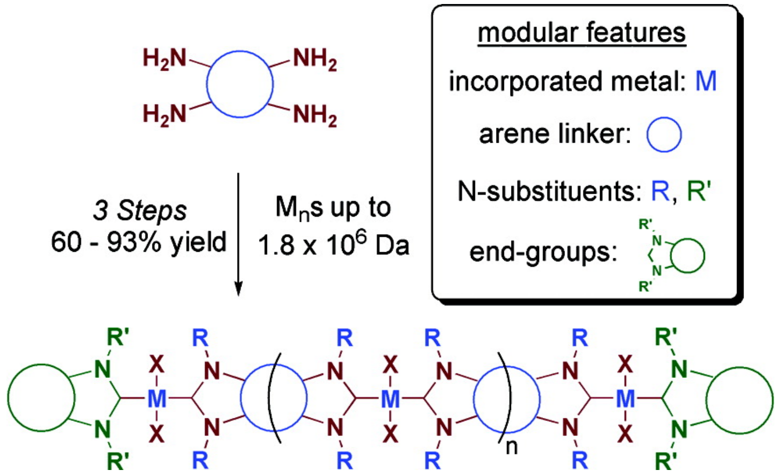
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

A Modular Approach to Main-Chain Organometallic Polymers

Andrew J. Boydston, Kyle A. Williams, and Christopher W. Bielawski

J. Am. Chem. Soc., **2005**, 127 (36), 12496-12497• DOI: 10.1021/ja054029k • Publication Date (Web): 20 August 2005



ACS Publications
High quality. High impact.

Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
COMMUNICATIONS

Published on Web 08/20/2005

A Modular Approach to Main-Chain Organometallic Polymers

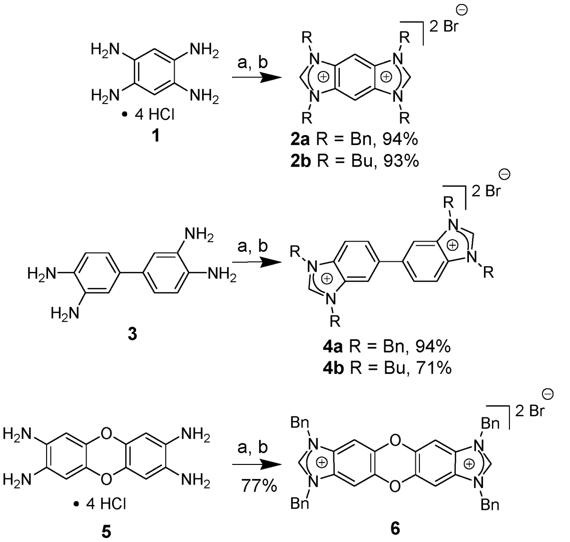
Andrew J. Boydston, Kyle A. Williams, and Christopher W. Bielawski*
Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78712
Received June 17, 2005; E-mail: bielawski@mail.cm.utexas.edu

Main-chain conjugated organometallic polymers (COMPs) are an interesting class of materials with desirable electronic and mechanical properties.[1] Unfortunately, access to these materials is often challenged by factors such as the need for inert atmospheres and anhydrous conditions, restrictive compatibilities of transition metals with contemporary polymerization protocols, and limited polymer stabilities and/or solubilities. Overcoming these restraints, which have prevented COMPs from reaching their full potential, requires development of new building blocks and polymerization strategies. Although a variety of binding interactions have been employed for integrating metals into organic polymers, Arduengo-type N-heterocyclic carbenes[2] (NHCs) remain an untapped resource. This is surprising, considering that NHCs offer broad structural diversity and generally display high affinities toward a wide range of transition metals.[3] We sought a versatile, direct, and simple route to bis(NHC)s connected via conjugated arenes. With the availability of these difunctional NHCs, we envisaged a new class of COMPs could be readily accessed.

We targeted rigid benzimidazole-based arene spacers to inhibit intramolecular metal chelation[4] and to ensure regiocontrol over metalation.[5] Toward this end, commercially available 1,2,4,5-tetraaminobenzene (**1**), 3,3′-diaminobenzidine (**3**), and known dioxintetraamine **5**[6] were condensed with formic acid[7] to provide the corresponding bis(imidazole)s. This cyclization protocol was conducted under ambient atmosphere and provided products in high purity (>95%) and high yields (>90%) after neutralization. As shown in Scheme 1, direct access to the respective bis(imidazolium) salts was accomplished via a single-step, 4-fold alkylation. Thus, the bis(imidazole)s described above were each treated with NaH in $PhCH_3$ followed by addition of alkyl bromide. After 1 h at 110 °C, DMF was introduced as a cosolvent (50% v/v) which facilitated dissolution of partially alkylated intermediates. After an additional 6 h at 110 °C, introduction of excess $PhCH_3$ precipitated the desired bis(imidazolium) bromides (**2**, **4**, and **6**) in good to excellent yields (74−99%).

