Abstract

A new class of main-chain organometallic polymers comprised of a bis(carbene) ligand with chelating phenolate moieties and various transition metals has been synthesized and characterized. A bis(azolium) precursor to the bis(bidendate) ligand was based on a benzobis(imidazole) framework and prepared from 1,3-dichloro-4,6-dinitrobenzene in three, chromatography-free steps in 78% overall yield. Direct metallation of the monomer was accomplished by addition of a stoichiometric amount of $Ni(OAc)_2$, $PdCl_2$, $PtCl_2$, or CuO which resulted in good to excellent yields of the respective organometallic polymer with molecular weights ranging from 67.5 to 363 kDa, relative to polystyrene standards. The polymers were found to be exceptionally air- and moisture stable and displayed thermal stabilities exceeding 350 °C (under nitrogen), as measured by thermogravimetric analysis. Electronic absorption measurements indicated the λ_{max} values of these polymers ranged between 287 and 319 nm depending on the incorporated metal. To gain insight into the microstructure of the polymer chains, a model Ni complex containing two chelating benzimidazolylidenes, analogous to the repeat unit of the polymer chains, was synthesized and characterized.

Introduction

The development of new organometallic materials has experienced explosive growth since the synthesis and isolation of the first stable, crystalline *N*-heterocyclic carbene (NHC) disclosed by Arduengo in the early 1990s.[1] Subsequently, an impressively broad range of NHCs, including many structural and electronic variants, have been reported.[2] Collectively, these compounds have been shown to coordinate to virtually every transition metal and often result in considerable performance enhancement in the respective metal catalyzed reactions.[3] Prime examples include Pd mediated carbon-carbon and carbon-heteroatom bond forming reactions, and Ru mediated olefin metathesis.[4]

In contrast, relatively little attention has been directed toward using NHCs as a means to construct organometallic polymeric materials.[5] Considering the large amount of synthetic and functional diversity inherent to NHCs, they are ideally suited for this purpose. However, to obtain polymeric materials, access to multifunctional NHCs capable of binding at least two transition metals with high fidelity is essential. Although a broad range of di-, tri-, and multifunctional NHC-based ligands are known,[3,4,6] they are often

poised (and designed) to preferentially bind to one metal center in a chelating or pincer-type fashion. Notable exceptions include examples from Lee,[7] Herrmann,[8] and Youngs[9] who have each shown that some pincer-type bis(carbene)s form bimetallic structures (with 1:1 NHC/metal stoichiometry). In particular, with Ag(I) salts, materials could be obtained that were polymeric in the solid-state and, interestingly, dissociated upon dissolution to afford the respective discrete bimetallic complexes. Bertrand[10] reported that non-chelating bis(carbene)s based on dialkylated 1,2,4-triazoles also afford solid-state polymers when reacted with Ag(I) salts.[11]

We have recently launched a program focused on utilizing multifunctional NHCs as the key constituents in producing soluble, processable, and high molecular weight materials, particularly those with tunable electronic properties and responsive characteristics.[12] We have shown that various linearly opposed bis(imidazolium) substrates can be easily prepared[12,13] and function as effective precursors to NHC-based organometallic materials; specifically, they can be copolymerized with transition metals to form high molecular weight main-chain organometallic polymers that retain their structure in solution.[11] One limitation of our initial approach was that the range of compatible transition metals was confined to Pd(II) and Pt(II) salts. Use of other metals such as Cu and Ni resulted in labile polymeric materials that rapidly underwent solvolysis upon introduction of protic media (e.g., H_2O, MeOH). A method for overcoming this constraint and expanding the scope of compliant transition metals in NHC-based organometallic polymers would ultimately provide increased control over their corresponding physical and electronic properties. This required the design and synthesis of a new difunctional NHC-based monomer that was appropriately functionalized to exhibit enhanced affinities toward transition metals.

An exemplary strategy for enhancing the chemical stability of metal-NHC interactions is to incorporate a bidentate or chelating scaffold into the NHC architecture. For example, enhanced stability of a Cu-NHC complex was demonstrated in Hoveyda's[14] use of imidazolylidene ligands containing *N*-aryloxy units. Grubbs[15] utilized *N*-(2-hydroxyphenyl) substituted imidazolium salts which ultimately complexed to Pd(II) species in a chelating-type fashion. While many other examples of mixed multidentate carbene ligands built on various types of imidazole-based frameworks are known,[14-16] related bidentate benzimidazolylidenes[17] have received less attention. For the purpose of forming macromolecular materials suitable for use in electronic applications, benzannulated systems are particularly attractive since the arene linkers maintain formal conjugation within the corresponding main chains of the polymeric materials and permit electronic tuning through further derivatization.[18] Installation of these structural features into an

annulated bis(azolium) framework designed for macromolecular applications presents specific synthetic challenges. In particular, metal complexation must proceed in high-yield and with high structural fidelity in order to obtain polymeric materials of significant molecular weights. In addition, to form main-chain polymers with transition metals that prefer four coordinate geometries (Cu(II), Ni(II), etc.), a desymmetrized difunctional NHC ligand where each "face" of the carbene monomer contains only one additional ligating *N*-substituent is required.

