



Phosphorus, Sulfur, and Silicon and the Related Elements

ISSN: 1042-6507 (Print) 1563-5325 (Online) Journal homepage: http://www.tandfonline.com/loi/gpss20

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To cite this article: Ya-Fan Lin, Chih-Hsun Liu, Chung-Hao Hu & Ching-Wen Chiu (2016) Non-chelating polydentate N-heterocyclic carbenes through assembly approaches, Phosphorus, Sulfur, and Silicon and the Related Elements, 191:4, 613-617, DOI: 10.1080/10426507.2015.1128918

To link to this article: <u>http://dx.doi.org/10.1080/10426507.2015.1128918</u>



Accepted author version posted online: 06 Feb 2016.



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Non-chelating polydentate N-heterocyclic carbenes through assembly approaches

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ABSTRACT

Bridging-type polydentate *N*-heterocyclic carbene (NHC) ligands are valuable building blocks for organometallic supramolecules. In order to quickly expand the ligand library of poly-NHC, we have assembled several bi-functional carbene precursors with spiroborate, phthalimide and metal-carboxylate to yield poly-NHC ligands with various denticities and geometries. Condensation of 4,5-dihyxdroxy-*N*,*N*'-diaryl-benzimidazolium and arylboronic acids leads to a spiroborate-linked bis-benzimidazolium salt, which can be further deprotonated to give a linear anionic bis-NHC. The second approach utilizes the dehydrative condensation of phthalic anhydride functionalized benzimidazole with poly-anilines to afford a series of poly-benzimidazole compounds, which can be converted into the corresponding poly-nuclear metal-NHC complexes after alkylation and metalation. The introduction of a benzoate group to bi-functional carbene precursor facilitates the assembly of poly-benzimidazolium salts with metal salts leading to MCl₂ (M=Zn, Co)-linked C_{2h} symmetric bis-benzimidazoliums and a penta-Zn cluster-linked tetra-benzimidazolium.

ARTICLE HISTORY

Received 3 December 2015 Accepted 3 December 2015

KEYWORDS

N-Heterocyclic carbine; multi-dentate ligands; non-chelating

GRAPHICAL ABSTRACT



Introduction

Being a strong σ -donating ligand to metals, *N*-heterocyclic carbenes (NHCs) have been widely applied in transition metal and main-group metal complexes.^{1–10} In addition to monodentate NHC, poly-functional NHC ligands have also attracted much attention for their ability to stabilize highly reactive low-valent metal centers through chelation.^{11–22} Another important advance of poly-NHC ligands is their application in the construction of organometallic supramolecules, including linear polymers, planar molecular rectangles, three-dimensional (3D) molecular cages, and porous organometallic polymers.^{23–31} However, the synthesis of poly-NHC ligands is not trivial, especially the one that maintains the relative ylidene position after metalation.^{32–36}

Recently, we have tried to prepare symmetrical multi-dentate NHC ligands through assembly methods. To this end, we have designed three bi-functional benzimidazolium derivatives that serve as carbene precursors and assembly linkages simultaneously (Figure 1). Assembly of these bi-functional building blocks with appropriate molecular platforms affords multi-dentate carbene ligands with various denticities and geometries. Besides, since the ylidene carbon in all cases lie on the rotational axis of the building block, the twisting angles between the benzimidazolium units and the central molecular platform do not affect the relative position and orientation of the metal-carbene bond. Such molecular design could potentially lead to crystalline organometallic polymers.



Figure 1. Design of building blocks.

