Inorganic and Organometallic Macromolecules

Design and Applications

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Editors

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Preface

Polymeric materials of the 21st century often contain atoms that are not present in traditional polymers. Polymers containing nontraditional atoms are now of interest because of their unique properties. This book demonstrates the breadth of these properties and some of the specialized analytical techniques that have been developed to characterize them.

Chapters 1, 2, 3, 4 and 7 emphasize the emerging special properties of materials dealing with the transmission of light for the purpose of communication, as well as other efforts. Later chapters deal with the use of materials in treating a variety of disease-causing microbes—including viruses responsible for pandemic herpes and the common cold (Chapter 8), cancers (Chapter 11), and bacterial infections (Chapter 17). The interaction of these materials for future biological investigations is investigated in Chapters 5 and 6.

Chapter 12 provides a comprehensive review of the application of Mössbauer spectroscopy to metal-containing polymers and Chapter 13 reviews the application of a new mass spectrometry technique. The use of metal-containing polymers as catalysts is described in Chapters 1, 9, and 10. Their use as precursors for advanced ceramics (Chapter 14), high temperature materials (Chapter 15), and flame retardants (Chapter 16) is also discussed. The unusual property of selected materials to spontaneously form fibers is described in Chapter 18.

This book includes a cross-section of novel polymeric materials containing nontraditional atoms and emphasizes current chemical, biological, engineering, ceramic, and optical areas of application. It is intended for those interested in the general areas of biomedicine, catalysis, electronics and light, thermal stability, and analysis of materials. The polymers reported in this volume represent early research but are inidicative of future application.

Contents

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Synthetic Versatility and Structural Modularity in Organometallic Polymers

Andrew J. Boydston and Christopher W. Bielawski

1 Background

With regard to tunability within a functional material, there are two primary areas of general discussion: (1) versatile synthetic strategies and (2) breadth of compatible structural features within the monomeric scaffold. These two issues rarely avoid some degree of overlap, yet a universal solution to both within any polymer design is nontrivial. Synthetic versatility can be further broken down into having either multiple access routes to obtaining the general monomer template or having a versatile and multifunctional monomer that can partake in more than one type—or in mechanistically distinct—polymerizations (e.g., copolymerizations) with high control. Structural modularity is inherently dependent on several factors: The polymerization method, the stability of the metal center, and the location of the metal's center (i.e., whether main- or side-chain metal incorporation). However, assuming general compatibility of the reaction conditions with the functional groups desired, the monomer design should accommodate installation of said groups.

Synthetically, there are a handful of methods for preparing main-chain organometallic polymers. This chapter provides an introduction to the methods that involve homo- and copolymerization of organometallic monomers, copolymerization of organometallic with organic monomers, and copolymerization of inorganic reagents with organic monomers such that those bonds formed to the metal involved are the ones that lead to polymer formation. There are multiple strategies for each type

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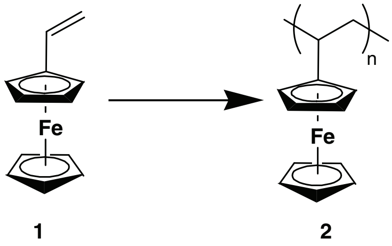
of polymerization method and additional details can be found in later chapters. Each method of polymer formation has been studied for years. Although many intricate details could be elaborated, for the purposes of this chapter only a brief overview will be given.

1.1 Polymerizations of Organometallic Monomers

Synthesis of functionalized organometallic compounds is often an entry point into structurally simple metal-containing polymers. With the vast body of knowledge available for small-molecule synthesis of metal complexes, it is of no surprise that this method is widely utilized and spans multiple subclasses of macromolecules. Many groups have had success in designing ligands with reactive sites either distal to the point of contact with the metal or proximal, such as arenes bearing halogens poised for substitution. The stability of the organometallic polymer is often determined by the binding affinity between the ligand and the transition metal incorporated within the polymer chain.

1.1.1 Olefin and Alkyne Polymerization

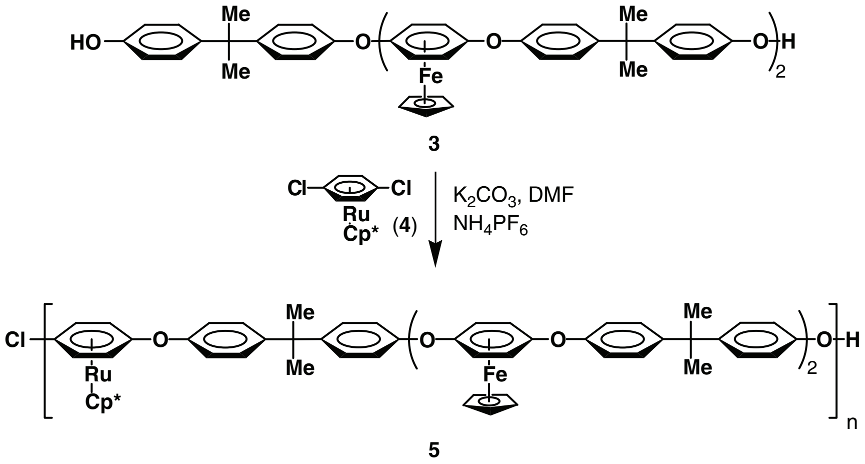
The polymerization of vinyl ferrocene (**1**) by Arimoto and Haven (Scheme 1.1) is regarded as the birth of organometallic polymers [1]. Since that report, the surge of additional methods and monomer structures suitable for alkene polymerizations has strengthened considerably. Typically, olefin polymerization approaches are used to obtain side-chain organometallic polymers, although many examples of main-chain systems have also been achieved. An attraction of this approach is that, assuming reasonable stability of the organometallic moieties, virtually any robust alkene or alkyne metathesis reaction compatible with organic monomers is compatible with organometallic variants as well. Whereas less focus has been placed on alkyne metathesis, one of the key features of this method is its ability to generate an organometallic polymer with a fully conjugated all-carbon backbone [2].



