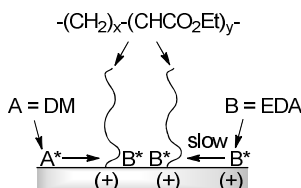


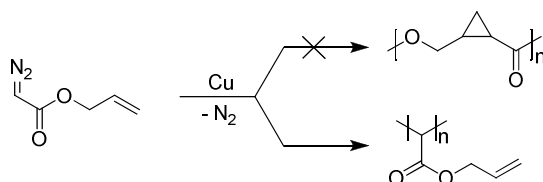
Figure 2. Schematic representation of electron-deficient gold surface by coordination of electronegative ester groups.

Electron-deficient gold atoms are believed to serve as reactive centre for insertion polymerization.⁶⁸ This is probably also the reason why the presence of copper atoms enhances the reaction. The electropositive copper atoms increase the interactions with the methyldiene units, and thereby shift the reaction from a biradical-type mechanism to an insertion-type mechanism, so that chain termination processes are suppressed.⁶⁷

1.4.3 Low molecular weight polymers/oligomers from polar functionalized diazo compounds (homogeneous processes)

Compared to unfunctionalized diazoalkanes, polar functionalized diazo compounds are much more challenging substrates in C1 polymerization. A few early reported examples of reactions of metal complexes with diazoesters show formation of only dimerization products dialkyl fumarate and maleate.^{59,64,69} However, already in 1909 Loose reported the reaction of Cu-bronze with EDA or methyl diazoacetate (MDA), leading to dialkyl maleate and fumarate and *possibly* higher oligomers.⁷⁰ Complete conversion of the starting material afforded the alkenes in 70% yield, but in addition a dark brown, highly viscous oil was obtained. It was suggested that this product is a trimer or even a higher oligomer, but at that time this could not be proven.

In 2002, Liu and co-workers found a polymer of carbalkoxycarbenes as an unexpected product when they attempted to perform copper-powder mediated cyclopropanation polymerization with allyl diazoacetate (Scheme 14).⁷¹ Analysis by NMR spectroscopy showed the absence of cyclopropane rings and with IR spectroscopy the absorption of a C=C double bond was observed. Instead of the expected cyclopropanation-polymerization a carbene-polymerization reaction had occurred. The polymer/oligomer with a molecular weight of 3000 Da (M_w) and a polydispersity of 1.2 was isolated as a solid.



Scheme 14. Synthesis of a polymer of carbalkoxycarbenes instead of cyclopropanation polymerization.

Since 2003, Ihara and co-workers have further investigated transition metal mediated polymerization reactions of diazocarbonyl compounds. A variety of new polymers/oligomers containing different functional groups were prepared. They called these procedures “poly(substituted methylene) synthesis”. The reactions involve (co-)polymerization of a variety of diazo compounds such as diazoacetates,^{72,73} saturated and unsaturated diazoketones with aliphatic or aromatic side groups,^{74,75} cyclic diazoketones,⁷⁶ bifunctional diazocarbonyl compounds⁷⁵ and diazoacetamides⁷⁷ (Figure 3) by mainly Pd^{II}-based catalysts.

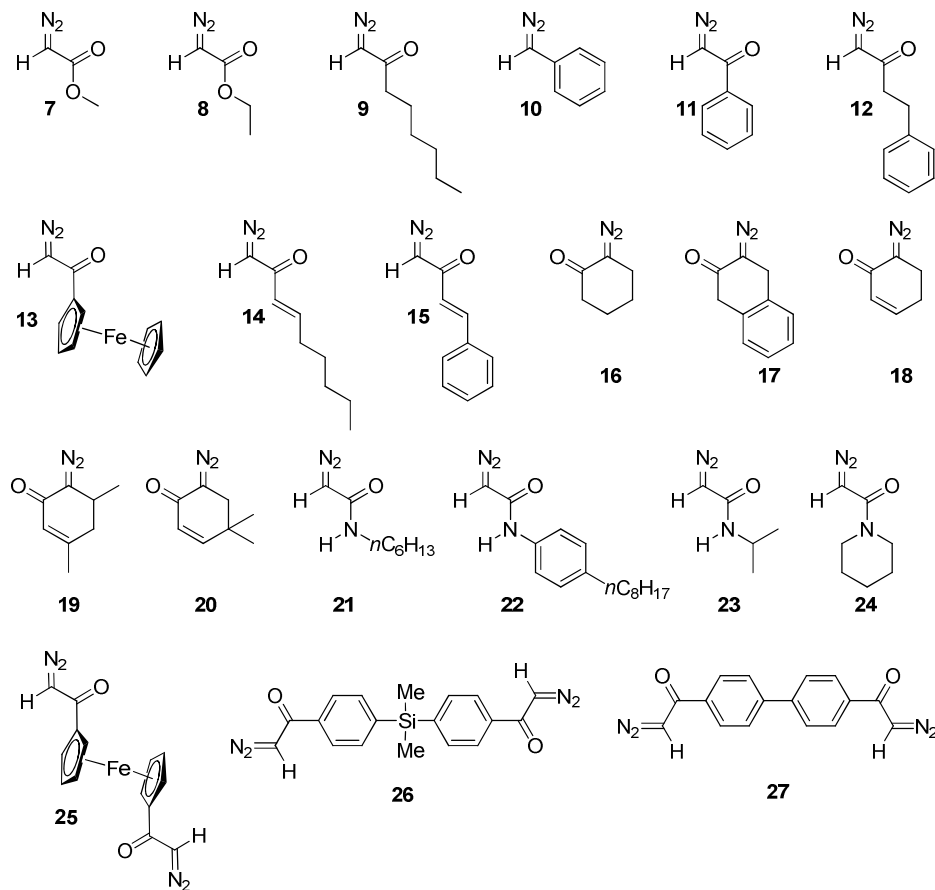


Figure 3. Diazo compounds used for “poly(substituted methylene) synthesis”.