Synthetic methods used to prepare NHC-metal complexes typically utilize one of three strategies: 1) reaction of an azolium salt with an electrophilic metal species possessing basic counterions or coordinating anions,[19] 2) generation of the free carbene followed by introduction of an unsaturated or electrophilic metal species,[2,3] or 3) formation of a Ag(I)-NHC complex followed by ligand transfer to the desired transition metal.[20,21] While each of the above described methods are superb for constructing small-molecule systems, at first glance none seemed directly amenable to high molecular weight polymer formation. For example, Herrmann demonstrated that Ni-imidazolylidene complexes can be obtained directly from their respective imidazolium salts in 30% yield using $Ni(OAc)_2$.[22] However, the reaction must be conducted in the melt under vacuum using anhydrous reagents. Synthesis of benzimidazolylidene-based Ni complexes using this methodology is unsuccessful, however, due to the fact that the resulting complexes decompose at the high reaction temperatures (150 °C). Recently, Hahn accomplished the first synthesis of benzimidazolylidene-Ni(II) complexes using an elegant adaptation of Herrmann's procedure by combining benzimidazolium salts with tetrabutylammonium salts at elevated temperatures under vacuum.[23] The ammonium salts were melted to give an ionic liquid solvent system which allowed for reduced reaction temperatures (120 °C) and ultimately provided the desired Ni complexes in 28 – 60% yield, provided the benzimidazolium and tetrabutylammonium salt counterions were appropriately matched. Since reaction yields of >95% are necessary to obtain high molecular weight polymer, the development of a new method for forming Ni benzimidazolylidene complexes was needed.

Considering alternatives to metallation of azolium salts directly, free carbene generation is compatible with essentially all transition metals known to form complexes with NHCs. Caveats of this approach include a two-step procedure under inert atmospheres and the use of dry solvents to avoid destruction of the free carbene. When carbene dimerization can occur, the resulting enetetraamines[24] are extremely sensitive toward oxygen and often subject to rearrangement or fragmentation depending on the nature of the *N*-substituent.[25] Additionally, although annulated bis(imidazolylidene)s can be manipulated as either

their free carbenes[13b] or respective homopolymers[26] en route to bimetallics and metallo-polymers, this imposes limitations on compatible solvents and high molecular weight materials are generally precluded by limited solubilities in common organic solvents (e.g., THF, benzene, PhCH$_3$). One method that has been employed with a diverse array of conditions, solvents, and substrates is Lin's NHC-transfer method.[27] However, disposal of stoichiometric Ag salts and confirmation of quantitative Ag exchange is not desirable for macromolecular applications.

With these considerations in mind, we targeted a ligand design that alleviated the need for strict use of inert atmospheres and allowed access to stable NHC complexes via direct metallation of benzimidazolium salts in a single step and in high yields. Herein, we report our efforts to expand the range of transition metals that can be incorporated into the main-chains of organometallic polymers containing NHCs via direct metallation of bis(azolium) salts bearing chelating *N*-phenol moieties.

Results and Discussion

The synthesis of the bis(bidentate) benzobis(imidazolium) monomer was accomplished as shown in Scheme 1. Treatment of commercially available 1,5-dichloro-2,4-dinitrobenzene **1** with 2-aminophenol (4.0 equiv) in refluxing EtOH provided 1,5-bis[(2-hydroxyphenyl)amino]-2,4-dinitrobenzene **2** in nearly quantitative yield after isolation by precipitation of the reaction mixture into an excess of H$_2$O followed by vacuum filtration. We envisioned that reduction of the nitro groups followed by formylative cyclization of the resulting tetraamino intermediate could be accomplished using a "one-pot" protocol. This was successfully executed by using a mixture of NaO$_2$CH/HO$_2$CH in the presence of catalytic amounts of Pd/C which effectively hydrogenated the nitro groups *in-situ*. Within 1-2 h, the intense red-orange color associated with dinitroarene **2** had dissipated indicating complete reduction had been accomplished. Continued heating ultimately provided the formylatively cyclized product **3** which was obtained in 84% yield from **1** after removal of Pd/C via filtration and neutralization of the filtrate with aqueous base to cause precipitation of the desired benzobis(imidazole). Finally, alkylation with 1-bromobutane provided bis(azolium) dibromide **4** in 93% yield after isolation and in 78% overall yield from **1**.