Results and discussion

Spiro-borate linkage

Inspired by the work of boronate-based covalent organic framework,³⁷⁻⁴⁰ we have designed a benzimidazolium salt ($[1]^+$) that contains two hydroxyl groups at 4,5-position for dehydrative condensation with arylboronic acid.³⁰ The synthesis of the catechol-benzimidazolium building unit is straightforward. After the amination of 4,5-dibromoveratrole, formylative cyclization of diamine compound afforded 4,5-dimethoxy-N,N'-dimesitylbenzimidazolium, which can then be demethylated with BBr₃ to yield the anticipated building unit [1][Br] (Scheme 1). Initial attempt to assemble building unit $[1]^+$ with benzenediboronic acid (BDBA) in 2:1 ratio in ethanol to give the corresponding linear bis-benzimidazolium salt $([2]^{2+})$ was unsuccessful due to the undesired cleavage of the aryl-boron bonds of BDBA. Instead, the mono-cationic spiroborate-linked bis-benzimidazolium salt ([3][Br]) was isolated exclusively. The ¹¹B resonance of $[3]^+$ detected at 15 ppm is consistent with the formation of a $[BO_4]^-$ unit. The structural connectivity of $[3]^+$ is further verified by X-ray diffraction analysis on a single crystal of [3][Br]. Two benzimidazolium units are brought together by a $[BO_4]^-$ linkage with a dihedral angle of nearly 90°, showing the lack of electronic communication between two azolium units. Therefore, $[4]^-$ could serve as a bridging ligand to two metal centers with dis-connected electronic communication between the two metal centers.

Interestingly, the $[BO_4]^-$ unit is robust toward KHMDS and KO^tBu, and the deprotonation of $[3]^+$ in tetrahydrofuran (THF) leads to the isolation of an anionic bis-NHC (K[4]) in excellent yield. The ¹³C NMR signal of the ylidene center observed at 224.5 ppm confirms the formation of free carbene in the solution.⁴¹ Further reaction of K[4] with BH₃(SMe₂) and

 $[Rh(COD)Cl]_2$ afforded the corresponding $[4-(BH_3)_2]^-$ and $[4-(Rh(COD)Cl)_2]^-$ complexes, respectively. Unfortunately, assembly of $[1]^+$ with arylboronic acid could only lead to the formation of a twisted linear ditopic NHC ligand $[4]^-$.

Phthalimide linkage

The second bi-functional building block that we designed is a phthalic anhydride containing benzimidazole (5), which can be assembled with polyamines and then converted into the phthalimide-linked poly-benzimidazoliums.³¹ Since phthalimide functionality is inert under normal pH and in the presence of bulky bases, metalation of these phthalimide-linked poly-azolium salts can be carried out to give the corresponding poly-nuclear NHC-metal complexes. Compound 5 can be readily obtained in multi-gram scale in few steps. Dehydrative condensation of 5 and aniline derivatives followed by second alkylation with ethyl iodide afforded the anticipated polybenzimidazolium salts in good to excellent yield (Scheme 2). Linear bis-benzimidaozlium ([6]²⁺), 2D tris-benzimidaozlium $([7]^{3+})$, and tetrahedral tetrakis-benzimidaozlium $([8]^{4+})$ were prepared from the assembly of bi-functional building block with di-amine, tri-amine, and tetra-amine, respectively. In other words, the size, denticity, and geometry of poly-benzidazolium salts could be easily controlled by the structure of the polyamino assembly platform.

To show that these phthalimide-linked poly-benzimidazoliums could serve as poly-NHC precursors, the corresponding poly-nuclear nickel ([6-(NiCpI)₂], [7-(NiCpI)₃], and [8-(NiCpI)₄]) and rhodium complexes ([6-(Rh(cod)I)₂], [7-(Rh(cod)I)₃], and [8-(Rh(cod)I)₄]) have also been prepared. Interestingly, reaction kinetics of these poly-nickel carbene



Scheme 1. Synthesis of bifunctional ligand [1][Br] and its reaction with BDBA to yield [3][Br].



Scheme 2. Assembly of poly-benzimidazolium salts from building block 5 and poly-amino molecular platforms.

complexes in hydrothiolation of terminal alkyne showed negligible correlation with ligand denticity and complex geometry. This observation implies that every [NHC-NiCpI] moiety of poly-nuclear nickel complexes is independent of each other.

Metal-carboxylate linkage

In an attempt to attain ligand topologies that are inaccessible with organic molecular platform, we then explored the potential to utilize the versatile coordination modes of carboxylate and transition metals to assemble poly-azolium units. To bring a carboxylic acid group to the C_2 axis of a benzimidazolium molecule, benzimidazole-5,6-dicarboxylic acid and 4-amino-benzoic acid were allowed to react in dimethylformamide (DMF) to yield the corresponding benzimidazole-carboxylic acid, which can then be converted into the anticipated benzimidazolium-carboxylic acid bi-functional ligand ([9a]⁺ and [9b]⁺) through stepwise deprotonation and alkylation with methyl iodide or benzyl bromide (Scheme 3).