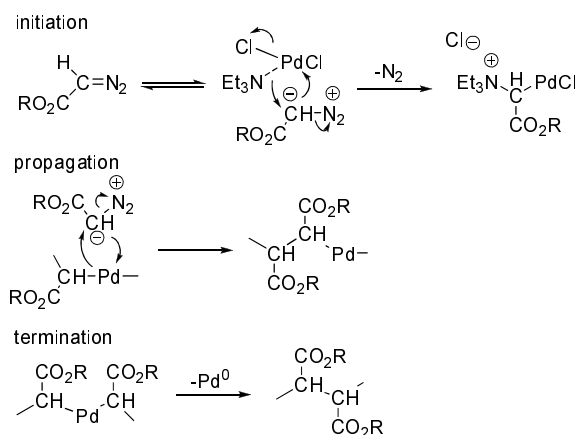
The first report deals with the polymerization of MDA (**7**) and EDA (**8**) by PdCl₂ affording low molecular weight polymers/oligomers in reasonable to good yields (M_n up to 750 Da, yields: 50-100%, see *e.g.* Table 2, entries 1 and 2).⁷² In the presence of an amine such as pyridine or triethylamine a polymeric product was obtained containing amine groups at both polymer ends. Spectroscopic data indicated that a polymethylene having ethoxycarbonyl substituents on all backbone

carbon atoms was formed. By MALDI-ToF mass spectrometry it was confirmed that the repeating unit is a carbene and not the dimerization product of two carbenes.

Table 2. Polymerization of diazo compounds with Pd and Pt-based catalyst systems (selected results)

Entry	Substrate	Catalyst	Yield (%)	M _n (Da)	M _w /M _n
1	7	PdCl ₂ + py	100	470	1.9
2	8	PdCl ₂ + py	100	700	1.8
3	9	PdCl ₂ (MeCN) ₂	13	890	1.3
4	11	PdCl ₂ (MeCN) ₂	25	420	1.4
5	12	PdCl ₂ (MeCN) ₂	16	650	1.3
6	13	PdCl ₂ (MeCN) ₂	39	490	1.5
7	14	PdCl ₂	46	2370	1.4
8	14	PtCl ₂	15	2440	1.3
9	14	PdCl ₂ (MeCN) ₂	50	2480	1.5
10	14	PdCl ₂ (MeCN) ₂ + py	22	2020	1.4
11	15	PdCl ₂ (MeCN) ₂	45	1720	1.3
12	18	PdCl ₂ (MeCN) ₂	24	1400	1.7
13	19	PdCl ₂ (MeCN) ₂	9	900	1.4
14	21	PdCl ₂ (MeCN) ₂	11	990	1.1
15	22	PdCl ₂ (MeCN) ₂	9	1890	1.1
16	10 + 8	PdCl ₂ (MeCN) ₂	28	750	1.3
17	14 + 10	PdCl ₂ (MeCN) ₂	31	1510	1.5
18	14 + 11	PdCl ₂ (MeCN) ₂	25	1690	1.2
19	14 + 12	PdCl ₂ (MeCN) ₂	27	1610	1.4
20	25 + 14	PdCl ₂ (MeCN) ₂	10	2580	1.7
21	25 + 15	PdCl ₂ (MeCN) ₂	29	1660	2.8
22	8	[IMesPd(NQ)] ₂ + NaBPh ₄	35	20700	1.5
23	8	[IPrPd(NQ)] ₂ + NaBPh ₄	34	24000	1.5

In the proposed mechanism, the reaction is initiated by nucleophilic attack of Et₃N on the α -carbon atom of the diazoacetate with formation of a metal-carbon bond (Scheme 15).



Scheme 15. Proposed mechanism for Pd-mediated polymerization of carbenes.

Propagation of the reaction is proposed to proceed *via* direct migration of the growing chain fragment to the α -carbon atom of the (coordinated) diazo compound with elimination of N₂. Thus, according to the authors the reaction does not proceed

via discrete carbene intermediates, which contrasts with quite some available mechanistic information pointing to carbenoid intermediacy in insertion reactions with diazo compounds, also for Pd (see section 1.5). The detection of an amine group at both ends of the polymer indicates that perhaps two polymer chains are formed on the same Pd center, and chain termination may have occurred by reductive elimination of two chains.

In later studies, mainly $\text{PdCl}_2(\text{MeCN})_2$ was used instead of PdCl_2 because of its better solubility in organic solvents. It appeared that the addition of pyridine, which gave good results in the polymerization of diazoacetates **7** and **8**,⁷² gave lower yields in polymerization of unsaturated diazoketones (see *e.g.* Table 2, entries 9 and 10).⁷⁴ Furthermore, indication of a chain-transfer mechanism and the fact that PdCl_2 without addition of amines affords polymers as well suggests that the reaction is not initiated by amines, but involves the attack of weak nucleophiles such as H_2O , MeCN or monomer. The reaction can also be initiated with Pd^0 sources such as $\text{Pd}_2(\text{dba})_3(\text{CHCl}_3)$, but the authors propose that these are oxidized to Pd^{II} *in situ*. This is in contrast to a recent report by Ortuño *et al.*, which shows that polymerization of diazomethane can be effected by Pd^0 nanoparticles formed *in situ* from $\text{Pd}(\text{OAc})_2$.⁷⁸

Pd mediated polymerization of other diazo compounds (especially diazoketones such as **14**) frequently led to incorporation of azo functionalities in the main chain, in varying amounts depending on the structure of the substrate. Some of these polymers are thus rather ill-defined random co-polymers, comparable to those observed in Al-mediated reactions (Scheme 5a, section 1.2.1).

The reactivity of other late transition metal halides towards monomer **14** was also investigated (*e.g.* FeCl_3 , RuCl_3 , CoCl_2 , RhCl_3 , NiBr_2 and PtCl_2), but only PtCl_2 afforded polymers/oligomers with similar molecular weight ($M_n = 2440$ Da), though lower yield (15%) compared to PdCl_2 ($M_n = 2370$ Da, 46%) under similar conditions (Table 2, entries 7 and 8). Also the previously mentioned incorporation of azo groups in the polymer obtained with PtCl_2 is higher than with PdCl_2 (Scheme 5, section 1.2.1).