<Insert Scheme 1>

As shown in Scheme 2, polymerizations were conducted by combining a stoichiometric amount of metal salt with **4**, in accord with our previously reported procedure.[12] Initial efforts focused on using PdCl$_2$ or

4

PtCl$_2$[28] in conjunction with **4**, however only low yields of polymeric materials (**5·Pd** and **5·Pt**) were obtained upon precipitation of the reaction mixtures into an excess of H$_2$O. We suspected that generation of HCl or HBr as a byproduct during the polymerization reaction was detrimental to complexation. After exploring various exogenous bases (i.e., K$_2$CO$_3$, Et$_3$N, NaHCO$_3$, NaOH, and KO^{t}Bu), it was found that addition of stoichiometric NaOAc (relative to each phenol moiety) gave the Pd- and Pt-based polymers **5·Pd** and **5·Pt**, in 99 and 95% yields respectively.[29] Using this protocol, we next tested the propensity of other transition metals to undergo copolymerization. Gratifyingly, treatment of either Ni(OAc)$_2$·4H$_2$O or CuO[30] with **4** in the presence of stoichiometric[31] NaOAc in DMSO at 50 – 80 °C provided the respective main-chain organometallic polymers **5·Ni** and **5·Cu** in 96 and 86% yields, respectively.

<Insert Scheme 2>

Each of the polymers noted above were characterized by NMR spectroscopy, gel permation chromatography (0.01 M LiBr/DMF eluent, 40 °C, relative to polystyrene standards), UV-Vis spectroscopy, and thermogravimetric analysis (TGA); key information is summarized in Table 1. Signals in the ^{1}H NMR spectra were broadened and shifted upfield relative to **4**; in addition, complete consumption of azolium protons was observed. The Pd- and Pt-based systems **5·Pd** and **5·Pt** were tan powders whereas the Ni- and Cu-based polymers **5·Ni** and **5·Cu** were dark brown and green-brown powders, respectively, and each displayed moderate to good solubility in polar solvents (e.g. DMF, DMSO, NMP). Although a multi-modal distribution was observed for the Ni-based polymer, analysis of the other polymers by GPC (relative to polystyrene standards) indicated M$_n$s ranged from 67.5 to 363 kDa, depending on the transition metal used, with PDIs typical of step-growth polymerizations (1.6 – 2.2). Qualitatively, each of the polymers were found to be stable toward water and oxygen as no signs of degradation (as determined by ^{1}H NMR spectroscopy and GPC analysis) were observed upon prolonged standing in wet, aerated solvents. Quantitative thermal analysis of polymers **5** by TGA indicated that their T$_d$s ranged from 329 and 362 °C. This represents a 30 – 70 °C increase in thermal stability in comparison with their analogous organometallic polymers containing (non-chelating) *N*-alkyl substituents.[12] Although chelation is a dominate contributor, the lack of counterions may also partially account for the enhanced relative stabilities. As shown in Figure 1, electronic absorption spectra of the polymers reveal a slight dependence on the incorporated metal with $_{max}$ values ranging from 287 to 319 nm. The Pd- and Pt-containing macromolecules show absorption spectra similar to those reported previously (containing only *N*-alkyl

substituents) which suggests that overall electronic contributions between the pendant anionic phenoxide moieties and the main chromophore are minimal. Thus, improved thermal stability is accomplished without compromising control over electronic characteristics.

<Insert Table 1>

<Insert Figure 1>

To gain a greater understanding of the polymer microstructure, we turned our attention to analyzing the structural characteristics of the metal centers formed along the main-chain of the polymer backbone. Accordingly, a model complex representative of the repeat units in the organometallic polymers described above was targeted. A relevant asymmetric benzimidazolium salt containing a pendant *N*-phenol group was synthesized as shown in Scheme 3. Aryl amination of 1-chloro-2-nitrobenzene (**6**) with 2-aminophenol under basic conditions and promoted with Cu provided the respective diaryl amine **7** in 80% yield.[32] The *in-situ* reductive cyclization protocol described above was successfully used to obtain mono-substituted benzimidazole **8** in 95% yield. Finally, alkylation was accomplished using 1-bromobutane in CH_3CN followed by removal of volatiles under vacuum to give benzimidazolium bromide **9** in near quantitative yield after isolation.

<Insert Scheme 3>

With **9** in hand we were poised to investigate the efficiency of metal complexation and the nature of the metal centers of the polymers. Considering the paucity of known benzimidazolylidene-Ni complexes and the relative limited number of synthetic protocols for preparing these compounds, we focused our attention on a Ni-based system. As shown in Scheme 4, azolium salt **9** was reacted with 0.5 equivalents of $Ni(OAc)_2 \cdot 4H_2O$ in the presence of NaOAc in DMSO at 50 – 80 °C and monitored by NMR spectroscopy.[29] Gratifyingly, the product of this reaction was isolated by precipitating the cooled reaction mixture into an excess of water, in analogy to our polymerization protocol, which provided the corresponding Ni complex **10** in excellent yield (95%). Although DMSO was used for consistency with the polymerization reactions, other polar solvents (e.g., THF, CH_3CN, EtOH) were also found to work well for efficient complexation, whereas reactions conducted in $PhCH_3$, PhH, and CH_2Cl_2 were unsuccessful and resulted in incomplete consumption of starting materials. The Ni complex **10** was found to be relatively