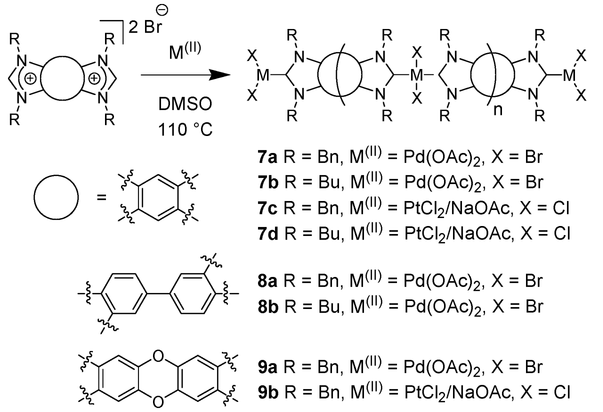
As shown in Scheme 2, polymerization and metal incorporation was carried out via a modified Herrmann−Schwarz−Gardiner method[8] by treatment of bis(imidazolium) bromides **2**, **4**, or **6** with $Pd(OAc)_2$ in DMSO at 110 °C.[9] After 1 h, the reaction solutions were precipitated into an excess of MeOH or H_2O which afforded polymers **7**−**9** in high yields (84−99%).[10] As expected, signals in the ^{1}H NMR spectra were relatively broad and shifted upfield in comparison with those of their respective bis(imidazolium) salt precursors. ^{13}C NMR spectroscopy was used to verify Pd was successfully incorporated into the backbones of the polymer chains. For example, the ^{13}C NMR spectrum of **8a** exhibited a resonance at 172 ppm which was diagnostic of an imidazol-2-ylidene-Pd bond.[4,11,12] As summarized in Table 1, absorption maxima for the polymer systems were clustered around 320 nm, and molar absorptivities (normalized per repeat unit) as high as 8.4×10^4 M^{-1} cm^{-1} were observed. Analysis of the polymers by gel permeation chromatography[13] (GPC) indicated their polydispersities were typical of step-growth polymerizations with number-average molecular weights (M_n's), ranging from 8.0×10^3 to 1.1×10^5 Da, dependent on the N-substituent and the bis(imidazole) structure. Likewise, the thermal stabilities of the polymers exhibited similar dependencies and began to degrade at 280−300 °C, as determined by thermogravimetric analysis.

Scheme 1 [a]



[a] Conditions: (a) HCO_2H, 110 °C, 2−36 h. (b) (i) NaH (2.0 equiv), $PhCH_3$, 110 °C; (ii) R−Br (6.0 equiv), 25 → 100 °C, 1 h.; (iii) DMF, 60 → 110 °C. Overall yields are indicated.

Scheme 2



Copolymerization of **4a** with $PdCl_2$ in the presence of NaOAc[14] (2.0 equiv) successfully produced a polymeric material with comparable molecular weight and yield as when prepared with $Pd(OAc)_2$. No reaction was observed when **4a** was treated with NaOAc in DMSO at 110 °C in the absence of metal. These results prompted us to explore the incorporation of other group X metals under similar reaction conditions. As shown in Scheme 2 and summarized in Table 1, copolymerizations of the bis(imidazolium) salts with $PtCl_2$/NaOAc afforded materials with remarkably high molecular weights; for example, the M_n of **7c** was found to be 1.8×10^6 Da.

10.1021/ja054029k CCC: $30.25 © 2005 American Chemical Society

Table 1. Physical Characteristics of Polymers **7**−**9**

polymer	yield (%)[a]	$M_n \times 10^3$ Da[b]	M_w/M_n	T_d (°C)[c]	λ_{max} (nm)[e]	Log(ϵ)[e,f]
7a	90	18.4	1.9	291	316	4.72
7b	84	103	1.8	[d]	314	4.72
7c	99	1760	1.3	294	329	4.45
7d	76	766	1.7	295	322	4.51
8a	85	26.1	2.0	284	308	4.80
8b	84	8.00	1.4	[d]	308	4.93
9a	98	106	1.5	299	323	4.63
9b	93	408	2.6	[d]	329	4.92

[a] Isolated yield. [b] Determined by GPC relative to polystyrene standards in DMF. [c] The decomposition temperature (T_d) is defined as the temperature at which 10% weight loss occurs determined by thermogravimetric analysis under N_2, rate = 10 °C/min. [d] Not determined. [e] Determined in DMF under ambient conditions. [f] Per repeat unit.