Some diazoketones proved more difficult to polymerize with the Pd-based catalysts. For example, saturated diazoketones **9** and **12** can be polymerized in only low yields (13% with $M_n = 890$ Da and 16% with $M_n = 650$ Da, respectively, entries 3 and 5).⁷⁴ Under the same conditions and with the same catalyst, $\text{PdCl}_2(\text{MeCN})_2$, unsaturated monomers **14** and **15** are polymerized in 50% ($M_n = 2480$ Da) and 45% ($M_n = 1720$ Da) yield, respectively (entries 9 and 11). The reason for the lower reactivity of the saturated substrates (**9** and **12**) compared to the diazoketones with a double bond next to carbonyl moiety (**14**) is not clear.

Polymerization of diazoketone **11** leads to very low molecular weight products in low yields ($M_n = 420$ Da, 25% yield, entry 4), which is explained by steric

hindrance at the metal during the polymerization.⁷⁴ Similar behavior is observed for ferrocenyl substituted diazoketone **13**; this substrate is oligomerized in moderate yield (39%, entry 6), but the low molecular weight corresponds with only dimers or trimers.⁷⁵ Cyclic diazoketones **16**, **17** and **20** can not be homo-polymerized at all.⁷⁶ Reacting unsaturated cyclic diazoketones **18** and **19** with $\text{PdCl}_2(\text{MeCN})_2$ does afford polymers, but in low yields (24% yield, $M_n = 1400$ Da and 9% yield, $M_n = 900$ Da, respectively, entries 12 and 13). The content of azo groups in the polymers of cyclic diazoketones is much higher (~25%) than for acyclic diazoketones (<10%). The low molecular weight polymer of monomer **18** could be partially (~40 mol%) post-modified by reacting it with the nucleophiles *n*-BuLi, PhLi or $\text{NaCH}(\text{CO}_2\text{Et})_2$.

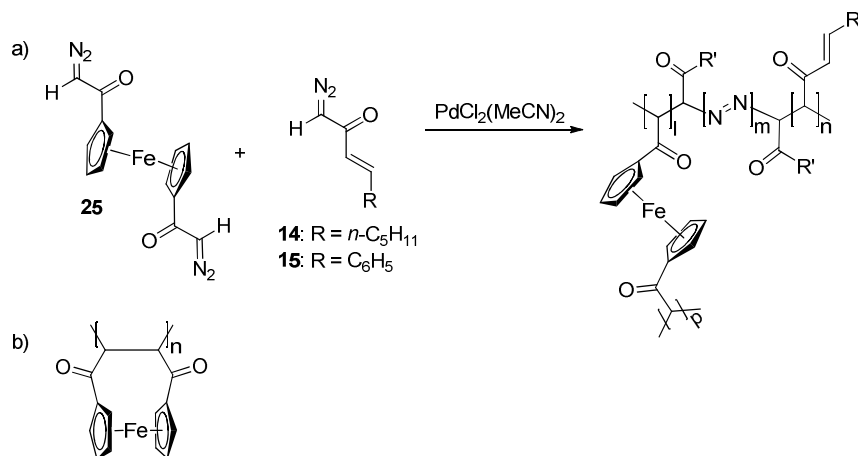
To broaden the scope of the reaction further, Ihara and co-workers polymerized diazoacetamides **21** and **22**, affording low molecular weight polymers/oligomers in low yield (11%, $M_n = 990$ Da and 9%, $M_n = 1890$ Da, respectively, Table 2, entries 14 and 15) with a relatively high azo group content (~20%).⁷⁷ Monomers **23** and **24** could not be homo-polymerized, probably due to steric crowding at the metal centre during polymerization.

The reactivity of some of the tested diazo compounds towards the catalyst was low and although some could not be homo-polymerized, co-polymerization of various combinations of monomers was investigated. The relative reactivity of the different monomers was mostly expressed in the composition of the corresponding co-polymers. For example, co-polymerization of **14** with monomers **11** or **12** affords random co-polymers/co-oligomers in low yields (~25% with $M_n \sim 1600$ Da, see *e.g.* Table 2, entries 18 and 19) with low incorporation of **11** and **12** compared to the feed ratio.⁷⁴ Also phenyldiazomethane (**10**) could be co-polymerized with **8** and **14** (yields: up to 38% with M_n up to 2000 Da, see *e.g.* entries 16 and 17).⁶⁵ The incorporation of the monomers corresponds more or less to the feed ratio, but there is also a significant amount of azo groups incorporated in the polymers. Monomers found to be unsuitable for homo-polymerization could be co-polymerized; **16**, **20**, **23** and **24** with **15** and **17** with **14** (M_n up to 1400 Da).^{76,77} Also here the incorporation of the less reactive monomers is low.

If the reaction follows an insertion-type mechanism (either as proposed by the authors in Scheme 15, or *via* discrete carbene intermediates as shown in Scheme 12), it should be possible to co-polymerize diazocarbonyl compounds with other monomers that react *via* insertion into the Pd-C bond. Therefore, Ihara and co-workers examined the co-polymerization of diazocarbonyl compounds with phenylacetylene, 1-heptyne and *t*-butyl isocyanide.⁷⁹ In the co-polymerizations of **14** with phenylacetylene or **15** with 1-heptyne a polymer containing both monomers was formed with a lower incorporation of the acetylenes than predicted by the feed ratios. Co-polymerization of EDA (**8**) with 1-heptyne or phenylacetylene results in low molecular weight oligomers with a composition similar to the feed ratio in low

yields (~20% yield, M_n ~1000 Da and ~30% yield, M_n ~700 Da, respectively). *t*-Butyl isocyanide was co-polymerized with **15** mediated by $\text{Ni}(\text{acac})_2 \cdot 2\text{H}_2\text{O}$ with two equivalents of (*S*)-(-)-1-phenylethylamine. The incorporation of both monomers was similar to the feed ratio, but the molecular weights were again low (M_n ~ 800 Da). On the basis of elemental analysis the amino end-group and incorporation of azo units were determined. The fact that diazocarbonyl compounds can be co-polymerized with acetylenes and isocyanides supports an insertion-type mechanism.