stable toward ambient moisture and oxygen and showed good solubility in common organic solvents (e.g., THF, $CHCl_3$, Et_2O, CH_2Cl_2, $PhCH_3$), attributable to the incorporation of the solubilizing *N*-butyl groups. Mass spectral analysis supported formation of a 2:1 ligand/metal complex which was further confirmed by X-ray diffraction analysis after quality crystals of **10** were obtained by slow diffusion of hexanes into a saturated solution of **10** in THF. As shown in Figure 2, the ORTEP diagram of the molecular structure of this complex indicated that the metal center adopted a *cis* geometry,[33] which to the best of our knowledge is the first Ni complex comprised of two benzimidazolylidenes of this relative configuration. The metal center displayed a distorted square-planar arrangement with C-Ni-C, C-Ni-O (*cis*), and O-Ni-O bond angles of 94.5, 89.0, and 90.5° respectively. The C-Ni bond lengths in **10** were shortened (1.84 Å) relative to bis(benzimidazolylidene)-Ni(II) halide complexes (1.89 – 1.91 Å).[23] These differences can be rationalized by the trans effect associated with each respective complex. The N-C-N bond angles of complex **10** (106°) were as expected for azolylidene-Ni(II) complexes.[22,23,33] The phenol ring was slightly rotated with a dihedral angle of 27° relative to the plane of the benzimidazolylidene suggesting diminished electronic communication between the two moieties, consistent with the UV-Vis data of the corresponding polymers **5**.

<Insert Scheme 4>

<Insert Figure 2>

Interestingly, the butyl groups in Ni complex **10** showed diastereotopic signals in the ^{1}H NMR spectrum, with some signals appearing markedly upfield in comparison with other NHC-Ni complexes. Specifically, NCH_2 resonances typically appear between $\delta = 4.5$ and 6.5 ppm, depending on the nature of the alkyl group.[16,22,23] In contrast, the protons associated with the methylene units of complex **10** were diastereotopic (e.g. NCH_2: $\delta = 4.2$ and 3.6 ppm). This can be explained from the X-ray data which revealed a π-facial interaction of each butyl group with the benzimidazolylidene moiety of its complementary ligand. Complex **10** also displayed a ^{13}C resonance at _ = 173 ppm (solvent = $CDCl_3$) which was intermediate with known benzimidazolylidene (~184 ppm)[23] and imidazolylidene (~170 ppm)[34] Ni(II) complexes. Thermogravimetric analysis of **10** indicated that the phenolic chelating moiety likely contributes to good thermal stability as the onset of mass loss occurred at 286 °C (rate = 10 °C/min, N_2 atmosphere).

Conclusion

In summary, we describe the synthesis and characterization of a new class of main-chain organometallic polymers comprised of bis(carbene)s and various transition metals. The approach builds upon our recently reported procedure for preparing analogous polymers by extending the range of transition metals that may be incorporated into the main chains of the polymers. This goal was accomplished through the synthesis of an annulated benzobis(imidazolium) salt bearing N-phenolic substituents followed by direct metallation with Pd, Pt, Ni, or Cu salts. The resulting organometallic polymers contained a benzobis(imidazolylidene) with pendant N-phenol groups that coordinated to the transition metals in a chelating type fashion. This resulted in polymeric materials with molecular weights up to 363 kDa (relative to polystyrene standards) and PDIs typical of step-growth polymerizations. A slight dependence of the electronic properties of these polymers on the incorporated transition metals was found in their electronic absorption spectra, but was in accord with their non-chelated analogues. In contrast, the relative thermal stabilities of this series of polymers were enhanced by intramolecular metal chelation and the lack of counterions associated with the electrophilic metal centers. Collectively, this suggested that the thermal stabilities of our first generation materials were increased without a comprise in their electronic characteristics. The bonding geometry and integrity of the new polymer systems were confirmed by solution- and solid-state characterization of a model complex designed to mimic the repeat unit of the polymer chain. In particular, a benzimidazolium salt possessing a pendant N-phenol moiety was reacted with $Ni(OAc)_2$ which afforded the corresponding discrete bis(bidentate) Ni-NHC complex in excellent yield. The geometry of the Ni complex was found to be exclusively *cis* and useful for gaining insight into the microstructure of its corresponding polymer chains. Future efforts will focus on exploring the utility of these polymers in catalysis and further examining their physical characteristics with an emphasis on their potential in electronic applications.

Experimental Section

Materials and Methods: ^{1}H and ^{13}C NMR spectra were recorded using a Varian Unity Plus 300 or 400 spectrometer and were routinely run using broadband decoupling. Chemical shifts (δ) are expressed in ppm downfield from tetramethylsilane using the residual protonated solvent as an internal standard (DMSO-d_6, ^{1}H 2.49 ppm and ^{13}C 39.5 ppm; CDCl$_3$ ^{1}H 7.26 ppm and ^{13}C 77.0 ppm). Coupling constants are expressed in hertz (Hz). HRMS (CI) were obtained with a VG analytical ZAB2-E instrument. UV-vis spectra were recorded using a Perkin Elmer Instruments Lambda 35 spectrometer. GPC data was recorded using a Waters HPLC system consisting of HR-1, HR-3, and HR-5E Styragel® columns arranged in

series, a 1515 pump, and a 2414 RI detector. Molecular weight data is reported relative to polystyrene standards in DMF (0.01 M LiBr) at 40 °C (column temperature). Decomposition temperatures (T_ds) were defined as the temperature at which 10% mass loss occurred and were determined using a TA Instruments TGA-Q500 under nitrogen atmosphere. All solvents and reagents were of reagent quality and used as obtained from commercial sources.