To facilitate metal–carboxylate coordination, bases were added to deprotonate carboxylic acid to give the corresponding benzimidazolium-carboxylate zwitterion. Unfortunately, only one type of ligand topology was achieved through the metal–carboxylate coordination. In the presence of pyridine, neither $Zn(NO_3)_2$ nor $Zn(OAc)_2$ formed coordination compounds with

[9]⁺. However, heating ZnCl₂ and [9a][I] in acetonitrile at 80 °C for two days resulted in a colorless di-zinc cluster (10). A related di-cobalt cluster (11) was also obtained in a similar manner (Scheme 4). Single crystal X-ray diffraction studies revealed that both 10 and 11 adopt a dimeric structure comprising two metal ions and two zwitterionic ligands. As shown in Figure 2, the two benzimidazolium moieties are anti-parallel to each other with an inversion center located at the centroid of the eight-membered ring, leading to a C_{2h} symmetry of bis-benzimidazolium complex. Two metal centers (Zn or Co) and two carboxylate groups are linked in a syn-anti-fashion to form an eight-membered ring in chair form conformation. Complex 10 features a Zn(II)-Zn(II) distance of 3.870 Å, while the two Co(II) are separated by 3.725 Å in 11. The biggest structural difference between 10 and 11 is the torsion angles formed by phenyl and benzimidazolium plane (29.46° for 10 and 42.21° for 11). Thus, an intermolecular $\pi - \pi$ stacking of phthalimide groups is found in the crystal structure of **10** because of a better coplanarity in **10**.

When [9b][Br] was allowed to react with two equivalents of $Zn(ClO_4)_2$ in the presence of 1,8-diazabicyclo[5.4.0]undec-7ene (DBU) in THF/NMP (v/v = 8:1) at 140 °C under solvothermal condition, a tetrakis-benzimidazolium linked by a pentazinc cluster ([12][ClO₄]₂) was isolated. The aminobenzoic acid group of $[9b]^+$ was removed under the harsh reaction condition to give the corresponding benzimidazolium-phthalate



Scheme 3. Synthesis of benzimidazolium-carboxylic acid ligands ([9][X]).



Scheme 4. Synthesis of metal-carboxylate-linked bis- and tetrakis-benzimidazoliums.

fragment (13), which then coordinated with Zn metal centers (Scheme 4). Structural analysis of $[12][ClO_4]_2$ shows that [12]²⁺ possesses five coplanar zinc ions, two terminal bromides, two capping NMP molecules, two μ_3 -hydroxo ligands, and four benzimidazolium-phthalate units. The hydroxo group binds to three neighboring zinc ions with Zn-O distances varied from 1.948(8) to 2.111(8) Å. Interestingly, the two carboxylate groups of benzimidazolium-phthalate moiety have different linkage types. One bridges two zinc ions in a syn-syn orientation, and the other provides a single binding site to the metal. Each benzimidazolium-phthalate ligand is capable of binding to three zinc ions with ortho-dicarboxylate functionalities. As a result, four benzimidazolium units are brought together through a complicated coordination to five Zn(II) ions. The selected structural parameters of $[12]^{2+}$ are listed in Figure 3. The four C2 carbons of benzimidazolium moieties are essentially coplanar in a rectangular arrangement with the C2...C2 distances of 11.3 Å and 13.8 Å. Unfortunately, the extremely poor solubility of $[12][ClO_4]_2$ in organic solvents prohibited further deprotonation or metalation of the molecule.

In conclusion, three different linkage groups were designed to connect two or more benzimidazolium units with organic or inorganic assembly platforms. Although the condensation of $[1]^+$ with arylboronic acid could only give the linearly opposed bis-NHC, the orthogonal arrangement of two NHC moieties in [4]⁻ may find interesting application in ferromagnetically coupled bi-metallic complexes. Meanwhile, the reaction of 5 with poly-amino compounds successfully afforded the anticipated poly-benzimidazolium salts that could be metalated to give the corresponding poly-NHC metal complexes. The assembly concept can be further extended to inorganic metal-carboxylate linkage. However, all attempts toward deprotonation or direct metalation of the metal-carboxylate-linked bis- and tetrakisbenzimidazolium were unsuccessful due to either the poor solubility of these complexes or the undesired dissociation of metalcarboxylate linkages.