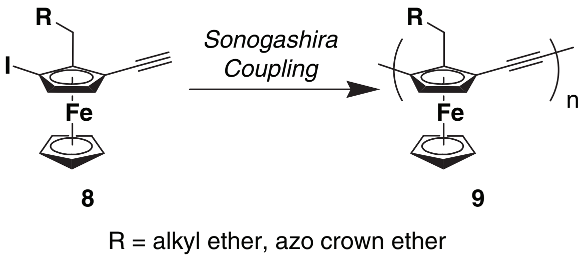
Scheme 1.1

1.1.2 Substitution and Condensation Reactions

The S_NAr approach and polycondensation reactions are excellent methods for generating organometallic polymers. Most of the examples in these areas involve use of an organic moiety as a comonomer and are highlighted in Section 1.2. With regard to structural complexity and control, perhaps the most exemplary organometallic polymers are alternating bimetallic polymers. As shown in Scheme 1.2, isolation of Fe-complex (**3**) (Scheme 1.3) and subsequent reaction with cationic Ru complex (**4**) gave an alternating bimetallic polymer with excellent control [3]. This route has several key advantages. First, each organometallic monomer can be constructed and characterized independently. Second, the use of a heterocoupling copolymerization reaction gives perfect control over the alternating positioning of each metal-containing moiety within the polymer chain. Finally, the number of metal combinations within metallocene chemistry is vast, thus modularity in this system should be high.



Scheme 1.2



Scheme 1.3

1.1.3 Electropolymerization

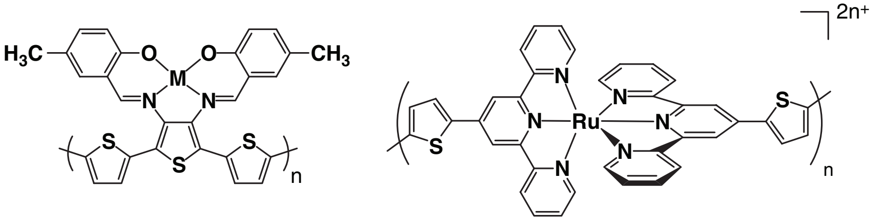
Electrochemical polymerization [4] is another attractive route to synthesizing metal-containing polymers from discrete organometallic monomers. Most often, the polymers obtained are not main-chain, but rather side-chain organometallics (Figure 1.1, **6**) [5]. There are, however, some examples of main-chain organometallic polymers obtained by electropolymerization. Constable, for example, made use of a functionalized Ru(terpy)$_2$ complex bearing electropolymerizable thiophenes on the periphery to achieve polymers such as Figure 1.1, **7** [6].

1.1.4 Alkyne Cross-Coupling Reactions

The examples of homopolymerizations discussed so far are of AA-type monomers. A convenient method for controlled AB-type monomer polymerizations is to use alkyne cross-coupling methodologies. For example, highly functionalized monomers (**8**) were prepared by Plenio [7] that featured an aza crown ether as well as an iodo and ethynyl group poised for homopolymerization (Scheme 1.3). It is at the heart of our discussion to point out that Plenio and coworkers had previously reported polymers showing interesting optical activity with structures also based on **9** (Scheme 1.3) [8]. The synthesis of polymers having very different potential applications, yet stemming from a common synthetic design demonstrates the importance of modularity.

1.1.5 Ring-Opening Polymerization

Ring-opening polymerization (ROP) has seen broad utility for synthesizing main-chain organometallic polymers. Initially reported by Rauchfuss [9], and thoroughly developed by Manners and coworkers [10], the transformation from **10** to **11** (Scheme 1.4) has been optimized to include various conditions for polymerization such as thermal, anionic, photo, and metal-mediated polymerizations; Both solution and solid-state polymerization have also been reported. Molecular weights on the order of 10^6 Da have been achieved and the ability to prepare monomers of varying functionality has assisted



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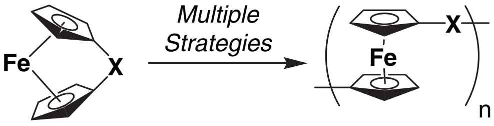
7

Figure 1.1 Examples of polymers obtained via electropolymerization of organometallic monomers



10 **11**

Scheme 1.4

in overcoming any inherent solubility limitations. Bridging groups have included hydrocarbon, sulfur, boron, tin, germanium, phosphorus, and silicon bridges as well as various segments obtained from block copolymerizations.

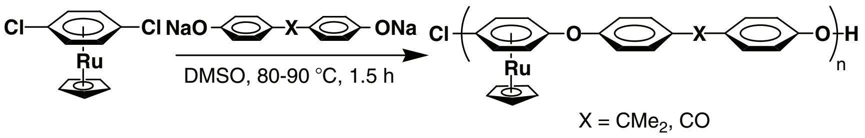
1.2 Copolymerization of Organometallic with Organic Monomers

1.2.1 Alkene Polymerizations

The majority of reactions available for alkene polymerization can be used to copolymerize organometallic and organic substrates. There has been substantial progress in this area since Pittman first described the radical polymerization of acrylate functionalized metal-arene complexes in the early 1970s [11]. Although some monomers underwent homopolymerization smoothly, typically an organic comonomer was necessary to obtain macromolecular products of significant molecular weight. It is noteworthy that in addition to organic comonomers, organometallic substrates have also been used to obtain mixed-metal copolymers. This method is also compatible with contemporary, highly controlled polymerization methods. For example, Frey and coworkers reported the living free radical polymerization of vinyl ferrocene with styrene [12].

1.2.2 Substitution and Condensation Reactions

Similar to the all-organometallic polymers discussed previously, substitution and condensation reactions are also widely used for the copolymerization of organic and organometallic monomers. The S_NAr approach utilizes almost exclusively the application of the metallocene as an electrophile because the halogen is activated by metal complexation to the arene. Since the report by Segal on the polymerization of CpRu complexed with *p*-dichlorobenzene (**12**) along with various bis(phenate) ions (Scheme 1.5) [13], this method has been developed to include a wide range of structures. The greatest structural variations are found in the organic comonomers (Figure 1.2); However, polyhalogenation of the metallocene offers an avenue for structural tuning as well. Extending from their work with Cp^*Ru-dichlorobenzene complexes [14], Dembek and coworkers have demonstrated the ability to generate



12 **13**

Scheme 1.5

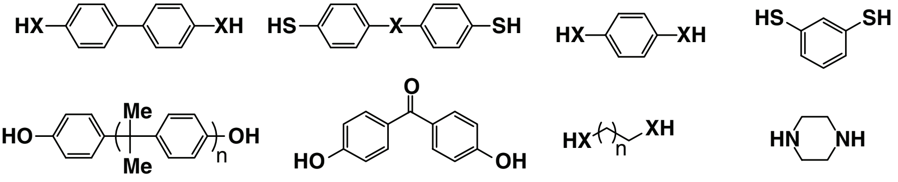
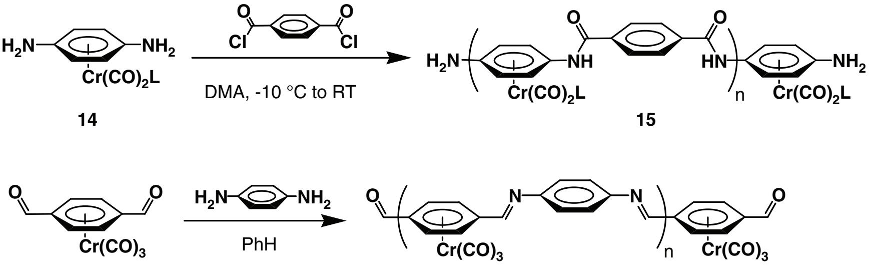


