Carbene Ligands

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Synthesis and Study of Janus Bis(carbene)s and Their Transition-Metal Complexes**

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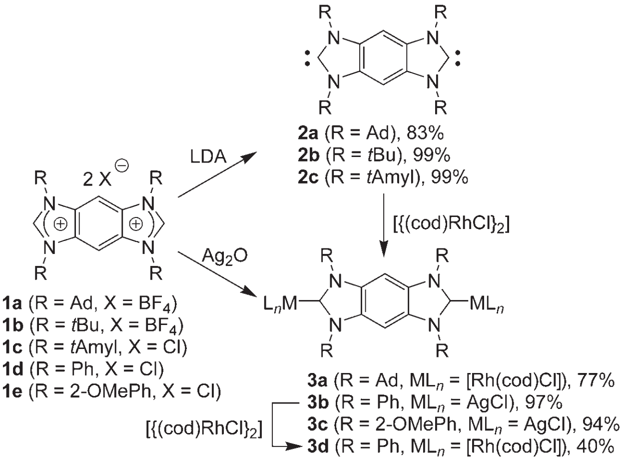
The construction of new organic–inorganic hybrid materials with interesting structural features and technologically useful functions is a vibrant area of research with considerable potential.[1] The key to growth in this field is the development of new, tunable molecular scaffolds that can bridge transition metals. Ideal linkers should be readily accessible, exhibit high affinities toward a broad range of transition metals, and possess modular features amenable for precisely manipulating their inherent physical and electronic characteristics. Stable N-heterocyclic carbenes (NHCs),[2] and in particular imidazolylidenes,[3] fulfill these requirements. These carbenes have been found to form robust complexes with nearly every transition metal[2,4] and both the basic *N*-heterocyclic nucleus, and its substituents on the N atoms can be acutely modified.[5] As a result, an impressive amount of attention has been devoted toward optimizing and understanding the interaction of carbenes with various transition metals to form monometallic complexes.[2–6] However, comparatively less attention has been directed toward the development of discrete, multitopic carbenes that are poised to bind multiple transition metals.[7,8] Herein, we report the synthesis and characterization of benzobis(imidazolylidene)s, a new class of Janus[9] bis(carbene)s, composed of two linearly opposed imidazolylidenes annulated to a common arene backbone. Their utility in preparing new organometallic materials is also demonstrated.

Requisite benzobis(imidazolium) salts **1** possessing a range of substituents on N were synthesized by Pd-catalyzed aryl amination of 1,2,4,5-tetrabromobenzene followed by formylative cyclization or by reductive cyclization of the respective 2,5-diamino-1,4-benzoquinonediimine, according to our previously reported procedures.[10] Independent treatment of **1a–c** with 2.2 equivalents of lithium diisopropylamide (LDA) in THF at RT caused precipitation of products **2a** and **2b**, which were subsequently isolated by filtration in yields of 83 and 99%, respectively (Scheme 1). While **2a** and **2b** were only slightly soluble in common organic solvents (for example, THF, toluene, and benzene), a highly soluble derivative featuring *N-tert*-amyl groups (**2c**) was obtained in 99% yield, after LiCl had been precipitated with excess toluene and removed by filtration.[11]



Scheme 1. Synthesis of benzobis(imidazolylidene)s and their related transition-metal complexes. Ad = adamantyl, cod = cycloocta-1,5-diene.

The ^{13}C NMR spectra of products **2a–c** in C_6D_6 all exhibited a single, diagnostic signal between $\delta = 227$–231 ppm, indicative of highly symmetric structures (Scheme 1) and consistent with other known annulated imidazolylidenes.[12] A crystal of **2a** was obtained by vapor diffusion of pentane into a saturated toluene/THF solution (1:1 v/v) and analyzed using X-ray diffraction.[13] An ORTEP view of the molecular structure is shown in Figure 1, with selected bond lengths and angles listed in the caption. Notably, the N-C-N bond angle was found to be 104.8(2)°,[14] which is similar to that found in saturated imidazolylidenes[15] and benzimidazolylidenes.[12a] This promising result strongly suggested that the reactivity and affinity of each carbene "face" of the Janus ligand toward transition metals should be similar to that of their monotopic analogues.

Addition of an equimolar amount of [{(cod)RhCl}$_2$] to a THF solution of **2a** at RT resulted in the precipitation of the Rh complex **3a** as a yellow solid, which was isolated in 77% yield. Analysis of this complex by NMR spectroscopy

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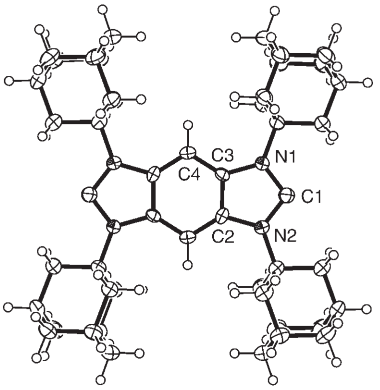