Figure 2. ORTEP drawing of (a) **10**, and (b) **11** with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg) for **10**: Zn–O1 2.0071(15), Zn–O2 1.9940(13), Zn–Cl1 2.2313(5), Zn–Cl2 2.2381(5), C1–O1–Zn 121.54(13), C1–O2–Zn 115.35(13), O1–Zn–O2 108.44(6), Cl1–Zn–Cl2 116.30(2), O1–Zn–Cl1 106.59(4), O1–Zn–Cl2 102.64(4), O2–Zn–Cl1 104.49(4), O2–Zn–Cl2 117.72(4). For **11**: Co–O1 2.0323(14), Co–O2 2.0209(14), Co–Cl1 2.2598(6), Co–Cl2 2.2506(6), C1–O1–Co 103.05(12), C1–O2–Co 122.38(12), O1–Co–Cl2 109.01(6), C11–Co–Cl2 110.89(2), O1–Co–Cl1 121.50(5), O1–Co–Cl2 103.97(4), O2–Co–Cl1 106.46(4), O2–Co–Cl2 103.66(4).



Figure 3. ORTEP drawing of [12][ClO₄]₂ with 50% probability ellipsoids: (a) side view, and (b) top view. Hydrogen atoms, counter anions, and solvent molecules are omitted for clarity. Selected bond distances (Å) and angles (deg): Zn1–O1 2.082(5), Zn1–O5 2.092(5), Zn1–O9 2.122(4), Zn2–O3 1.969(5), Zn2–O9 2.026(4), Zn2–O6 1.954(5), Zn2–Br1 2.2432(19), Zn3–O2 1.970(5), Zn3–O9 1.966(4), Zn3–O1 1.939(5), Zn3–O7 1.955(5), Zn1–O9–Zn2 113.0(2), Zn1–O9–Zn3 108.0(2), Zn2–O9–Zn3 126.9(2).

Acknowledgment

We would like to thank Dr. G.-H. Lee, Y.-H. Liu, and Prof. S.-M. Peng for structural determinations.

Funding

We would like to thank the Ministry of Science and Technology of Taiwan for funding (MOST 103-2113-M-002-005 and MOST 104-2811-M-002-130).

References

- 1. Díez-González, S. N-Heterocyclic Carbenes: From Laboratory Curiosities to Efficient Synthetic Tools; RSC Publishing, Cambridge, 2011.
- Herrmann, W. A.; Köcher, C. Angew. Chem. Int. Ed. 1997, 36, 2162-2187.
- Bourissou, D.; Guerret, O.; Gabbaï, F. P.; Bertrand, G. Chem. Rev. 2000, 100, 39-91.
- 4. Enders, D.; Niemeier, O.; Henseler, A. Chem. Rev. 2007, 107, 5606-5655.
- 5. Hahn, F. E.; Jahnke, M. C. Angew. Chem. Int. Ed. 2008, 47, 3122-3172.
- 6. Alcaide, B.; Almendros, P.; Luna, A. Chem. Rev. 2009, 109, 3817-3858.
- Díez-González, S.; Marion, N.; Nolan, S. P. Chem. Rev. 2009, 109, 3612-3676.
- Samojilowicz, C.; Bieniek, M.; Grela, K. Chem. Rev. 2009, 109, 3708-3742.
- Fevre, M.; Pinaud, J.; Gnanou, Y.; Vignolle, J.; Taton, D. Chem. Soc. Rev. 2013, 42, 2142-2172.
- Hopkinson, M. N.; Richter, C.; Schedler, M.; Glorius, F. Nature 2014, 510, 485-496.
- 11. Poyatos, M.; Mata, J. A.; Peris, E. Chem. Rev. 2009, 109, 3677-3707.
- Kernbach, U.; Ramm, M.; Luger, P.; Fehlhammer, W. P. Angew. Chem. Int. Ed. 1996, 35, 310-312.
- 13. Douthwaite, R. E.; Houghton, J.; Kariuki, B. M. *Chem. Commun.* **2004**, 698-699.
- Nieto, I.; Cervantes-Lee, F.; Smith, J. M. Chem. Commun. 2005, 3811-3813.
- Muñoz, S. B.; Foster, W. K.; Lin, H.-J.; Margarit, C. G.; Dickie, D. A.; Smith, J. M. Inorg. Chem. 2012, 51, 12660-12668.
- Gonell, S.; Poyatos, M.; Mata, J. A.; Peris, E. Organometallics 2012, 31, 5606-5614.
- Seitz, S. C.; Rominger, F.; Straub, B. F. Organometallics 2013, 32, 2427-2434.