Figure 1.2 Commonly used organic spacers for S_NAr copolymerization with di- or polyhalogenated metallocenes (X = O, S)



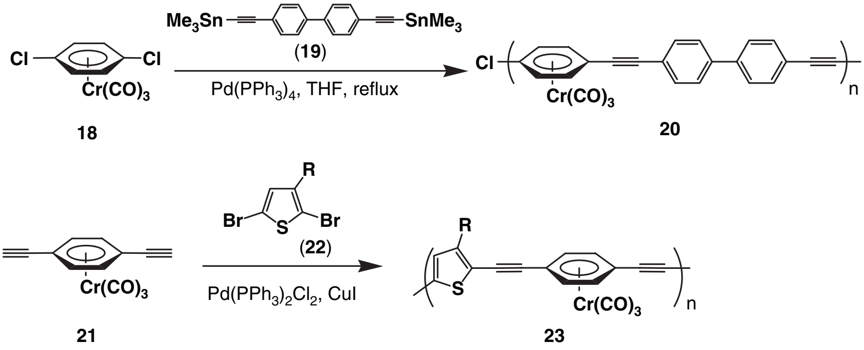
14 **15**

16 **17**

Scheme 1.6

highly branched materials using tri- and tetrachlorobenzene complexes [15]. This latter example illustrates the molecular and architectural complexity that can be achieved with this route while requiring only simple synthetic manipulations such as polyhalogenation of arenes followed by metal complexation.

Many examples exist of metal-arene complexes bearing nucleophiles poised for polycondensation to give polyesters, amides, imines, etc. As early as 1961, polycondensation reactions using diacid chloride variations of metallocenes [16] have been studied with various linkers such as 1,4-hydroquinone and *p*-phenylenediamine. Polycondensation reactions have the added versatility of using the organometallic monomer as either the nucleophilic or electrophilic partner. Examples of each are depicted in Scheme 1.6. Jin and Kim showed the use of phenylenediamine-$Cr(CO)_3$ complex (**14**) with terephthaloyl chloride to give the corresponding copolymer (**15**) in good yields (Scheme 1.6) [17]. Complimentary to this example, dehydration reactions to form polyimines were performed by Wright and Lowe-Ma using a Cr complex of terephthalaldehyde (**16**) and *m*-phenylenediamine (Scheme 1.6).



Scheme 1.7

Although this particular polymer showed limited solubility, the approach could be easily adapted to include monomers with increased solubilizing ability.

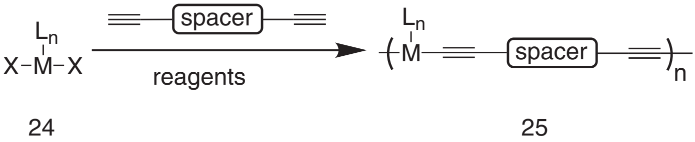
1.2.3 Cross-Coupling Reactions

Others have achieved an all-carbon backbone using standard cross-coupling techniques to install conjugated linkers. In these cases, the metal-arene complex has been employed in both roles (individually and dually) of the cross-coupling. As one partner, Wright used the metallocene (**18**) as the electrophile in combination with Stille reagent **19** under standard conditions to give the corresponding highly conjugated organometallic polymer (Scheme 1.7) [18]. As might have been expected from the linear rigid framework, these polymers displayed poor solubility despite a relatively low molecular weight (ca 7.8 kDa). Alternatively, Chujo and coworkers prepared a functionalized thienylene containing copolymer **23** using 1,4-diethynylbenzene chromium complex (**21**) in combination with dibromothiophenes (**22**) under Sonogashira conditions (Scheme 1.7). In these studies, polymers with molecular weights ranging from 13.5 to 24.4 kDa (PDIs = 3.2 – 3.6) were obtained and extensive π-delocalization was confirmed from comparative UV-Vis spectroscopy. Notably, the polymers were found to be semiconducting when undoped ($\lambda_s = 10^{-6}$ S/cm) [19].

1.3 Polymerizations Involving Metal-Binding Events During Polymerization

1.3.1 Metal-Containing Polyynes

The metal-containing polyynes are an interesting class of main-chain organometallic polymers that have been under investigation since the 1970s. These systems are known for their rigid-rod structures and electronic communication over the extensively



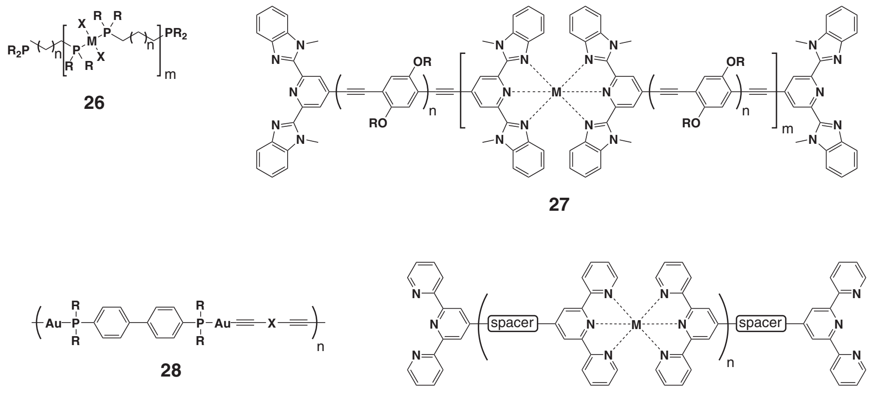
Scheme 1.8

delocalized π-system leading to interesting optical properties. Since Hagihara's initial report on Pd- and Pt-containing polymers [20], much optimization and development has followed. Synthetic avenues typically involve use of a metal(II) halide (**24**) in combination with an α,ω-diyne (**25**). As implied in Scheme 1.8, various linkers have been used and many transition metals have been explored as well as ligand effects at the metal center. Electronic and solubility tuning is also achieved through simple functionalization of the arene linkers. Mixed-metal bimetallics have also been obtained using metal-alkyne linkage in the polymerization step [21].