1,5-Bis(2-hydroxyphenyl)amino-2,4-dinitrobenzene (2): A 500 mL flask was charged with 1,5-dichloro-2,4-dinitrobenzene (10.0 g, 42.2 mmol), 2-aminophenol (18.4 g, 169 mmol), EtOH (250 mL) and a magnetic stir bar. The flask was equipped with a H_2O-jacketed condenser and the mixture was heated under reflux for 48 h. The resulting red solution was allowed to cool to ambient temperature and the volume was reduced to approximately half its original volume under reduced pressure. The red slurry was then poured into H_2O (200 mL) and allowed to stand for 1 h. The red solids that had formed were collected by vacuum filtration, rinsed with H_2O, and dried under vacuum to give **2** (15.9 g, 99% yield). This material was used without further purification. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.64 (br s, 2H), 9.04 (s, 1H), 7.21 (dd, J = 7.6, 1.2 Hz, 2H), 7.03 (t, J = 6.8 Hz, 2H), 6.92 (d, J = 7.4 Hz, 2H), 6.76 (t, J = 7.0 Hz, 2H), 6.30 (s, 1H); ^{13}C NMR (100 MHz DMSO-d_6): δ 150.8, 145.6, 128.3, 127.0, 125.0, 124.7, 124.6, 119.2, 116.3, 95.5.

Benzobis(azolium) dibromide 4: In an 500 mL flask, a suspension of 10% Pd/C (1.0 g, 0.94 mmol Pd) and NaO$_2$CH (22.6 g, 333 mmol) in formic acid (88%, 250 mL) was treated with dinitroarene **2** (10.6 g, 27.7 mmol) in several portions. The flask was then equipped with a H_2O-jacketed condenser and the mixture was heated under reflux for 48 h. Upon completion, the mixture was allowed to cool to ambient temperature, filtered through Celite and washed with 50 mL H_2O. The filtrate volume was then reduced under vacuum to ca 50 mL and then slowly added to a stirred aqueous solution saturated with Na$_2$CO$_3$. The resulting precipitate was collected by vacuum filtration, rinsed with H_2O, and dried under vacuum to give benzobis(imidazole) **3** (8.1 g, 85% yield) as a tan powder. The material was used directly in the next step without additional purification. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.2 (br s, 2H), 8.31 (s, 2H), 8.02 (s, 1H), 7.39 (d, J = 7.6 Hz, 2H), 7.30 (t, J = 7.6 Hz, 2H), 7.08 (d, J = 8.4 Hz, 2H), 6.95 (t, J = 7.2 Hz, 2H), 6.91 (s, 1H).

A Schlenk flask was charged with DMF (100 mL), benzobis(imidazole) **3** (11.8 g, 34.5 mmol), 1-bromobutane (22.2 mL, 207 mmol), and a magnetic stirbar. The flask was sealed and the slurry was stirred at 110 °C for 48 h during which time the mixture became homogenous for a short period of time and then heterogenous. Subsequently, the cooled mixture was poured into PhCH₃ (200 mL) and the solids were collected by vacuum filtration, rinsed with THF, and dried under vacuum to give 19.8 g (93% yield) of the bis(azolium) salt as a tan powder. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.77 (br s, 2H) 10.52 (s, 2H), 9.46 (s, 1H), 7.72 (dd, J = 8.0, 1.2 Hz, 2H), 7.53-7.49 (m, 3H), 7.22 (d, J = 8.4 Hz, 2H), 7.09 (t, J = 8.2 Hz, 2H), 4.80 (t, J = 6.8 Hz, 4H), 2.08 (pent, J = 7.4 Hz, 4H), 1.46 (sext, J = 7.4 Hz, 4H), 0.97 (t, J = 7.2 Hz, 6H), ^{13}C NMR (75 MHz DMSO-d_6): δ 152.2, 147.0, 132.5, 130.9, 130.0, 128.1, 120.0, 119.7, 117.5, 100.0, 98.9, 47.6, 30.2, 19.1, 13.5; HRMS m/z calcd for $C_{28}H_{31}N_4O_2$ [M-H$^+$] 455.2447, found 455.2447.