In an attempt to synthesize cross-linked polymers from diazo compounds, Ihara and co-workers employed diazoketones **25**, **26** and **27** (Figure 3).⁷⁵ Compound **25** was co-polymerized with **14** and **15** (Scheme 16a), but the products were still soluble in chloroform (entries 20 and 21, feed ratio: 1 : 3), meaning that probably almost no cross-links were formed. A possible explanation is the formation of mainly linear polymers by intramolecular cyclization of **25** (Scheme 16b). Also significant azo group incorporation (10-16%) was observed by elemental analysis.



Scheme 16. a) Co-polymerization of bifunctional diazoketone **25** with **14** and **15**; b) formation of linear polymers by intramolecular cyclization of **25**.

The more rigid bifunctional diazoketones **26** and **27** were more suitable for establishing cross-links; solid products insoluble in chloroform were obtained in high yields (64-96%) by co-polymerizing **26** or **27** with *e.g.* **14** (feed ratio: 1 : 3). In these co-polymers the azo group content is somewhat lower: up to 5%.

In 2009, Ihara *et al.* communicated the polymerization of EDA by palladium complexes of NHC-ligands in the presence of either NaBPh_4 or NaBARF_4 (Figure 4).⁷³ With these catalyst systems remarkably higher polymer molecular weights could be obtained than reported before (up to 24,000 Da; entries 22 and 23, Table 2). After purification the products were isolated as colorless solids.

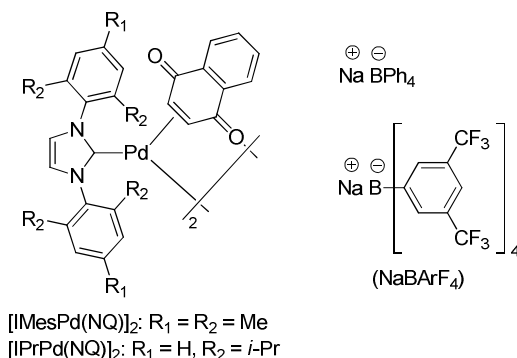


Figure 4. Pd-complexes of NHC-ligands with borate reagents used for polymerization of EDA.

In the ^1H and ^{13}C NMR spectra the backbone signals of the polymer are broad, but three different peaks could be distinguished. These three peaks were ascribed to triads and the authors believe that these findings show that with these Pd-NHC-complexes they can influence the polymer tacticity. MALDI-ToF mass spectrometry analysis of the polymers showed the presence of Na-adducts of species with a repeating unit of 86 Da, corresponding with $:\text{CHCO}_2\text{Et}$, and as end-groups H and a $\text{C}=\text{C}$ moiety. In the proposed mechanism the reaction is initiated by cationic $[(\text{NHC})\text{Pd}^{\text{II}}\text{H}]^+$. The authors propose that this species is formed in the first step from the Pd^0 -complex and THF, with or without the assistance of the borate reagent.⁷³ The propagation steps are similar to the ones described before (see Scheme 15). Subsequent termination by β -H elimination explains the unsaturated end-groups of the polymers. With these catalyst systems, incorporation of azo groups into the polymers does not take place.

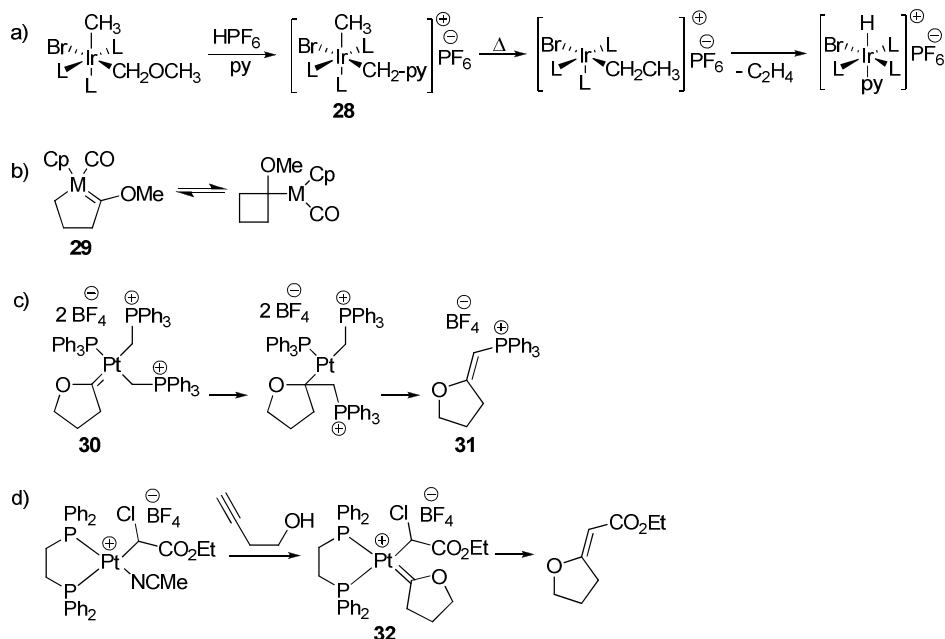
In general, the Pd-mediated polymerization of diazo carbonyl compounds reported by Ihara *et al.* can be applied for a broad range of diazo compounds, but affords only low molecular weight (co-)polymers/oligomers (M_n up to 2600 Da and with the Pd-NHC-systems up to 24,000 Da) and frequently leads to incorporation of substantial amounts of azo-functionalities in the main-chain. The oligomers are mostly isolated as brown viscous oils (sometimes brown solids) and all show broad signals in their NMR spectra, indicating that they are most likely atactic.