1.3.2 Coordination Polymers

When one considers the vast body of knowledge that is nearly taken for granted regarding neutral donor ligands in metal complexes, it is not surprising that many researchers have used these moieties in the design of organometallic polymers. The task put forward would seem to simply be one of attaching two known ligands at either end of an extended and/or rigid linker. Whereas this is essentially the overall scheme, achieving macromolecular materials in this way is simple in theory, but nontrivial in its execution. Common donor moieties have historically been phosphines, mono-, bidentate-, or tridentate amines, ethers, imines, nitriles, and thio compounds. High binding affinities are necessary to generate high-molecular-weight materials, and often characterization of the polymers is hampered by the inherent tendency toward depolymerization, especially in dilute solutions typical of gel permeation chromatography (GPC), UV-Vis, and mass spectroscopy.

High-molecular-weight materials have been obtained using difunctional bis(phosphines) as in the reports by Sijbesma (Figure 1.3, **26**) [22]. In these studies, it was found that simply combining either Pd(II) or Pt(II) salts with a bis(phosphine) produced macromolecular materials. Although a common concern with coordination polymers of labile ligands is there inherent lack of structural integrity and strength, the polymers reported by Sijbesma were sufficiently stable to form fibers. Studies were conducted to establish the nature of the metal center and conditions to control linear versus cyclic oligomerization. Bis(phosphine)s of conjugated linkers have also been used. Examples reported by Puddephatt [23] use Au(I) capped bis(acetylides) in combination with



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28

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Figure 1.3 Various scaffolds of coordination polymers synthesized from copolymerization of an organic linker with a transition metal salt

bis(phosphine)s to produce macromolecular coordination polymers (Figure 1.3, **28**). Interestingly, they demonstrated that coordination of AuCl to the bis(phosphine) followed by reaction of the bis(acetylide), in a manner analogous to those described in Section 1.3.1, also produced to polymeric materials. Coordinating amines are also widely used. Prior to Puddephatt's report, Takahashi had used pyridines linked through hydrocarbon chains to coordinate between metal centers providing cationic metallo-polyynes of interesting structure and properties [24]. However, when amines are used it is more common that each binding pocket is made up of a di- or triamine. Difunctional linkers derived from terpyridyl (terpy) ligands, for example, offer a very high binding affinity and many structural derivatives used for polymer formation (Figure 1.3, **29**) are known [25]. In these cases, a range of conjugated and otherwise functionalized spacers have been used to connect two terpy moieties. Rowan and Weder have used a pyridine-based chromophore functionalized with two benzimidazoles to form metal binding sites on the ends of *p*-phenyleneethynylene oligomers. In the presence of Zn(II) or Fe(II), supramolecular polymers such as **27** were obtained [26]. Closely related are various diamine linkers which have also been used to make organometallic coordination polymers. Rehahn's work [27] exemplifies some of the key features of polymers in this subclass. Using phenanthrolines connected through rigid conjugated spacers, polymers containing Cu(I) or Ag(I) were synthesized. The properties of these polymers are quite interesting because macromolecular structure can be solvent-controlled. In noncoordinating solvents, a linear structure having a "classical" polymeric form is obtained, and concentration dependence of molecular weight and structure is not observed. In more coordinating solvents, aggregates are assumed to be formed which, at high dilution, appeared as cyclic oligomers.

2 Research and Discussion

2.1 New Approach to Modular Difunctional Monomers

The various methods described so far for achieving organometallic polymers offer several key features. Multiple transition metals can be incorporated and various polymerization protocols have been presented. Coordination polymers, although often too labile for practical implementation in devices, display dynamic behavior that may be optimized for controlled reversible polymerizations. Metal-arene and metallocene polymers have the versatility of being either main-chain or side-chain organometallic macromolecules, with occasional hybrids of the two being studied. Incorporation of the metal moieties can be accomplished pre-, post-, and during polymerization (or copolymerization) with equal diversity in the mode of polymerization. From a survey of the body of work available on organometallic polymers, it seems apparent that a universal monomer scaffold of high tunability would offer the particular features: (1) Monomer synthesis should be simple and straight-forward with high overall yield, and the general structure should have multiple access routes to facilitate modification; (2) the steric environment around the metal should be easily manipulated, predictable, and modular; (3) a broad range of transition metals should be compatible without the need to significantly alter the polymerization method; (4) sites for functionalization should be apparent and easily manipulated to control both physical and electronic features, preferably independent of one another; (5) the polymers should display "bench-stability" toward moisture and air while dually exhibiting controllable dynamic behavior at the metal center; (6) the polymerization protocol should be robust, proceed under mild conditions, and not require the need for inert atmosphere or dry solvents, and (7) high molecular weights should be obtainable as well as control over molecular weight and end groups.

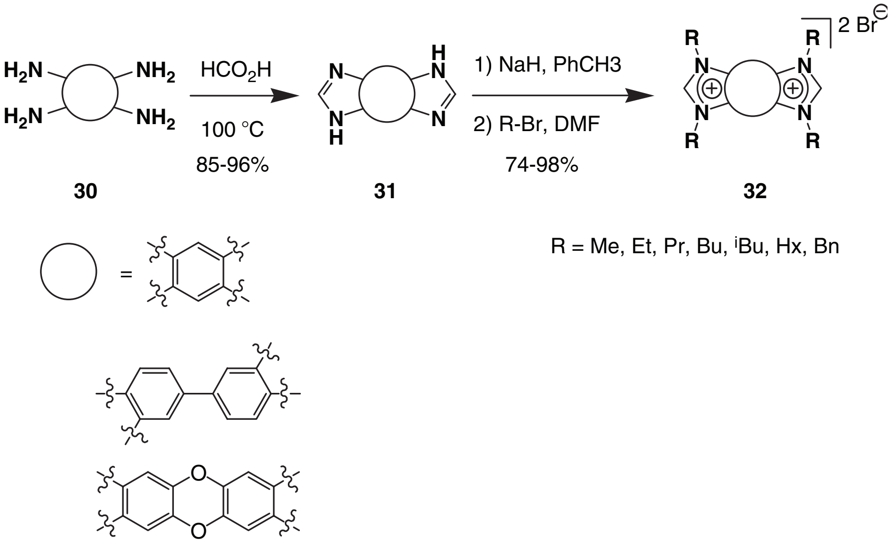
Many of the most efficient strategies for organometallic polymer synthesis (with regard to controllability and molecular weight) make use of highly developed polymerization reactions optimized initially for all-organic substrates. Many of the polymers synthesized under these criteria are inherently side-chain type and offer restricted communication between metal centers. Additionally, polymerization protocols often require the need for inert atmosphere and dry solvents due to the sensitivity of either the organometallic moiety or the reactivity of the comonomers. With regard to metallocene-based systems, it is important to note that because the point of attachment, and synthetic focus, is primarily on functionalization of the arene, the same sites used for electronic and steric tuning are often coincident with those used for attachment of polymerizable functional groups. Although for an S_NAr approach there are plenty of handles for structural tuning, one exception is that the organometallic complex must almost always be designated as the electrophilic partner because the substitution reaction relies on activation of the arene-halide bond after metal complexation. This last issue is resolved for polycondensation reactions and when precise stoichiometric control and pristinely pure reagents are used, excellent control over molecular weight can be achieved.