2-(2-Nitro-phenylamino)-phenol (7): 1-Chloro-2-nitrobenzene (**1**) (1.39 g, 8.82 mmol), 2-aminophenol (915 mg, 8.38 mmol), CuO, (210 mg, 2.65 mmol), K_2CO_3 (2.44 g, 17.6 mol), and a magnetic stirbar were combined in a 500 mL flask. The flask was fitted with a H_2O-jacketed condenser and DMF (200 mL) was added. The mixture was stirred in an oil bath at 120 °C for 12 h. The cooled reaction mixture was then diluted with PhCH₃ (100 mL) and filtered through a plug of silica gel using 100 mL CH_2Cl_2 as eluent. The filtrate was concentrated under vacuum and purification by flash chromatography on silica gel (30% _ 80% CH_2Cl_2/hexanes gradient) provided 1.63 g (80% yield) of the desired material as an orange-red solid. ^{1}H NMR (400 MHz, CDCl₃): δ 9.01 (br s, 1H), 8.21 (dd, J = 8.4, 1.6 Hz, 1H), 7.40-7.35 (m, 1H), 7.28-7.20 (m, 2H), 7.07 (dd, J = 8.0, 1.2 Hz, 1H), 6.99 (ddd, J = 7.8, 7.6, 1.2 Hz, 1H), 6.84-6.79 (m, 1H), 6.77 (dd, J = 8.6, 1.4 Hz, 1H), 5.63 (br s, 1H). ^{13}C NMR (100 MHz CDCl₃): δ 152.2, 144.0, 136.1, 133.6, 128.9, 127.8, 126.5, 124.9, 121.4, 118.1, 116.3, 116.2.

***N*-Butyl-*N*´-(2-hydroxyphenyl)-benzimidazolium bromide 9**: A 100 mL flask was charged with a magnetic stirbar, formic acid (88%, 60 mL), NaO_2CH (1.77 g, 26.1 mmol), and 10% Pd/C (460 mg, 0.43 mmol Pd). To this mixture was added nitroarene **7** (2.00 g, 8.69 mmol) and the flask was fitted with a H_2O-jacketed condenser and stirred in an oil bath at 110 °C for 7 h. Upon completion, the cooled reaction mixture was filtered through celite with the aid of ca 25 mL H_2O and the volume of the filtrate was reduced to ca 10 mL under reduced pressure. The acidic solution was then slowly added to a vigorously stirred

aqueous solution of saturated Na_2CO_3 (ca 250 mL). The resulting solids were collected by vacuum filtration, rinsed with H_2O, and dried under vacuum to give 2.12 g (93% yield) of monosubstituted benzimidazole **8** as a tan solid. This material was used without additional purification. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.29 (s, 1H), 7.72 (br s, 1H), 7.34 (d, J = 7.6 Hz, 1H), 7.29-7.22 (m, 4H), 7.11 (d, J = 8.4 Hz, 1H), 6.89 (t, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 152.2, 144.4, 143.0, 134.3, 129.7, 127.5, 122.9, 122.9, 121.9, 119.6, 119.5, 117.0, 111.1.

Benzimidazole **8** (347 mg, 1.65 mmol) was dissolved in a mixture of CH_3CN (5.0 mL) and 1-bromobutane (0.53 mL, 4.95 mmol) in a screw-cap vial. A magnetic stirbar was then added and the vial was sealed with a Teflon-lined cap and placed in an oil bath at 100 °C and stirred for 12 h. After cooling to ambient temperature, the reaction was transferred to a round-bottom flask with the aid of ca 3 mL MeOH. The crude material was then concentrated under reduced pressure to provide benzimidazolium bromide **9** in near quantitative yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.75 (s, 1H), 10.11 (s, 1H), 8.21 (d, J = 8.0 Hz, 1H), 7.76-7.69 (m, 3H), 7.58-7.51 (m, 2H), 7.22 (d, J = 0.8 Hz, 1H), 7.11 (ddd, J = 8.0, 7.6, 1.2 Hz, 1H) 4.59 (t, J = 7.2 Hz, 2H), 1.96 (pent, J = 7.2 Hz, 2H), 1.39 (sext, J = 7.2 Hz, 2H), 0.95 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 152.2, 143.2, 132.1, 131.7, 130.8, 127.9, 127.2, 126.7, 112.0, 119.8, 117.3, 114.0, 46.8, 30.5, 19.1, 13.4; HRMS m/z calcd for $C_{17}H_{19}N_2O$ [M$^+$] 267.1497, found 267.1494.

General polymerization procedure: Bis(azolium) dibromide **4** (1.0 mmol, 1.0 equiv) was dissolved in DMSO (5 mL). To the solution was added the metal salt (1.0 mmol, 1.0 equiv) and NaOAc (4.0 mmol, 4.0 equiv if $PdCl_2$, $PtCl_2$, or CuO; 2.0 mmol, 2.0 equiv if Ni(OAc)$_2$ or Cu(OAc)$_2$). The solution was stirred at 80 °C for 24 – 48 h and monitored by ^{1}H NMR spectroscopy. Upon completion, the mixture was allowed to cool and added dropwise into H_2O (50 mL). The resulting precipitate was collected via vacuum filtration, rinsed with H_2O and dried under vacuum.