Figure 1. ORTEP view of **2a** (ellipsoids at the 50% probability level). Selected bond lengths [Å] and angles [°]: C1-N1 1.369(3), C1-N2 1.368(3), N1-C3 1.411(3), N2-C2 1.408(3), C2-C3 1.402(3), C3-C4 1.388(3); N1-C1-N2 104.8(2).

confirmed that the stoichiometry between the Rh centers and bis(carbene) nucleus was 2:1. A single ^{13}C NMR resonance appeared at $\delta = 198$ ppm, and two distinct sets of olefinic ^{1}H NMR signals were observed at 3.0 ppm (*cis* to the carbene) and 5.0 ppm (*trans* to the carbene), which was suggestive of a square planar geometry for each of the metal centers.[16] The structure of **3a** was confirmed by X-ray diffraction analysis after a suitable crystal was obtained by slow cooling of a hot $CHCl_3$ solution (Figure 2). Although key bond lengths were in accord with known NHC–Rh complexes,[16] a notable exception were the positions of the Rh atoms, which were displaced perpendicularly from the plane of the benzobis(imidazolylidene) by 0.75 Å. This unusual structural feature was attributed to the substantial steric bulk of the *N*-adamantyl groups balanced by the high affinity of imidazolylidenes for Rh^I.[17]

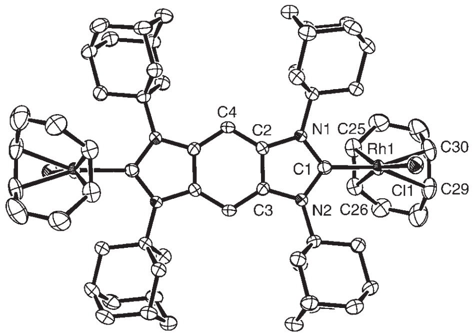


Figure 2. ORTEP view of **3a** (ellipsoids at the 50% probability level). Selected bond lengths [Å] and angles [°]: Rh1-C1 2.073(3), Rh1-C25 2.125(3), Rh1-C26 2.131(3), Rh1-C29 2.184(3), Rh1-C30 2.197(3), C1-N1 1.387(4), C1-N2 1.406(4), N1-C2 1.406(4), N2-C3 1.395(4), C2-C3 1.401(4), C2-C4 1.397(4); N1-C1-N2 105.7(2). Hydrogen atoms have been removed for clarity.

In cases where the free bis(carbene)s were not isolable (**1d–e**),[18] an alternative method of forming metal complexes was desired. Attention shifted toward the versatile Ag-mediated carbene-transfer protocol developed by Wang and Lin,[19] for accessing organometallic complexes.[20] Bis(azolium) salts **1d** and **1e** were respectively treated with 1 equivalent of Ag_2O in CH_2Cl_2 (23 °C) and CH_3CN (40 °C) (Scheme 1). Following filtration of the inorganic salts that precipitated during the reaction, concentration of the resulting solutions afforded products **3b** and **3c** in excellent yields (97 and 94%, respectively). Crystals of **3c** were obtained by slow diffusion of hexanes into a saturated CH_2Cl_2 solution and analyzed using X-ray diffraction. As shown in Figure 3, the structure is essentially linear along its main axis with a C1-Ag1-Cl1 bond angle of 176°; the *N*-aryl substituents are rotated out of the plane of the benzobis(imidazolylidene) with an average dihedral angle of 69°. Interestingly, in the solid state, the complexes arranged themselves in infinite rows that appeared to be governed by intermolecular argentophilic interactions.[20]

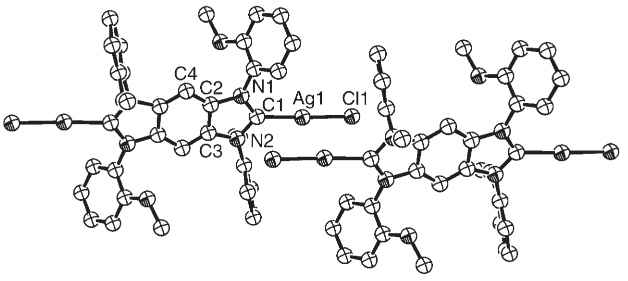
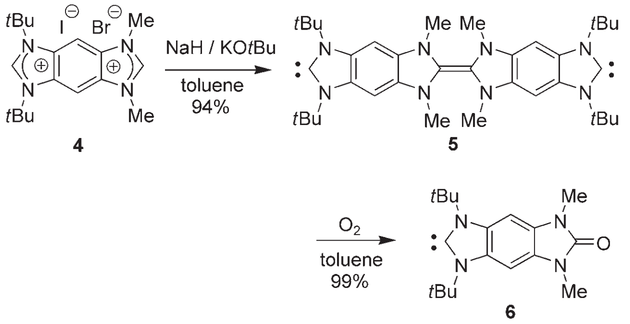


Figure 3. ORTEP view of **3c** (ellipsoids at the 50% probability level). Selected bond lengths [Å] and angles [°]: Ag1-C1 2.072(11), Ag1-Cl1 2.236(3), C1-N1 1.352(12), C1-N2 1.360(11), N1-C2 1.409(11), N2-C3 1.409(12), C2-C3 1.411(12), C2-C4 1.353(13), Ag···Ag 3.3054(15); N1-C1-N2 106.4(9). Hydrogen atoms have been removed for clarity.