Though the list of criteria for a highly modular design seems daunting, there appeared to be an organometallic scaffold that would potentially lend itself to a solution to such extraordinary demands. We envisioned the use of heterocyclic carbenes in a new fashion to achieve organometallic polymers exhibiting all of the features listed above. Prior to our contributions, there were very few reports of bis(carbene)s used in the synthesis of macromolecular organometallic materials beyond labile Ag-based aggregates [28]. This was surprising considering the features of heterocyclic carbenes that are desirable for polymer formation such as broad structural diversity and tunable affinities toward virtually every transition metal. Our design would require the construction of a monomer bearing two facially opposed heterocyclic carbene moieties linked through a rigid organic framework that would give control over the site of metallation and shepherd complexation away from intramolecular chelation. Years of effort produced stable and isolable N-heterocyclic carbenes. The task of a bis(carbene) target, however, seemed loftier, especially considering the precedence for challenges in preparing such a class of difunctional ligands [29]. Our current research remains focused on the design and synthesis of new structures and incorporation of stable bis(carbene) moieties into macromolecules that are engineered to execute useful tasks.

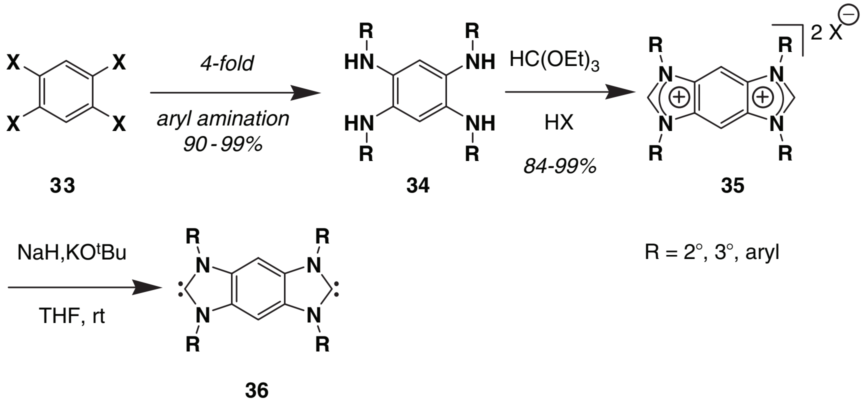
2.2 Difunctional Heterocyclic Carbenes as Linkers

Our original series of bis(carbene) structures focused on a practical synthesis that could demonstrate modularity primarily of the conjugated linker between the metal centers. This was accomplished using tetraamino arenes bearing various aromatic frameworks including benzo, biphenyl, and dioxin-based chromophores (Scheme 1.9). Cyclization of the tetraamines (**30**) with formic acid gave each bis(imidazole) (**31**) in excellent yield and high purity. Fourfold alkylation was accomplished by first treating the bis(imidazoles) each with NaH in refluxing $PhCH_3$ followed by introduction of the electrophile. Addition of dimethylformamide (DMF) as cosolvent at this point in the reaction facilitated dissolution of partially alkylated intermediates and the final products (**32**) were precipitated from the cooled reaction mixture cleanly in good to excellent yields. This protocol was both rapid and high yielding, however the installation of N-substituents was limited to primary halides. Expanding the possible N-substituents involved finding additional pathways to the monomer template.

Installation of larger substituents was accomplished using a two-step high-yielding protocol (Scheme 1.10) [30] involving a fourfold aryl amination to give tetraamines (**34**); using a modified version of Harlan's procedure [31]. Our initial efforts focused on bulky aliphatic amines, but were later extended to include functionalized arylamines as well. Interestingly, although tetraamino arenes are typically plagued by oxidative instability, we found that large alkyl groups (e.g., ^{t}Bu, ^{t}Oct, Ad) significantly suppressed the rate of oxidation. These compounds can be stored for days under ambient atmosphere. Alternatively, more reactive tetraamines were isolated as their respective hydrochloride salts and found to be highly resistant to



