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Synthesis of New Dipyrido-Annulated N-Heterocyclic Carbenes with Ortho Substituents

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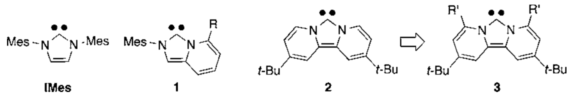
Supporting Information

ABSTRACT: A method for the introduction of various substituents at the 4 and 8 positions of 2,10-di-*tert*-butyldipyrido[1,2-*c*;2′,1′-*e*]imidazolium salts, is described. The new imidazolium salts bearing substituents (R′ = Cl, SPh) at the 4 and 8 positions are synthesized in three-step procedures, and carbenes generated from the imidazolium salts can be used to give the corresponding rhodium complexes. The role of the 4,8-substituents can be either bystanders or coordinating ligands according to the nature of the metal moiety.

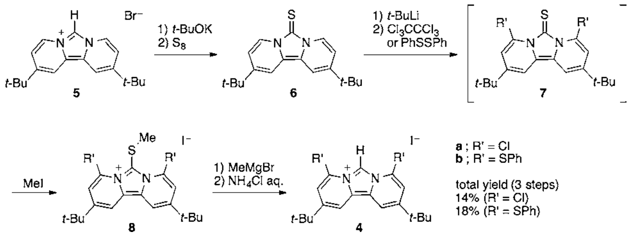
N-Heterocyclic carbenes (NHCs) have been widely utilized as versatile ligands for transition-metal catalysts and for stabilization of low-valent main-group elements.[1,2] Modification of the electronic properties and fine-tuning of the geometry of NHCs have resulted in the development of unique ligands and excellent catalysts.[3−5] On the other hand, pincer-type ligands[6] have also found widespread use because of their characteristic activation and stabilization properties. Among pincer-type complexes, those with fixed backbones such as anthracene-based compounds[7] or semifixed complexes such as the 7-6-7 cored complexes[8] reported by us have been found to be unique in themselves. Thus, it would be well worthwhile to investigate pincer-type complexes with a carbene coordinating site in the center. However, carbene-centered pincer compounds are much less common,[9,10] and there was no precedence on such compounds with a rigid backbone that we were aware of. Because carbene−pincer complexes with fixed backbones were expected to show chemistry intrinsic to their rigid structure, we decided to devote our efforts in this direction. Because of its structural similarity to the anthracene system, the dipyrido-fused NHC was chosen as the platform for investigations. Studies on pyrido-derived NHCs bearing rigid bi- or tricyclic structures have been limited. Lassaletta et al.[11a] synthesized bicyclic **1** along with some metal complexes, and Glorius et al.[11b] extended the utility of this ligand system by introducing a variety of new substituents at R. Weiss and Kunz studied dipyrido-annulated NHCs such as **2** and their transition-metal complexes (Scheme 1).[12,13] However, the synthesis of bipyridine-derived NHCs **3** bearing ortho substituents R′, other than a few undocumented benzo-fused derivatives, had not yet been achieved. Herein, we report on a method for the simple synthesis of ortho-substituted dipyrido-annulated NHCs **3** (R′ = Cl, SPh) and their application to rhodium complexes.

Scheme 1



Our method involves the following three-step procedures: (i) preparation of thiourea **6** from the reported imidazolium salt **5**;[12c] (ii) dilithiation of **6** with 2 equiv of *t*-BuLi and electrophilic trapping with hexachloroethane or diphenyl disulfide to give **7a** (R′ = Cl) and **7b** (R′ = SPh), respectively, followed by conversion to **8a** and **8b** with MeI; (iii) reaction of **8a** and **8b** with MeMgBr and workup with aqueous NH_4Cl to furnish **4a** and **4b**. The overall yields from **5** were 14 and 18%, respectively (Scheme 2).