1.5 Mechanistic information from synthetic model reactions relevant for C1 polymerization

The above sections clearly show that in terms of functional group tolerance, transition metal catalyzed polymerization of (functionalized) diazo compounds outperforms all other C1 polymerization techniques. There is still much to gain in this field though, especially in improving the yields and gaining control over the molecular weight (distribution) and the polymer stereoproperties. For that reason we need a full detailed mechanistic insight in all possible initiation and termination

processes (M_w and PDI), possible side-reactions, as well as an understanding of factors influencing the stereoselectivity of the propagation steps. In this section we thus summarize the available (although limited) mechanistic information from experimental model studies.

In most cases C1 polymerization reactions from diazo compounds are proposed to proceed *via* migratory insertion involving carbene intermediates. *Cis*-carbene-alkyl transition metal complexes are very reactive, and since they are expected to undergo rapid alkyl migration to the carbene ligand, they are intrinsically difficult to observe. Nevertheless, with some tricks used to slow-down or prevent this elementary step in model reactions, such species could be isolated. Such methods include: (I) trapping of the metal-carbenoid with labile nucleophiles, (II) inducing ring-strain in the migration product, and (III) using electron donating and/or sterically encumbered substituents on the carbene ligand to slow down or prevent the insertion process. Method I was applied in model studies by Thorn *et al.* where a carbene unit (generated by MeOH elimination from a protonated Ir^{III} -CH₂OMe complex) was trapped with pyridine (**28** in Scheme 17a).⁸⁰



Scheme 17. Isolated late transition metal alkyl carbene complexes and the products of carbene migratory insertion and β -hydrogen elimination (L = PMe₃, py = pyridine, Cp = cyclopentadienyl, M = Fe or Ru).

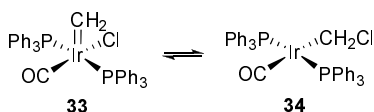
The pyridine-trapped methylene complex **28** (*N*-ylide) is stable at room temperature, but at 60°C it eliminates ethylene and forms an Ir-hydride complex. The reaction most likely proceeds *via* alkyl migration to a discrete carbene ligand, followed by β -hydrogen elimination. When the starting material was reacted with BrCH₂OMe, a

similar reaction took place and the ethyl complex could be isolated before β -hydrogen elimination occurred. Reactions with the analogous Rh^{III} complex led to similar products, but no intermediates could be detected.⁸¹

Jones and co-workers prepared some stable transition metal *cis*-carbene-alkyl complexes of iron and ruthenium (**29** in Scheme 17b) using ring-strain (method II).⁸² At room temperature, the iron complex undergoes migratory insertion to form the strained cyclobutane ring, but the ruthenium analogue does not react at all, not even after 3 days at 100°C. Migratory insertion of the carbene in the iron complex was estimated to be at least 10^7 times faster than for its ruthenium analogue. Generally, kinetic barriers for second-row transition metals are higher than for first row transition metals.

Another example of an isolated late transition metal alkyl carbene complex was reported by Stryker *et al.*⁸³ Platinum bis(phosphonium ylide) complex **30** (Scheme 17c) could be isolated and structurally characterized, because the carbene ligand is electronically stabilized and somewhat sterically protected (method III). However, upon heating the phosphonium salt **31** is formed by migration of a phosphonium ylide ligand to the Fischer carbene in **30**, followed by β -H elimination. A similar reaction was observed for the isolated *cis*-alkyl-carbene complex **32**. Interestingly, **32** was synthesized by reaction of EDA with $(\text{dppe})\text{PtCl}_2$, most likely *via* carbene insertion into the metal-chloride bond, followed by carbene formation with 3-butynol (Scheme 17d).⁸⁴ The overall reaction could be performed 'catalytically', with almost two turnovers.

Experiments of Mango and Dvoretzky clearly point to the intermediacy of carbene ligands in Ir catalyzed polymerization of diazomethane. Reaction of $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$ with diazomethane in diethyl ether leads to polymethylene *via* a detectable intermediate at low temperatures.⁸⁵ Elemental analysis and IR spectroscopy of the intermediate are consistent with either the iridium methylene complex **33**, or the insertion product **34** (Scheme 18).



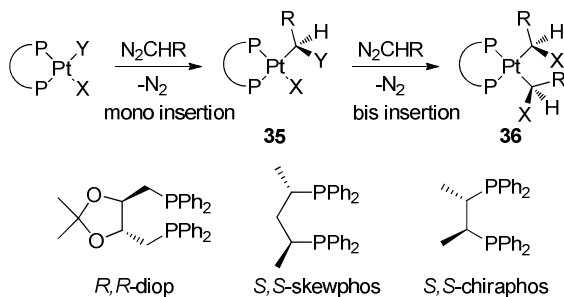
Scheme 18. Proposed structures for the reaction product of $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$ with diazomethane.

Complex **33** has a methylene moiety as a fifth ligand, *cis* to the chloro ligand. Chloride migration to this fragment leads to **34**. Interestingly, in the presence of styrene the methylene moiety is transferred to the styrene double bond, leading to cyclopropanation. The spectroscopic data and the behavior of the complex in solution suggest that in the solid state the complex exists in its more stable form **34**, while its reactivity in solution is determined by **33**. Chloride migration to the carbene ligand thus seems to be reversible, and it seems most logical that the

formation of **34** from $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$ and diazomethane also proceeds *via* the same discrete carbene intermediate **33**.

Similar conclusions were gathered in carbene migratory insertion reactions observed for palladium–halide complexes. Reaction of $[(\text{L})\text{Pd}^{\text{II}}(\text{Cl}_2)]$ with diazomethane leads to insertion of ‘methylene’ into both Pd–Cl bonds.⁸⁶ The isolable products are not very stable, and tend to eliminate ethene with regeneration of the starting bis-halide complex. This suggests that chloride-to-carbene migration is reversible also for Pd, thus providing a pathway for ethene elimination (similar to the equilibrium between **33** and **34** in Scheme 18).