Scheme 1.9

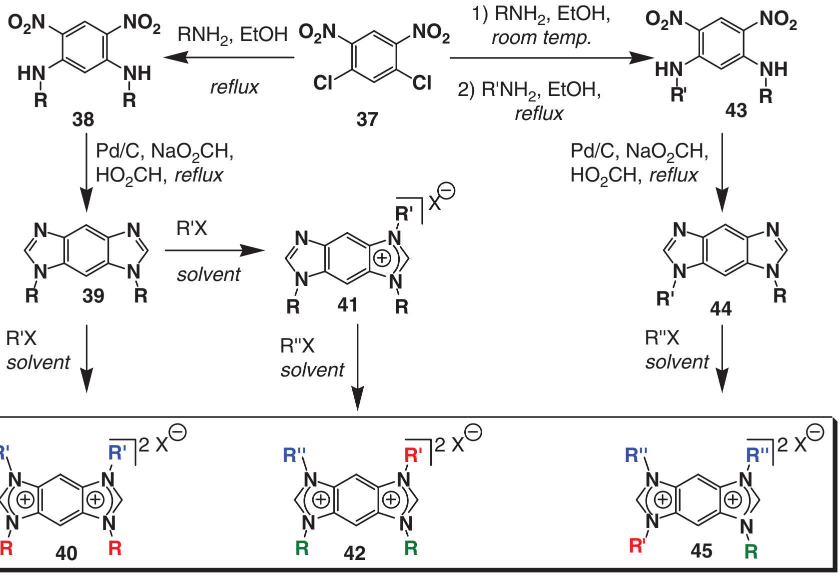


Scheme 1.10

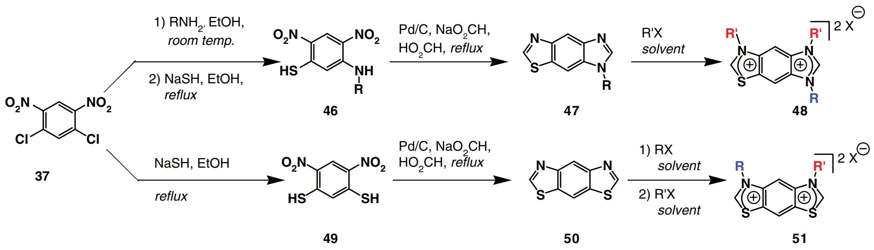
oxidation. Successful ring-closure was accomplished using triethylorthoformate and HCl to provide the bis(azolium) salts (**35**). In cases where increased solubility was desired, simply performing the double ring closure in the presence of HBF_4 in place of HCl provided the more soluble tetrafluoroborate salts. In cases involving very large N-substituents, deprotonation gives the stable bis(carbene)s (**36**) which can be isolated and stored indefinitely.

As mentioned previously, desymmetrization of monomers is often a focal point for accomplishing structural complexity. We have found that in addition to symmetric bis(azolium) salts, a short sequence was available to obtain high yields of asymmetric monomers as well. Ultimately, we have achieved a level of structural diversity arriving at bis(carbene) scaffolds bearing two or three different R-groups, and varying heteroatoms, with complete regiocontrol. This was accomplished using a double-S_NAr reaction, or two sequential S_NAr substitutions, with dichlorodinitrobenzene (**37**) and virtually any primary amine of choice. This effectively installs the first two R-groups regiospecifically. Following an *In situ* reduction-cyclization protocol optimized in our laboratories, the *N*,*N′*-disubstituted benzimidazoles are obtained in excellent overall yield and high purity. Alkylation is accomplished in high yield to give the bis(azolium) salts with varying substitution patterns.

In the first route shown in Scheme 1.11, substitution of two equivalents of an amine in refluxing ethanol provides the diamine (**38**) as it precipitates from the reaction mixture. This method is best employed when installing R-groups not compatible with alkylation via nucleophilic attack on alkyl halides. Following reduction and cyclization to give **39**, alkylation can be performed to give the bis(azolium) salt with two different R-groups regiospecifically. In further studies, we found that mono-alkylation of **39** could be controlled to give high yields of monoazolium salt (**41**). This compound proved to be a useful asymmetric building block in preparing alternating bimetallic polymers as will be discussed below. A second alkylation of **41** yielded the bis(azolium) salt (**42**) bearing three different R-groups. Three different R-groups can also be installed in cases where the desymmetrizing substituents are not compatible with alkylation. This is accomplished through temperature control during the S_NAr reaction. Treatment of **37** with an amine in EtOH at room temperature gave a nearly quantitative yield of the monoamine product. The second substitution was performed



Scheme 1.11



Scheme 1.12

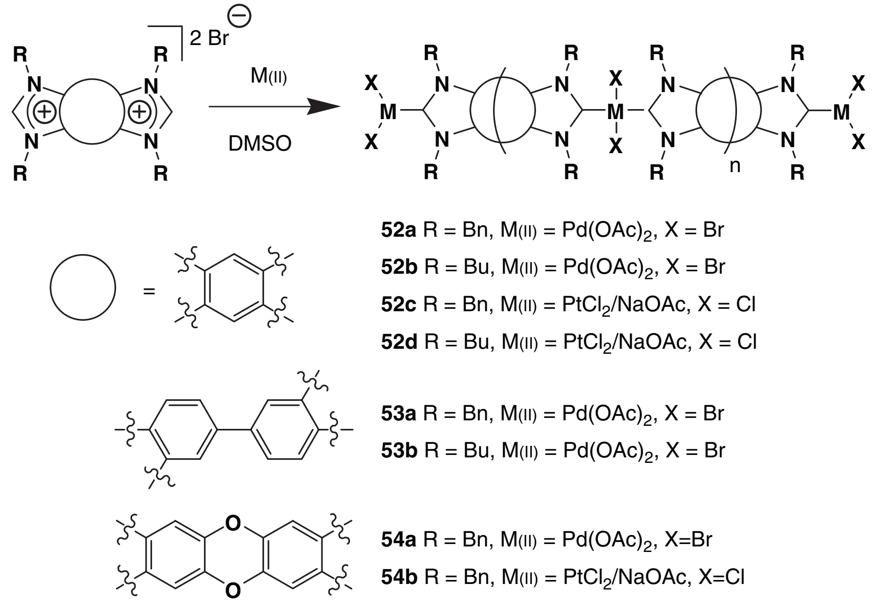
cleanly and in high yield which effectively desymmetrized the monomer template (**43**). Reduction and cyclization to give **44**, followed by alkylation, provided the bis(azolium) (**45**) that is complimentary in the R-group structure to **42**.

Heteroatom variation has been accomplished using NaSH as a nucleophile in the S_NAr reactions (Scheme 1.12). Treatment of **37** with an amine, followed by reaction with NaSH furnished asymmetric dinitroarene (**46**). Reduction and cyclization gave a hybrid structure (**47**) which was cleanly alkylated to give **48**. Use of excess NaSH with **37** yielded **49** which was used en route to bis(thiazole) (**50**). Alkylation could be performed stepwise, as in the synthesis of **42**, to ultimately yield asymmetric structures, such as **51**, bearing two thiazolium moieties.

In summary, in monomer syntheses there is broad flexibility with regard to heteroatom content, N-substituent functionality, electronic asymmetry, steric asymmetry (through judicious placement of different N-substituents), conjugation through arene linker, solubility, and overall function. Each synthetic route is streamlined to be short, high-yielding, and pose minimal technical difficulty. In the next section we will discuss how these attributes were used to obtain polymers of desired functionality.