- Blom, B.; Tan, G.; Enthaler, S.; Inoue, S.; Epping, J. D.; Driess, M. J. Am. Chem. Soc. 2013, 135, 18108-18120.
- Darmawan, N.; Yang, C.-H.; Mauro, M.; Raynal, M.; Heun, S.; Pan, J.; Buchholz, H.; Braunstein, P.; De Cola, L. *Inorg. Chem.* **2013**, 52, 10756-10765.
- Howell, T. O.; Huckaba, A. J.; Hollis, T. K. Org. Lett. 2014, 16, 2570-2572.
- 21. Schick, S.; Pape, T.; Hahn, F. E. Organometallics 2014, 33, 4035-4041.
- Li, Y.; Tang, J.; Gu, J.; Wang, Q.; Sun, P.; Zhang, D. Organometallics 2014, 33, 876-884.
- Boydston, A. J.; Williams, K. A.; Bielawski, C. W. J. Am. Chem. Soc. 2005, 127, 12496-12497.
- 24. Boydston, A. J.; Bielawski, C. W. Dalton Trans. 2006, 4073-4077.
- Boydston, A. J.; Rice, J. D.; Sanderson, M. D.; Dykhno, O. L.; Bielawski, C. W. Organometallics 2006, 25, 6087-6098.
- Williams, K. A.; Boydston, A. J.; Bielawski, C. W. Chem. Soc. Rev. 2007, 36, 729-744.
- Choi, J.; Yang, H. Y.; Kim, H. J.; Son, S. U. Angew. Chem. Int. Ed. 2010, 49, 7718-7722.
- Schmidtendorf, M.; Pape, T.; Hahn, F. E. Angew. Chem. Int. Ed. 2012, 51, 2195-2198.
- 29. Mejuto, C.; Guisado-Barrios, G.; Peris, E. Organometallics 2014, 33, 3205-3211.
- Su, J.-H.; Lee, G.-H.; Peng, S.-M.; Chiu, C.-W. Dalton Trans. 2014, 43, 3059-3062.
- Chen, Y.-H.; Peng, K.-E.; Lee, G.-H.; Peng, S.-M.; Chiu, C.-W. RSC Adv. 2014, 4, 62789-62792.
- 32. Williams, K. A.; Bielawski, C. W. Chem. Commun. 2010, 5166-5168.
- Gonell, S.; Poyatos, M.; Peris, E. Angew. Chem. Int. Ed. 2013, 52, 7009-7013.
- Gonell, S.; Alabau, R. G.; Poyatos, M.; Peris, E. Chem. Commun. 2013, 49, 7126-7128.
- Wang, Y.-T.; Chang, M.-T.; Lee, G.-H.; Peng S.-M.; Chiu, C.-W. Chem. Commun. 2013, 49, 7258-7260.
- Segarra, C.; Linke, J.; Mas-Marza, E.; Kuck D.; Peris, E. Chem. Commun. 2013, 49, 10572-10574.
- Niu, W.; O'Sullivan, C.; Rambo, B. M.; Smith, M. D.; Lavigne, J. J. Chem. Commun. 2005, 4342-4344.
- Niu, W.; Smith, M. D.; Lavigne, J. J. J. Am. Chem. Soc. 2006, 128, 16466-16467.
- Côté, A. P.; Benin, A. I.; Ockwig, N. W.; O'Keeffe, M.; Matzger, A. J.; Yaghi, O. M. Science 2005, 310, 1166-1170.
- El-Kaderi, H. M.; Hunt, J. R.; Mendoza-Cortés, J. L.; Côté, A. P.; Taylor, R. E.; O'Keeffe, M.; Yaghi, O. M. Science 2007, 316, 268-272.
- 41. Tapu, D.; Dixon, D. A.; Roe, C. Chem. Rev. 2009, 109, 3385-3407.