Similar reactions were reported for the analogous platinum complexes $[(\text{L})\text{Pt}^{\text{II}}(\text{X}_2)]$ (L = 1,5-cyclooctadiene or a chelating diphosphine ligand; X = Cl, Br or I). Reaction with close to stoichiometric amounts (~1-8 equivalents) of substituted and non-substituted diazo compounds generally leads to a single ‘carbene’ insertion into one or both of the metal-halide bonds. With diazomethane usually insertion into both metal-halide bonds occurs (**36**, see Scheme 19, $\text{R} = \text{H}$), while with substituted diazo compounds insertion into only one of the two halides occurs in most cases (**35**, $\text{X} = \text{Y} = \text{halide}$).^{87,88} Reactions with substituted diazo compounds and chiral diphosphine ligands leads to moderate to low diastereoselectivity (*d.e.* = 0-88%), which could not be increased by using a chiral diazo compound (*R,R*-menthyl diazoacetate).^{89,90} Insertion into the second metal-halide bond with substituted diazo compounds is much slower, but can occur with longer reaction times.⁹¹



Scheme 19. Mono and bis insertion products of reaction of Pt^{II} complexes with diazo compounds and chiral diphosphine ligands (X = halide, Y = halide or methyl).

The above model systems show that metal-carbon ‘carbene insertion’ is a viable chain-growth propagation mechanism. Although moderate, the reactions reported by Pringle and Bergamini *et al.* also reveal an influence of the auxiliary ligands on the stereochemical outcome of the ‘carbene insertion’ process.^{89,90} This is relevant for the development of stereoregular C1 polymerization reactions from functionalized diazo compounds.

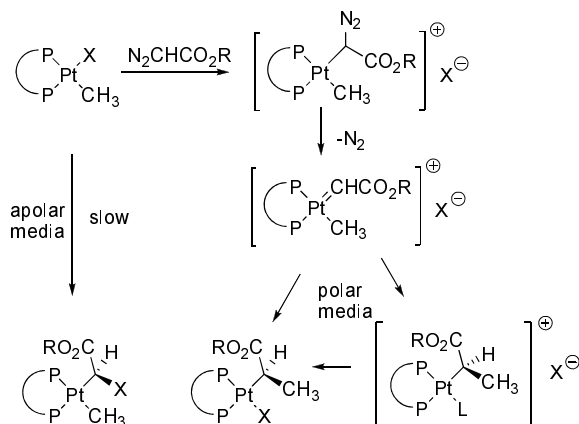
The above model systems further show that ‘carbene insertion’ reactions into metal-halide or other metal-ligand bonds is a viable chain-initiation mechanism, thus creating the required ‘growing-chain alkyl’ for C1 polymerization. At the same time, these model systems reveal that β -hydrogen elimination occurs easily, which is a likely chain termination/transfer pathway in the polymerization reactions. For the above model systems the ‘carbene insertion reactions’ are rather slow, which is quite remarkable for ‘unsaturated’ (16 valence electron) square planar d^8 metal complexes. The observed β -elimination reactions thus occur with competing rates. Combined, this suggests that for the formation of long polymers perhaps an additional vacant site (*i.e.* a 3-coordinate complex) is required for faster insertion than chain-transfer/termination.

Model reactions reported for the mixed Pt-alkyl-halide⁹²⁻⁹⁴ or Pt-aryl-halide⁹⁵ complexes provide additional hints in this direction. Reaction of [(chiral diphosphine)Pt^{II}X(Me)] with different diazo carbonyl compounds in polar solvents generally results in formation of Pt-C insertion products [(*S,S*-diop)Pt^{II}(X)(CH(Me)R)] (R = CO₂Et, X = Cl or Br) (**35**, Scheme 19, X = halide, Y = Me) with rather low diastereoselectivities.^{92,93} However, carbene insertion into the Pt-X and Pt-C bonds compete for these species, and the chemoselectivity strongly depends on the polarity of the solvent. Higher chemoselectivities towards Pt-C insertion were observed in polar solvents (MeCN, DMSO), while apolar solvents (benzene, CHCl₃) favor insertion into the Pt-X bond. With stronger Pt binding halides (I > Br > Cl), the chemoselectivity shifts from Pt-C insertion towards Pt-halide insertion (yields of Pt-C insertion products: 100%, 80% and 55% for X = Cl, Br and I, respectively). Interestingly, also decreasing the bite angle of the (diphosphine)Pt^{II} complex and the use of diazoesters instead of diazoketones favors Pt-C insertion over Pt-X insertion,⁹⁰ thus suggesting that ligand modification and substrate variation may have a substantial influence on the rate and selectivity of transition metal catalyzed C1 polymerization reactions of diazo compounds.

In polar solvents only the chiral diphosphine ligand controls the diastereoselectivity of insertion, while in apolar solvents the diastereoselectivity depends also substantially on the nature of the halide.⁹⁰ The authors further proved that the Pt-X insertion products are not intermediates towards the Pt-C insertion products, and Pt-C and Pt-X insertions must thus take place *via* different pathways.

All these observations point to the mechanism depicted in Scheme 20. Metal-carbene formation is preceded by dissociation of the halide to form a 3-coordinate intermediate to allow coordination of the diazo substrate. In the next step, carbon-carbon bond formation by methyl to carbene migration takes place in polar solvents, where the halide is sufficiently solvated. Slow metal-carbene formation from the diazo compound and the 4-coordinate square planar complex occurs without halide dissociation in apolar solvents (especially for the stronger binding halides). The

mechanism is consistent with independent pathways for Pt–C and Pt–X bond insertion. The formation of the carbene species is easier when X is a better leaving group, which explains the trend in selectivity concerning the halides. In polar solvents, halides have no influence on the diastereoselectivity because the halogen is lost before the chiral center is formed.



Scheme 20. Proposed mechanism for carbene migratory insertion into Pt–C and Pt–X bond.