Nickel complex 10: A 10 mL flask was charged with benzimidazolium bromide **9** (347 mg, 1.0 mmol), DMSO (4.0 mL), Ni(OAc)$_2$·4H$_2$O (124 mg, 0.50 mmol), NaOAc (82 mg, 1.0 mmol), and a magnetic stirbar. The mixture was placed in an oil bath thermostatted at 80 °C and stirred for 2 h at which time No-D NMR spectroscopy revealed complete consumption of **9**. The mixture was allowed to cool to ambient temperature and poured into H_2O (20 mL). The resulting tan solids were collected by vacuum filtration,

rinsed with H_2O, and dried under vacuum. Recrystallization of the crude material from CH_2Cl_2/hexanes gave 280 mg (95%) of the desired product as a yellow solid. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.91-7.89 (m, 1H), 7.67 (d, $J = 7.2$ Hz, 1H), 7.39 (d, $J = 8.4$ Hz, 1H), 7.30-7.29 (m, 3H), 7.17 (t, $J = 7.2$ Hz, 1H), 6.80 (t, $J = 7.4$ Hz, 1H), 4.23-4.16 (m, 1H), 3.64-3.57 (m, 1H), 2.32-2.28 (m, 1H), 1.32-1.24 (m, 2H), 1.11-1.04 (m, 1H), 0.55 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 172.5, 158.9, 135.3, 132.2, 128.2, 128.1, 123.7, 123.7, 122.4, 120.1, 113.9, 112.2, 109.9, 48.3, 32.1, 20.2, 13.3; HRMS m/z calcd for $C_{34}H_{35}N_4O_2Ni$ [M+H$^+$] 589.2113, found 589.2115; Crystal data for **10**: $C_{34}H_{34}N_4NiO_2$, $M = 589.36$, monoclinic, P21/n, $a = 12.8694(2)$ Å, $b = 10.3815(2)$ Å, $c = 21.7249(4)$ Å, α= 90°, β= 96.904(1)°, γ = 90°, $V = 2881.48(9)$ Å^3, $Z = 4$, $D_c = 1.359$ g cm^{-3}, _ = 0.712 mm^{-1}, $F_{(000)} = 1240$, _ = 0.71073 Å, yellow plates, crystal size 0.20 x 0.16 x 0.12 mm, 11823 reflection measured ($R_{int} = 0.0282$), 6579 unique, $R1 = 0.0407$ for $I>2\_(I)$ and 0.0725 for all data. The data were collected at 153(2) K using an Oxford Cryostream low temperature device. The structures were solved by direct methods and refined by full-matrix least-squares on F2 with anisotropic displacement parameters for the non-H atoms using SHELXL-97 (Sheldrick, G. M. University of Gottingen, Germany, 1994). Data for this structure was deposited with the Cambridge Crystallographic Data Centre (12 Union Road, Cambridge CB2 1EZ, UK).

Supporting Information Available: A CIF file containing X-ray structural data, atomic coordinates, thermal parameters, bond distances, and bond angles for complex **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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28) Pd(OAc)$_2$ was found to be equally effective. For reactions involving PdCl$_2$, PtCl$_2$, or CuO, 2.0 equivalents (relative to metal) of NaOAc was added.

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31) A 4:1 ratio of total acetate ions relative to bis(azolium) salt **4** was used.

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Figures and Schemes:

Scheme 1. Synthesis of bis(phenolic) benzobis(imidazolium) monomer **4**.
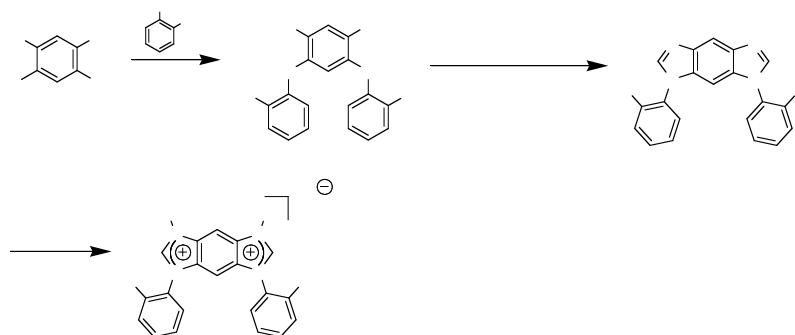
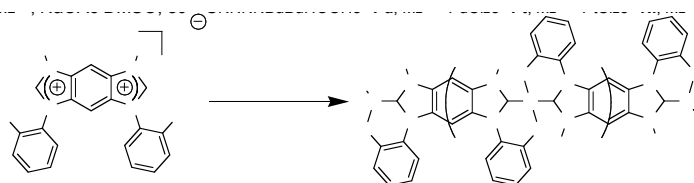**Scheme 2**. Copolymerization with various transition metals to form organometallic polymers **5**.

Table 1. Physical characterization and absorption maxima of polymers **5**.