Treatment of bimetallic Ag complex **3b** with an equimolar amount of $[\{(cod)RhCl\}_2]$ in CH_2Cl_2 at 50 °C for 24 h afforded the bimetallic Rh complex **3d** as an orange-brown powder in 40% yield (Scheme 2).[21] Although solution and solid-state[22] structural analyses indicated that **3d** and **3a** are superficially similar, a key difference is that the Rh atoms were now coplanar with the benzobis(imidazolylidene). Considering that the *N*-phenyl groups were rotated by an average of 63° relative to this same plane (minimizing any electronic contributions), and both complexes showed a similar *trans* effect (average Rh–olefin separation in **3a**: 2.20 Ås, in **3d**: 2.19 Ås), the size of the substituents on the N atoms appeared to dominate structural features about the metal centers.

Finally, we focused on the synthesis of bis(azolium) **4**, a desymmetrized precursor that was envisioned to provide a Janus bis(carbene) with differential characteristics at each carbene "face". The dissimilar environments of the 1,3-dimethyl- and 1,3-di-*tert*-butylimidazolium fragments were manifested in the ^{1}H NMR spectrum ([D$_6$]DMSO) of **4**, which exhibits signals at $\delta = 9.9$ and 9.0 ppm, respectively. Deprotonation of **4** using 2.1 equivalents of NaH (and catalytic KO*t*Bu) in toluene at 120 °C resulted in selective dimerization to afford enetetraamine **5**, which was subsequently isolated in 94% yield (Scheme 2). Crystals suitable for X-ray analysis were obtained by slow cooling of a saturated toluene solution



Scheme 2. Selective dimerization and oxidation of a desymmetrized Janus bis(carbene) precursor.

of **5**, and an ORTEP view of the structure of this compound is shown in Figure 4. Key bond lengths and angles of the benzimidazolylidene fragments were consistent with those of **2b**,[13] and the torsion angle about the enetetraamine was 15.2°, consistent with that of the dimer of 1,3-dimethylbenzimidazolylidene.[16a] The structure of **5** in solution was confirmed by treatment with O_2, which rapidly and selectively oxidized the enetetramine moiety to afford urea **6** (Scheme 2).[23]

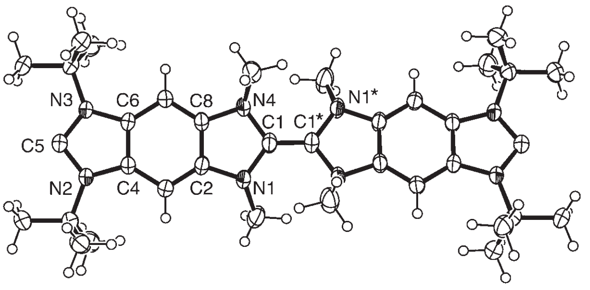


Figure 4. ORTEP view of **5** (ellipsoids at the 50% probability level). Selected bond lengths [Å] and angles [°]: C5-N3 1.366(3), C5-N2 1.371(3), N3-C6 1.406(2), N2-C4 1.404(3), C4-C6 1.397(3), C1-N1 1.426(3), C1-N4 1.424(3), N4-C8 1.416(3), N1-C2 1.408(2), C2-C8 1.399(3), C1-C1* 1.349(4); C1-N4-C18 117.79(18), N2-C5-N3 104.00(17), N1-C1-N4 108.48(16).

In summary, we report the first Janus bis(carbene)s with facially opposed imidazolylidenes annulated to a common arene core. Synthetic routes employed to obtain these compounds were modular and high yielding, and permitted access to derivatives with *N*-alkyl or *N*-aryl substituents, as well as a desymmetrized variant. The promise of the Janus bis(carbene) ligands was borne out through synthesis of a variety of new homobimetallic complexes; efforts toward heterobimetallic complexes are currently underway.

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[13] The crystal structure of **2b** was also determined and found to be similar to that of **2a**.[24]

[14] For comparison, X-ray structures were determined for the bis(azolium) salts **1a**[24] and **1e**.[10b]

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[17] These structural characteristics are consistent with [(cod)RhCl(1,3-diadamantylbenzimidazolylidene)].[24]

[18] Attempts to deprotonate **1d** and **1e** resulted in dark red solutions of polymeric materials, see: J. W. Kamplain, C. W. Bielawski, *Chem. Commun.* **2006**, 1727.

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[21] Deprotonation of **1d** followed by addition of [{(cod)RhCl}$_2$] also afforded complex **3d**, although in lower yields (34 %).

[22] The X-ray crystal structure of **3d** was determined (structure not shown). Crystals were obtained by slow diffusion of hexanes into a saturated CH_2Cl_2 solution of **3d**.[24]

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[24] See the Supporting Information for additional details.