In 1986, McCrindle *et al.* reported repetitive insertions of carbenes from diazomethane into the Pt–C bond of [(cod)PtCl(Me)], resulting in formation of ethyl and propyl platinum complexes.⁹⁶ The proposed mechanism is similar to the one shown in Scheme 20. The authors defined the requirements for an effective catalyst for polymerization of diazomethane; a suitable migrating group (growing chain alkyl) and intermediate carbenes that undergo migratory insertion rather than being captured by an anion. This hypothesis was tested by abstracting the chloride from the platinum before reaction with diazomethane. Indeed, the use of the 3-coordinate species [(cod)Pt(Me)]⁺ in reaction with diazomethane led to formation of a large amount of polymethylene (along with free 1,5-cyclooctadiene and platinum metal). In another experiment, a chelating phosphine ligand was used in order to stabilize the carbene species. In the reaction of [(1,3-bis(PPh₂)propane)PtCl(Me)] with diazomethane, Pt–(CH₂)_n–Me species were observed (*n* ~ 8). These results strengthen the above hypothesis that 3-coordinate alkyl d⁸ transition metal complexes (*e.g.* L₂Pd^{II}–R) are the active catalysts in late transition metal mediated C1 polymerization of diazo compounds (see also sections 1.4.3).

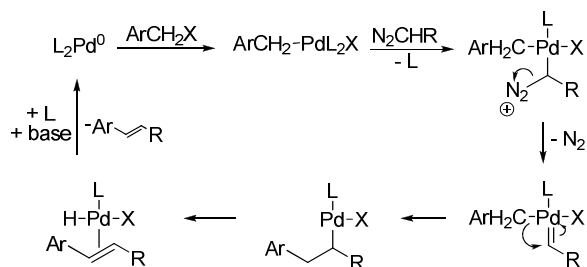
Summary of the mechanistic implications

We can summarize the lessons learned from these model reactions in the context of their mechanistic implications for late transition metal mediated C1 polymerization of diazo compounds as follows: (A) Repetitive ‘carbene insertions’ in transition-metal carbon bonds seems a viable chain-growth mechanism. (B) The

stereochemical outcome of the insertion steps is influenced by the auxiliary ligands, providing opportunities for stereoregular polymerization reactions. (C) Chain-initiation *via* nucleophilic attack of an external nucleophile, or migration of a coordinated anionic ligand, to a carbene ligand seems a viable chain-initiation mechanism. (D) Chain-termination/transfer with these late metals most probably proceeds *via* β -hydrogen elimination. (E) Square-planar 16 valence electron d^8 species are not unsaturated enough, and require an additional vacant site (*i.e.* 3-coordinate complexes) for 'carbene formation' from diazo compounds at appreciable rates.

1.6 Catalytic C–C bond forming carbene insertion reactions leading to products other than polymers

A large ratio of the carbene insertion rate constant over the chain-termination/transfer rate constant (k_p/k_t) is an important parameter for tuning the reaction to form high molecular weight polymers in C1 polymerization. Smaller k_p/k_t ratios generally lead to unwanted oligomeric or dimeric products. However, slow carbene insertion can also be beneficial for the development of new reactions, providing opportunities to discover new catalytic C–C bond forming methods. This was nicely demonstrated by Van Vranken, Solé and their co-workers. They employed carbene insertion reactions into Pd–C bonds as a new tool in catalytic C–C bond forming reactions. The Van Vranken group first applied trimethylsilyldiazomethane (TMSDM) as a carbene precursor to prepare styrene derivatives from benzyl halides.⁹⁷ The reaction is believed to proceed as shown in Scheme 21.⁹⁸



Scheme 21. Proposed mechanism for carbene insertion into Pd–benzyl bonds.

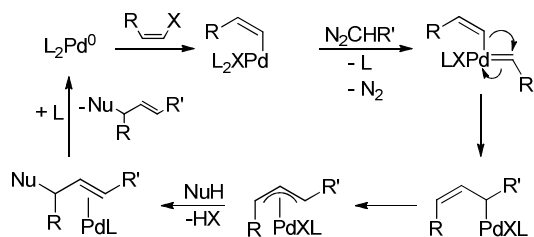
After oxidative addition of the benzyl halide, a metal carbene species is formed from the diazo compound, which undergoes migratory insertion into the Pd–C bond of the benzyl ligand. Finally, β -hydrogen elimination results in the styrene derivatives and a hydride complex. The latter is deprotonated with an external base to reform the starting Pd^0 complex. As such, this reaction resembles Heck-type C–C bond formations, but uses carbenes instead of olefins. Although the products of

these reactions (Scheme 21) are also accessible *via* traditional Heck coupling reactions of aryl halides with acrylates, this new reaction potentially has a larger substrate scope; various carbene sources with different R-groups are commercially available or easily prepared according to known procedures.

The SiMe₃ functionality introduced in the above method (by using TMSDM) is easily lost through desilylation,⁹⁷ but ester functional groups introduced by using for example ethyl diazoacetate (EDA) as a substrate remain in the product; ethyl cinnamates with different substituents on the phenyl ring were obtained in yields up to 74%.⁹⁸

Insertion of carbenes from EDA or TMSDM into Pd–Ar bonds was demonstrated by Solé *et al.*, affording new azapalladacycles⁹⁹ and by Van Vranken *et al.* resulting in indenylsilanes.¹⁰⁰ In both studies the authors describe side reactions with TMSDM due to desilylation. Wang *et al.* reported the Pd catalyzed cross-coupling of carbenes from α -substituted diazocarbonyl compounds with boronic acids, affording 2-phenylacrylates.¹⁰¹ Barluenga and co-workers showed that cross-coupling can also be performed with *N*-tosylhydrazones and aryl halides, leading to polysubstituted olefins.¹⁰² The *N*-tosyl-hydrazone is believed to decompose and generate a diazo compound *in situ*, which participates in the reaction (similar to those depicted in Scheme 21).