Metal	Yield (%)[a]	M_n (kDa)[b]	M_w/M_n	T_d (°C)[c]	λ_{max} (nm)[d]
Ni	96	[e]	[e]	362	287
Pd	99	67.5	2.20	342	312
Pt	95	363	1.59	340	316, 372 (sh)
Cu	86	150.0	1.96	329	319

[a]Isolated yields. [b]Determined by GPC relative to polystyrene standards in DMF with 0.01 M LiBr at 40°C. [c]The decomposition temperature (T_d) is defined as the temperature at which 10% weight loss occurs as determined by

thermogravimetric analysis under N_2, rate = 10 ºC/min. ^{d}Determined in DMF under ambient conditions. ^{e}Multi-modal distribution.
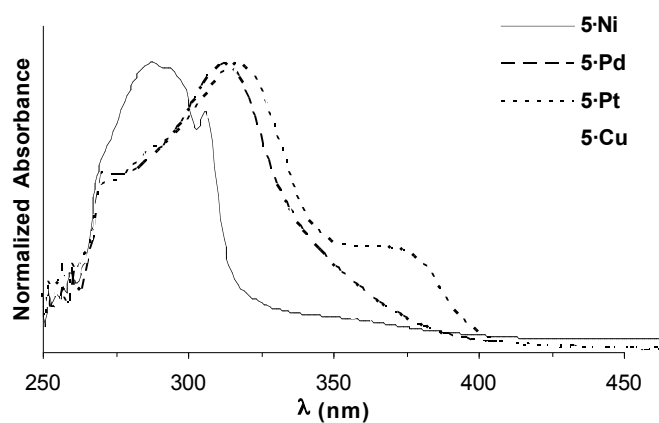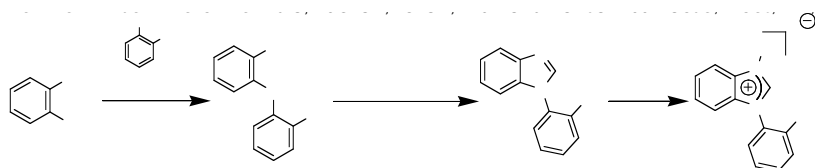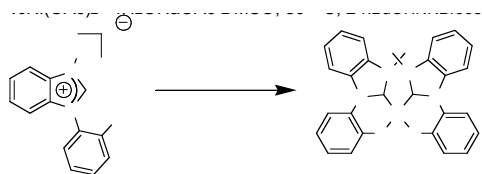

Figure 1. Electronic absorption spectra of polymers **5** in DMF at room temperature.

Scheme 3. Synthesis of phenol-substituted benzimidazolium salt **9**.

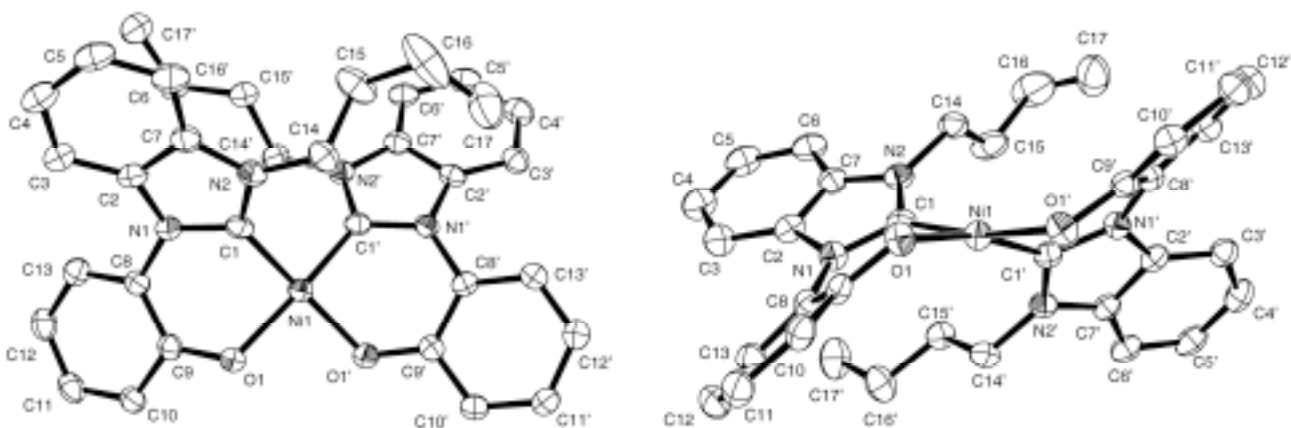**Scheme 4**. Synthesis of model complex **10**.

Figure 2. Two views of the molecular structure of Ni complex **10**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ni1-C1, 1.839(2); Ni1-O1, 1.895(5); N1-C1, 1.367(3); N2-C1, 1.364(3); N1-C2, 1.411(3); C2-C7, 1.388(3); O1-C9, 1.324(2); C1-Ni1-C1´, 94.5(3); C1-Ni1-O1´, 168.9(6); C1´-Ni1-O1´, 89.0(3); C1-Ni1-O1, 88.3(9); C1´-Ni1-O1, 167.1(7); O1´-Ni1-O1, 90.4(8); C9-O1-Ni1, 118.0(2); N1-C1-N2, 106.2(7); C1-N1-C2, 110.3(4); N1-C2-C7, 105.9(8); O1-C9-C8, 124.0(2); C9-C8-N1, 117.5(4); C1-N1-C8, 121.7(8); N1-C1-Ni1, 124.1(5); N2-C1-Ni1, 129.3(1); C1-Ni1-O1-C9 52.0(6); C1-N1-C8-C9, 26.7(3).