Scheme 2



With the new substituted carbene precursors **4a** and **4b** in hand, we attempted generation of the corresponding carbenes (Scheme 3). The reaction of **4a** (R′ = Cl) with NaHMDS or *t*-BuOK in deuterated solvents such as THF-d_8 or C_6D_6 resulted in a color change from a yellow suspension to a clear brown solution. ^1H NMR measurements revealed that the imidazolium proton at 9.97 ppm in $CDCl_3$ was absent. However, the generated carbene **3a** gradually decomposed in THF-d_8 at room temperature, and the signal for the carbenic atom could not be observed by ^{13}C NMR. On the other hand, **3a** was stable in C_6D_6. In this case, poor solubility hampered ^{13}C NMR measurements. Fortunately, similar treatment of **4b** (R′ = SPh) with LiHMDS in THF-d_8 at room temperature led to the formation of thermally

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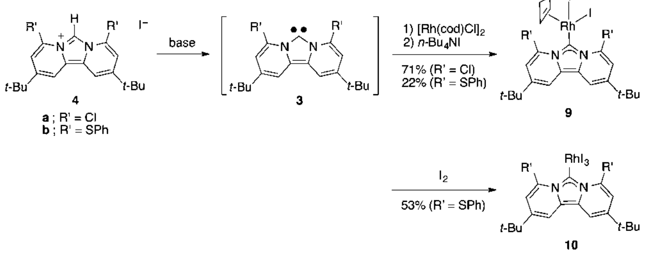
Scheme 3



stable carbene **3b**. ^{13}C NMR measurements of **3b** showed a signal that could be assigned to the carbenic atom at 193.7 ppm. In comparison with the reported chemical shifts of the ortho-unsubstituted dipyrido-annulated NHC (196.3 ppm in THF-d_8)[12c] and the classical Arduengo carbene (211.4 ppm in C_6D_6),[1] the carbene signal of **3b** was slightly high-field-shifted. This could probably be because of some degree of "hidden" carbon(0) character, as suggested by experiments[13d] and theory[14] for dipyrido-annulated NHCs.

Although **3a** with electron-withdrawing chlorine atoms was not very stable in THF, trapping of in situ generated **3a** with $[Rh(cod)Cl]_2$ followed by treatment with *n*-Bu_4NI resulted in formation of the expected metal complex [Rh(cod)(**3a**)I] (**9a**) in 71% yield. A similar reaction with **3b** was also successful, and **9b** was obtained in 22% yield.

Contrary to the relative stability of the free carbenes **3a** and **3b**, **9a** (R′ = Cl) is more stable than **9b** (R′ = SPh; Figure 1) in solution. In the solid state, both complexes are stable even in the open air. In CH_2Cl_2 or THF, **9b** gradually decomposed at room temperature under argon, whereas **9a** showed no signs of decomposition even in the open air. The structures of **9a** and **9b** were confirmed by X-ray diffraction analysis. There are no distinct structural differences between the two regardless of the difference in the substituents R′. The average Rh−$C_{C=C}$ distances trans to the carbene [2.203(5) Å (R′ = Cl); 2.209(12) Å (R′ = SPh)] are longer than those trans to the iodide [2.133(5) Å (R′ = Cl); 2.12(1) Å (R′ = SPh)] because of the stronger trans influence of the carbene. The Rh−$C_{carbene}$ distances of **9** [2.029(5) Å (R′ = Cl); 2.015(11) Å (R′ = SPh)] are essentially the same and slightly longer than that of a reported rhodium complex coordinated by ortho-unsubstituted **2** [2.007(4) Å].[12d] This is probably because of steric hindrance in **9**. In both complexes, the average Rh−Cl or Rh−S distance [Rh−Cl, 3.1288(12) Å; Rh−SPh, 3.056(3) Å] is shorter than the sum of the van der Waals radii (Rh−Cl, 3.8 Å; Rh−S, 3.9 Å) but not within an ordinary coordinating distance.[15] Furthermore, there are only small torsions in the angles involving these substituents. Thus, for these complexes, the ortho substituents can be considered to be spectator substituents with minimal interaction, as expected for rhodium(I). Oxidation of complex **9b** with I_2 furnished complex **10** bearing rhodium(III) in 53% yield. X-ray diffraction analysis of a single crystal of **10** revealed interactions between the sulfur atoms and rhodium(III) (Figure 2). The average distance was significantly shorter [2.386(3) Å] than that in **9b** and similar to that of a reported hemistable carbene−sulfur bidentate rhodium(I) complex (2.35−2.37 Å).[15] In addition, the S−C_{ipso}−N angle was found to be contracted to 111.5(6)°. Thus, complex **10** can be considered to be the first pincer NHC ligand with a rigid tridentate backbone. These results suggest that it is possible to alter the function of the ortho substituents according to the nature of the central metal moiety, as in the case of ordinary flexible pincer−ligand systems. This may be attributed to the widened space between the two potential coordinating sites created by the presence of the planar five-membered ring in the center of the three-ring system.