In a recent study, Van Vranken and co-workers synthesized vinyl silanes by reacting vinyl halides, TMSDM and a nucleophile (amine¹⁰³ or stabilized carbon¹⁰⁴ nucleophiles) in the presence of a Pd catalyst. In the mechanism the vinyl halide is oxidatively added to Pd, after which the carbene is formed (see Scheme 22). Migratory insertion of the carbene into the Pd–vinyl bond yields an η^1 -allyl complex, which can form an η^3 -allyl complex. Attack by the nucleophile leads to the product (Scheme 22). The use of EDA as a carbene precursor and amines as nucleophiles yields α,β -unsaturated γ -amino acids in one step.¹⁰⁵



Scheme 22. Proposed mechanism of synthesis of vinyl silanes (R' = SiMe₃) and γ -amino acids (R' = COOEt, Nu = amine).

1.7 Conclusions

C1 polymerization provides interesting opportunities to prepare new polymers which are not (easily) accessible by conventional olefin polymerization techniques. As such, Lewis acid and transition metal mediated polymerization of carbenes (from their precursors, such as diazo compounds or sulfur ylides) provide valuable alternative synthetic protocols in polymer synthesis.

Scope & Limitations

Although C1 polymerization is a very promising research area, our mechanistic understanding and the developments and applications of most of the reported C1 polymerization techniques are still far from mature. For many of the reported C1 polymerization techniques it proved difficult to obtain high molecular mass polymers, and control over the polymer tacticity is often poor. Another limiting factor in this research field is the limited stability or poor accessibility of some of the applied C1 monomer precursors. Carbon functionalized sulfur ylides are synthetically not easily accessible and diazoalkanes are potentially explosive. On the other hand, a wide variety of diazoketones and diazoesters, which are much more stable than diazoalkanes (and therefore relatively safe to work with, even in large scale applications) are readily available. However, so far only a limited amount of catalysts proved capable of polymerizing such substrates and the products are usually atactic and of low molecular weight.

The Lewis acid mediated reactions are valuable from different perspectives, as these 'living polymerization' techniques allow the preparation of various telechelic polymethylenes. Especially the boron-mediated 'polyhomologation' reaction with sulfur ylides is an elegant procedure to make high molecular weight polymethylenes, which at the same time makes it possible to introduce a wide variety of specific functional groups at both polymer chain-ends in a controlled fashion. Thereby a large polymer structural diversity becomes possible, such as tris-polymethylene substituted alcohols, bis-polymethylene substituted adamantanes, cyclic polymethylenes and a variety of block-copolymers. Such control over (both) chain-end functionalities is difficult to achieve with traditional olefin polymerization, if not impossible.

Lewis acid mediated C1 polymerization techniques do not allow the polymerization of polar functionalized C1 monomers, but this is possible with some late transition metal C1 polymerization catalysts. Several homogeneous and heterogeneous catalysts are capable of producing polymers from a variety of diazo compounds.

Related carbene insertion reactions are also of interest for the development of new C–C bond forming catalytic reactions. Reactions related to traditional Pd cross couplings, but using carbenoid precursors replacing the olefinic substrates are examples of such new developments.

1.8 Outline of this thesis

A major challenge in traditional olefin polymerization is the synthesis of stereoregular polymers from polar functionalized monomers. C1 polymerization techniques could offer interesting possibilities to prepare *stereoregular* polymers with a densely functionalized main-chain structure. To achieve this, a better mechanistic understanding of the known transition metal mediated reactions is required to bring these reactions to the next higher level. Especially control over the stereoproperties of the polymers and the chain termination and/or chain transfer processes is needed. This thesis describes the development of Rh-mediated carbene polymerization methodologies for the preparation of unprecedented stereoregular and highly functionalized polymers.

In Chapter 2 the Rh-mediated polymerization of ‘carbenes’ from diazoesters will be introduced. This method leads to highly *stereoregular* and high molecular weight polymers with an ester group on *every* carbon of the carbon-chain. The stereoproperties of the polymer are determined by chain-end control, resulting in a *syndiotactic* polymer. The method is not only limited to ethyl diazoacetate; also other diazoesters can be homo-polymerized.

In the third Chapter supramolecular ligands are employed in an attempt to steer and control the carbene polymerization reaction. Supramolecular assemblies of [(cod)(NHC)Rh] complexes with Zn^{II}-templates are reacted with ethyl diazoacetate. Higher molecular weight polymers are obtained with these catalysts, but the effect of the Zn^{II}-templates is general; without the formation of the assemblies the same results are observed.

A study into the mechanism is discussed in Chapter 4. Ligand variation in combination with the results described in Chapters 2 and 3 leads to the conclusion that the active species for the polymerization is stabilized by the diene ligand. Kinetic experiments show low initiation (1-5% of the added pre-catalyst becomes active in the polymerization) for the Rh(diene)-catalyst systems described in the Chapter. Computational investigations provide an insight in the propagation steps and an explanation for the syndiospecificity of the carbene insertion polymerization reaction.

Chapter 5 describes an approach to decrease side product formation. The use of Me₂cod-based Rh precursors leads to very high molecular weight polymers. Remarkably, excellent polymer yields are attainable upon ‘aging’ these catalysts for prolonged times in air.

The investigations into initiation, termination and chain-transfer mechanisms are discussed in Chapter 6. Several Rh-alkyl/aryl complexes are evaluated in the polymerization reactions and end-group analysis of both the polymeric and oligomeric products of the reaction is described. Several species turn out to be active in Rh-mediated carbene transformations to dimers, oligomers and polymers, which adds to the complexity of these reactions.

In the last Chapter the synthesis and characterization of syndiotactic copolymers of different diazoesters is described. The formation of random and block copolymers from these diazoesters is confirmed by different techniques; NMR spectroscopy, size-exclusion chromatography, thermal analysis and 2D liquid chromatography. The thermal and mechanical material properties of the homo- and copolymers, investigated by several techniques (thermo gravimetric analysis, differential scanning calorimetry, polarizing optical microscopy, dynamic mechanical thermal analysis), are also included in this Chapter.

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