Scheme 3

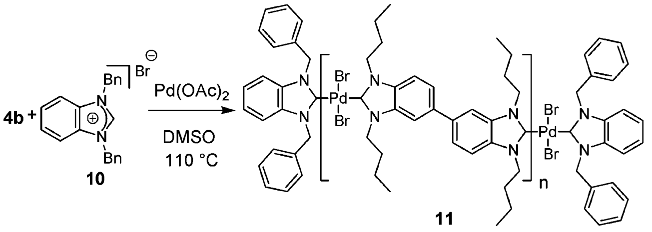


Table 2. Experimental and Theoretical Molecular Weight Data for **11**

polymer	$X_{n,theo}$[a]	$X_{n,NMR}$[b]	$M_{n,NMR}$ (×10³ Da)[b]	$M_{n,GPC}$ (×10³ Da)[c]
11a	10	8.9	6.4	4.8
11b	20	23	17	8.5
11c	40	47	34	11

[a] Theoretical number average of monomer units per polymer chain given by (2[**4b**]$_o$/[**10**]$_o$). [b] Determined by ^{1}H NMR spectroscopy. [c] Determined by GPC relative to polystyrene standards in DMF.

As with Pd, molecular weights were found to be dependent on the organic moiety; however, the transition metal obviously played a dominant role. Unfortunately, no polymeric materials were obtained with $Ni(OAc)_2 \cdot 4H_2O$, which may reflect the reduced affinity of NHCs for Ni.[15]

Since the metal centers in the main chain of the polymers are coordinatively unsaturated, we envisioned altering the physical properties of the macromolecules via a post-polymerization modification.[16] For example, treatment of **8a**, which is virtually insoluble in THF,[17] with 2 equiv of PCy_3 or PPh_3 resulted in rapid dissolution. GPC and ^{1}H NMR analysis of the phosphine-bound polymer confirmed the macromolecular structure was not compromised. Phosphine ligation to Pd was confirmed by ^{31}P NMR spectroscopy (δ = 25 ppm).[18]

Precise control of molecular weight is essential for tailoring or fine-tuning the physical characteristics of polymeric materials.[19] Chain transfer agents (CTAs) have been used extensively to control molecular weights of polymers obtained from equilibrium polymerizations.[20] Since coordination of NHCs to Group X metals is dynamic,[21] inclusion of monofunctional NHCs as CTAs during these polymerizations should provide an effective handle for controlling molecular weight. As shown in Scheme 3, copolymerization of **4b** with $Pd(OAc)_2$ in the presence of various amounts of *N*,*N*′-dibenzylbenzimidazolium bromide (**10**)[22] provided the corresponding end-functionalized polymers **11**. Integration of the benzyl end-groups ($PhCH_2$− δ = 6.2 ppm) with respect to the butyl groups ($ArNCH_2$− δ = 4.8 ppm) along the polymeric backbone indicated the molecular weights of the polymers were in excellent agreement with their theoretical values based on complete incorporation of the CTA (Table 2).

In conclusion, we have developed a highly efficient route to a new class of organometallic polymers with metal centers linked together via conjugated, difunctional NHCs. The polymerizations did not require anhydrous conditions or inert atmospheres, and the entire process, from commercial materials to polymeric products, was accomplished in three simple manipulations with minimal technical difficulty. The physical properties of the polymers were found to be dependent on both the transition metal and the modular structural characteristics of the NHC, and could be further modified through post-polymerization ligation. Control over both molecular weight and end-groups was also demonstrated through the inclusion of chain transfer agents during polymerization. Combined with the ability to prepare polymers with high molecular weights, these modular building blocks should open new opportunities in polymer synthesis, conductive polymers, nonlinear optics, and electronic devices. Full investigation of the electronic and physical characteristics of the polymers presented herein will be reported in due course.

Acknowledgment. We thank the University of Texas at Austin and the U.S. Army Research Office (W911NF-05-1-0430) for their generous financial support.