2.3 Bis(carbene)-Based Organometallic Polymers

All of the bis(azolium) salts presented above undergo smooth copolymerizations with Pd(II) and Pt(II) salts in the presence of acetate anion in polar solvents (e.g. dimethyl sulfoxide [DMSO], DMF, N-methylpyrrolidone [NMP], CH_3CN) as described in our original report in this area [32]. Treatment of our bis(azolium) salts with $Pd(OAc)_2$ or $PtCl_2$/NaOAc in polar solvents between 50 and 110 °C effectively executed the copolymerization and metal incorporation to yield the bis(carbene)-based main-chain organometallic polymers (**52–54**) in high yield after precipitation into MeOH or H_2O (Scheme 1.13). Our first studies focused on monomer bearing aliphatic alkyl groups as described in Scheme 1.8. Molecular weight analysis by GPC revealed polydispersities typical of step-growth polymerizations. For this series, M_n was higher for Pt-containing polymers than for the structurally analogous Pd-containing systems. Notably, very high M_n (up to 1.8×10^6 Da) were obtained



52a R = Bn, M(II) = $Pd(OAc)_2$, X = Br
52b R = Bu, M(II) = $Pd(OAc)_2$, X = Br
52c R = Bn, M(II) = $PtCl_2$/NaOAc, X = Cl
52d R = Bu, M(II) = $PtCl_2$/NaOAc, X = Cl

53a R = Bn, M(II) = $Pd(OAc)_2$, X = Br
53b R = Bu, M(II) = $Pd(OAc)_2$, X = Br

54a R = Bn, M(II) = $Pd(OAc)_2$, X=Br
54b R = Bn, M(II) = $PtCl_2$/NaOAc, X=Cl

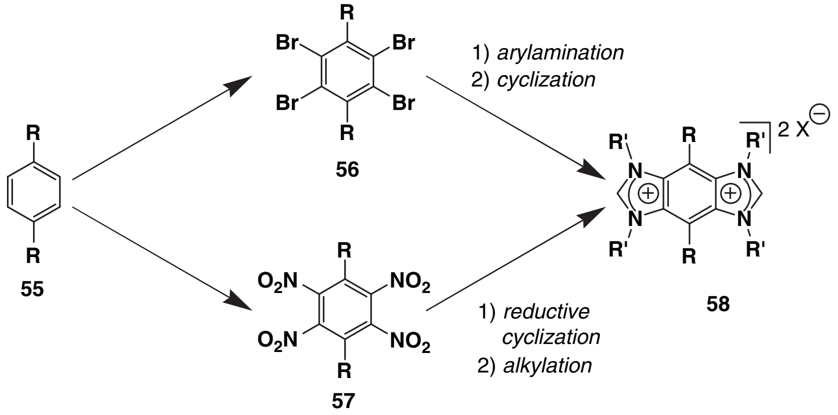
Scheme 1.13

with this method. The electronic absorption spectra revealed a fairly narrow range of absorption maxima (308–329 nm). Thermal stability was measured by thermal gravimetric analysis (TGA) under nitrogen atmosphere and T_d was consistently found to be between 280 and 300 °C for polymers of this structure.

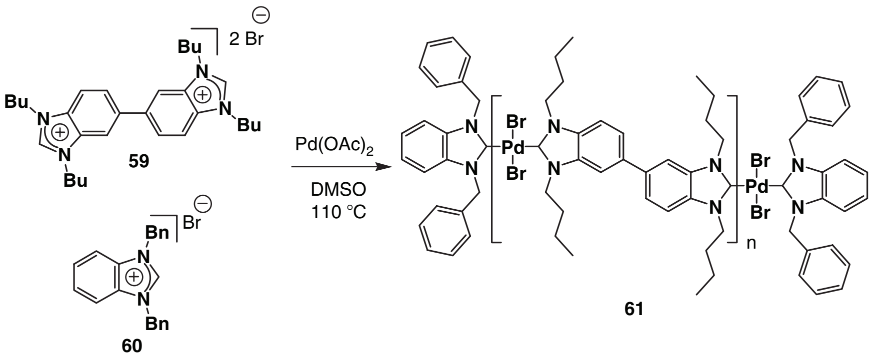
One key limitation in this synthetic route was the incompatibility of using metals other than Pd and Pt. Of specific interest initially was the failure to polymerize using Ni(II) salts, which have also demonstrated nonreactivity in attempts to generate analogous small molecule Ni-NHC complexes via Herrmann's procedure [33]. To verify the stability of the resultant Ni-based polymers, we generated the free bis(carbene), which reversibly formed the corresponding homopolymer [34], and subsequently added anhydrous $NiCl_2$. This method provided the desired polymer as a stable macromolecule. Another alternative route utilized Lin's Ag-mediated NHC transfer reaction. Treatment of the bis(azolium) salts with Ag_2O produced thick gels when solvated which, when reacted with divalent metal halides, led to the corresponding organometallic polymers. This method, however, produces a stoichiometric amount of metal waste and results in difficulty confirming complete transmetallation. Procedures for small molecule NHC-Ni complexes are known [35] that involve monomeric azolium salts with predried $Ni(OAc)_2$ at high temperature under vacuum either neat [36] or in an ionic liquid [33].

In general, the polymers in this series were poorly soluble in most common solvents (THF, CH_2Cl_2, dioxane, CH_3CN), but readily dissolved in more polar solvents such as DMF, DMSO, and NMP. Subsequent changes have involved simply using longer alkyl chains for the N-substituents (e.g., hexyl) which resulted high-molecular-weight polymers that exhibited good solubility in solvents such as THF, $CHCl_3$, CH_2Cl_2, and dioxane. Alternatively, when increased solubility is desired in combination with relatively small N-substituents, installation of additional functionality on the arene is useful. For example, we are working toward producing bis(azolium) salts with varying chain-length alkyl groups on the arene (Scheme 1.14). Fourfold electrophilic aromatic substitution was performed on 1,4-dialkyl benzenes (**55**) to give either tetrahalo (**56**) or tetranitro (**57**) products. Reductive cyclization of the tetranitro followed by alkylation, or four-fold aryl amination of the tetrahalo followed by cyclization, should afford the corresponding bis(azolium) salts (**58**) which should exhibit markedly improved solubilities.