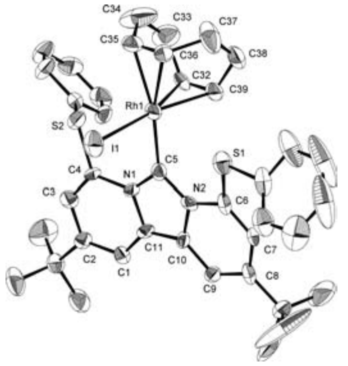


Figure 1. ORTEP drawing of **9b** with the thermal ellipsoids shown at the 50% probability level. All hydrogen atoms are omitted for clarity. The structure of **9b** was modeled as a pseudomerohedral twin. The application of twin law, [1 0 0/0 −1 0/0 0 1], improved the R1 residual from 20% to 7%. Selected bond lengths (Å) and angles (deg): Rh1−I1 = 2.6875(11), Rh1−C32 = 2.11(1), Rh1−C39 = 2.12(1), Rh1−C35 = 2.212(12), Rh1−C36 = 2.206(12), Rh1−C5 = 2.015(11), C5−N1 = 1.362(13), N1−C11 = 1.415(13), C1−C11 = 1.415(4), C1−C2 = 1.369(13), C2−C3 = 1.444(15), C3−C4 = 1.34(1), C4−N1 = 1.396(11), C5−N2 = 1.359(12), N2−C10 = 1.415(13), C9−C10 = 1.404(13), C8−C9 = 1.365(14), C7−C8 = 1.457(16), C6−C7 = 1.351(15), C6−N2 = 1.429(13), C10−C11 = 1.372(13); N1−C5−N2 = 103.0(9), S1−C6−N2 = 115.5(8), S2−C4−N1 = 119.2(7).

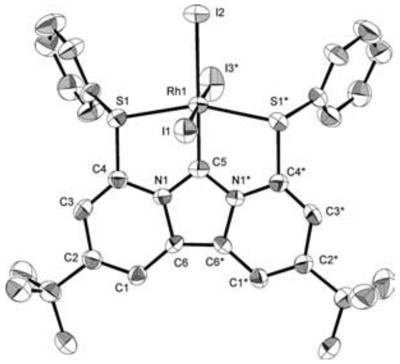


Figure 2. ORTEP drawing of **10** with the thermal ellipsoids shown at the 50% probability level. All hydrogen atoms and the solvent molecule are omitted for clarity. Selected bond lengths (Å) and angles (deg): Rh1−I1 = 2.698(2), Rh1−I2 = 2.712(2), Rh1−I3* = 2.652(2), Rh1−S1 = 2.386(3), Rh1−C5 = 1.892(12), C5−N1 =, N1−C6 =, C1−C2 = 1.373(13), C2−C3 = 1.469(13), C3−C4 = 1.343(13), C4−N1 = 1.370(11), C6−C6* = 1.399(17); N1−C5−N1* = 104.3(10), S1−C4−N1 = 111.5(6).

In conclusion, we have developed a method for the preparation of new dipyrido-annulated NHC carbenes with ortho substituents. The corresponding rhodium complexes from the carbenes are also reported, where the ligand can serve as either a monodentate or a tridentate. Noteworthy is pincer complex **10** with sulfur substituents as ligands, which happens to be the first carbene-centered pincer complex with a fixed scaffold. The synthetic approach should be useful for the preparation of various ortho-substituted derivatives and thus allows for fine-tuning of the steric and/or electronic properties of the carbenic atom. The introduction of other transition metals and low-valent main-group elements, in addition to the preparation of other ortho-substituted derivatives, is in progress.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallography details and CIF files of compounds and experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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