Supporting Information Available: Detailed experimental procedures and characterization of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) For recent reviews, see: (a) Holliday, B. J.; Swager, T. M. *Chem. Commun.* **2005**, 23. (b) Pittman, C. U. *J. Inorg. Organomet. Polym. Mater.* **2005**, *15*, 33. (c) Moorlag, C.; Sih, B. C.; Stott, T. L.; Wolf, M. O. *J. Mater. Chem.* **2005**, *15*, 2433. (d) Bunz, U. H. F. *J. Organomet. Chem.* **2003**, *683*, 269. (e) Nguyen, P.; Gómez-Elipe, P.; Manners, I. *Chem. Rev.* **1999**, *99*, 1515. (f) Roncali, J. *J. Mater. Chem.* **1999**, *9*, 1875. (g) Pickup, P. G. *J. Mater. Chem.* **1999**, *9*, 1641.

(2) (a) Arduengo, A. J., III. *Acc. Chem. Res.* **1999**, *32*, 913. (b) Arduengo, A. J., III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361. (c) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290.

(3) For recent reviews, see: (a) Scott, N. M.; Nolan, S. P. *Eur. J. Inorg. Chem.* **2005**, 1815. (b) Crudden, C. M.; Allen, D. P. *Coord. Chem. Rev.* **2004**, *248*, 2247. (c) Kavel, K. J.; McGuinness, D. S. *Coord. Chem. Rev.* **2004**, *248*, 671. (d) Peris, E.; Crabtree, R. H. *Coord. Chem. Rev.* **2004**, *248*, 2239. (e) Arnold, P. *Heteroat. Chem.* **2002**, *13*, 534.

(4) For selected examples see: (a) Chiu, P. L.; Chen, C. Y.; Zeng, J. Y.; Lu, C. Y.; Lee, H. M. *J. Organomet. Chem.* **2005**, *690*, 1682. (b) Marshall, C.; Ward, M. F.; Harrison, W. T. A. *Tetrahedron Lett.* **2004**, *45*, 5703.

(5) Grundemann, S.; Kovacevic, A.; Albrecht, M.; Faller, J. W.; Crabtree, R. H. *J. Am. Chem. Soc.* **2002**, *124*, 10473.

(6) Chichak, K.; Jacquemard, U.; Branda, N. R. *Eur. J. Inorg. Chem.* **2002**, 357.

(7) Wagner, E. C.; Millett, W. H. *Org. Synth.* **1939**, *19*, 12.

(8) This method, and variations thereof, are well-known for making bidentate and bis(NHC) organometallic complexes, see: Herrmann, W. A.; Schwarz, J.; Gardiner, M. G. *Organometallics* **1999**, *18*, 4082.

(9) Polymerizations proceeded at temperatures as low as 50 °C, although longer reaction periods were required (3 h).

(10) Prolonged standing of **7b** in H_2O or 10% HCl (aq) did not affect spectroscopic or molecular weight characteristics.

(11) Frøseth, M.; Netland, K. A.; Tornroos, K. W.; Dhindsa, A.; Tilset, M. *J. Chem. Soc., Dalton Trans.* **2005**, 1664.

(12) Based on analogous small molecule reactions (cf. 8), polymer end groups were assumed to be MX_2; however, due to their high molecular weights, conclusive evidence was not obtainable using ^{1}H or ^{13}C NMR spectroscopy.

(13) M_n's are reported relative to polystyrene standards in DMF.

(14) The use of stronger bases (e.g., NaOH, Et_3N) gave inferior yields of polymer.

(15) Louie, J.; Gibby, J. E.; Farnworth, M. V.; Tekavec, T. N. *J. Am. Chem. Soc.* **2002**, *124*, 15188.

(16) Boaen, N. K.; Hillmyer, M. A. *Chem. Soc. Rev.* **2005**, *34*, 267.

(17) Polymers **7**−**9** exhibit good solubility in highly polar aprotic solvents (e.g., DMF, DMSO, and NMP).

(18) This is consistent with the reported ^{31}P chemical shift for $(PCy_3)_2PdCl_2$ (δ = 21.2 ppm); see: Rüegger, H. *Magn. Reson. Chem.* **2004**, *42*, 814.

(19) Odian, G. *Principles of Polymerization*, 3rd ed.; Wiley-Interscience: New York, 1991.

(20) Goethals, E. J. *Telechelic Polymers: Synthesis and Applications*; CRC Press: Boca Raton, FL, 1989.

(21) (a) Gstöttmayr, C. W. K.; Böhm, V. P. W.; Herdtweck, E.; Grosche, M.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1363. (b) Titcomb, L. R.; Caddick, S.; Cloke, F. G. N.; Wilsona, D. J.; McKerrecherb, D. *Chem. Commun.* **2001**, 1388.

(22) Claramunt, R. M.; Elguero, J.; Meco, T. *J. Heterocycl. Chem.* **1983**, *20*, 1244.

JA054029K