One key feature of the bis(NHC) organometallic polymers is their reversibility, or "dynamicity." The dynamic nature of the copolymerization prompted us to investigate the use of chain-transfer agents to modulate both polymer molecular weight and end-group structure (Scheme 1.15). Copolymerization with $Pd(OAc)_2$ in



Scheme 1.14

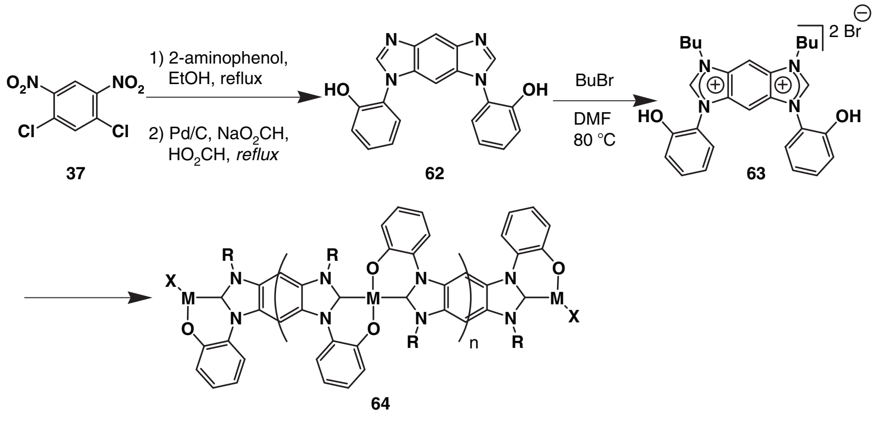


Scheme 1.15

the presence of monfunctional benzimidazolium bromide (**60**) as a CTA produced end-capped polymers (**61**). In these experiments, excellent agreement was observed between the theoretical DP based on loading ratios of **60/59** and experimental DP determined by ^{1}H nuclear magnetic resonance (NMR) analysis. Later studies have focused on using the reversible polymer formation to design dynamic copolymers of varying monomer structure and self-healing networks.

Postpolymerization modification is yet another method of tailoring polymer properties and can be considered a modular attribute of a macromolecule [37]. Given that the metals in the bis(NHC) polymers are coordinatively unsaturated, the use of an exogenous ligand added postpolymerization was expected to bind to the metal thus altering the physical and electronic properties of the polymer. Addition of PPh_3 or PCy_3 to a suspension of polymer **53a** in THF quickly affected complete dissolution of the phosphine-bound polymer. Ligation was confirmed by ^{1}H and ^{31}P NMR spectroscopy.

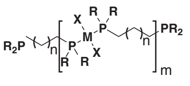
Generation of bis(NHC)-based organometallic polymers containing varying transition metals of choice was a key breakthrough. Unfortunately, metals typically showing poor hydrolytical stabilities as NHC complexes (e.g., Cu) were impractical using our first generation of monomer scaffolds. To address this issue, we targeted a monomer that would increase the affinity of the NHC ligand for the metal. Considering examples from similar small-molecule organometallic complexes, we focused on using phenolic imidazoles to generate an additional (ionic) bond with the metal. Using similar chemistry to that described previously, dichloro-dinitrobenzene (**37**) was reacted with 2-aminophenol, followed by reduction-cyclization to yield **62** (Scheme 1.16) [40]. Alkylation arrived at the desired monomer (**63**) in high overall yield. Optimization studies revealed that polymerization was most successful with the addition of an exogenous weak base to level the mineral acid generated from reaction of the phenol with the metal halide. After successful formation of both Pd- and Pt-containing polymers with the new monomer design, we targeted transition metals such as



Scheme 1.16

Ni and Cu. Typically, small-molecule analogs are synthesized via a full deprotonation of both the phenol and the azolium under inert atmosphere, followed by introduction of a soluble (ligated) metal salt [38]. Alternatively, Hoveyda has successfully employed Lin's NHC transfer reaction to obtain naphtholic NHC-metal complexes [39]. Additionally, no studies on benzimidazolium salts functionalized with phenol substituents had been reported. Subjecting Ni(II) and Cu(II) salts to our polymerization conditions in the presence of stoichiometric NaOAc produced excellent yields of the corresponding polymers. Incorporation of these transition metals could be done directly under ambient atmosphere in high yields. Increased thermal stability of the systems was also observed. All of the phenolic polymers are air and moisture stable, and TGA analysis under nitrogen atmosphere revealed T_d ranging from 340 to 362 °C. In comparison to the analogous Pd- and Pt-based polymers bearing N-alkyl groups (**52**), thermal stabilities increased by approximately 50 °C via incorporation of phenoxide substituents. Varying the transition metal had a small, but discernable, impact on the electronic absorption spectra. Each absorbs in the infrared with λ_{max} ranging from 287 (Ni) to 319 nm (Cu). The increased binding affinity appeared to be tailored independently of the overall electronic nature. That is, the phenolic Pd and Pt systems exhibit λ_{max} values nearly identical to the related *N*-alkyl polymers (**52**).

Two independently impressive displays of polymer design lie in areas involving directionality (head-to-tail selectivity) and mixed-metal systems. We are working toward accomplishing these goals using our bis(carbene) approach. Further use of the phenol ligand, in combination with "left–right" desymmetrization, led to a designer monomer with the potential to form a discrete directional polymer via head-to-tail ordering of the bis(carbene) linker. Specifically, sequential temperature-controlled S_NAr reactions using an aliphatic amine followed by introduction of 2-aminophenol gave an asymmetric diamine of structure **43**. Carrying through to the corresponding organometallic polymer gave materials under study for the potential to exist as depicted in the form shown in Figure 1.4. Use of **41** to form a transition metal complex with terminal imidazole functionality poised to ultimately generate an alternating bimetallic polymer with excellent control over metal placement could lead to polymers of the structure **66** (Figure 1.4). The broad combinations of transition metals compatible with our polymerization protocols should bring about new opportunities for electronic fine-tuning.



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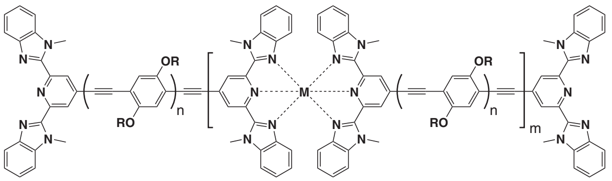

Figure 1.4 Directional polymers and mixed-metal polymers from bis(carbene) monomers

3 Further Considerations and Outlook

We have demonstrated the high level of modularity that is achieved by using bis(carbene) scaffolds as monomer for organometallic polymers. Many handles exist that allow tuning of nearly every desirable feature of the polymers including solubility, thermal stability, metal compatibility, dynamicity, and electronic communication. The frontier of this approach to main-chain organometallic polymers will be pushed further and faster with the addition of structurally variable monomer architectures and will span many areas of material science. The use of cross-linked networks of our systems are already being investigated for application in conductive self-healing materials. Other areas of research involve dynamic polymers as "heat-activated" catalysts. Conductivity optimization through redox matching of the heterocyclic carbenes and the transition metals will ultimately lead to improvements on the already semiconducting (undoped) properties observed from our polymers. All of these areas are facilitated by the common theme of a modular design that not only allows versatility in the metal involved in the polymer, but also in the steric and electronic features of the organic moieties. The changes in design have been brought about quickly and efficiently due to a monomer template that has many avenues for synthesis and ultimately new applications.

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