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Deprotonation Attempts on Imidazolium Salt Tethered by Substituted Phenol and Construction of Its Magnesium Complex by Transmetalation

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*Summary: Several attempts to deprotonate the imidizolium salt 1-methyl-3-(4,6-di-tert-butyl-2-hydroxybenzyl)imidazolium bromide, H_2[CO]Br (**4**), tethered by substituted phenol to yield anonic carbene species M[CO] (M = Li, Na) resulted in the formation of {Na[ON](THF)}$_2$ (**5**) and {Li[ON](THF)}$_2$ (**6**) (1-methyl-2-(4,6-di-tert-butyl-2-hydroxybenzyl)imidazole, H[ON]) after warming to room temperature from −78 °C due to 1,2-aryloxy migration. Treatment of in-situ-generated M[CO] with 1.0 equiv of MesMgBr (Mes = 2,4,6-$Me_3C_6H_2$) produced a rare magnesium NHC complex, {Mg[OC](Mes)}$_2$ (**8**). Both **5** and **8** have been characterized by an X-ray diffraction study.*

Introduction

N-Heterocyclic carbenes (NHC) and their metal complexes have been the focus of intense research in organometallic chemistry and homogeneous catalysis for the past decade.[1] In particular, functionalized carbene metal complexes derived from imidazolium precursors have been successfully developed as highly active precatalysts to promote a variety of important organic transformations, such as C−C coupling reactions.[2−5] Some NHC complexes with hemilabile donor functions have also been reported to be highly active in ethylene and norbornene polymerization.[6−12] The majority of these precatalysts contain NHC as ancillary ligands that are derived from imidazolium salts. It is known that most carbenes can be derived from their precursors by deprotonation using strong base or silver carbene reagents.[13] To the best of our knowledge, strong bases, such as M[N(SiMe$_3$)$_2$)] (M = Na, K) or n-BuLi are good reagents for the preparation of free anionic carbene ligands, but in most cases the resultant salt derivates are difficult to isolate due to their instabilities at room temperature, so metal complexes bearing anionic carbene ligands are much less established than their neutral counterparts.[14−19] Moreover, only a few studies on s-block metal carbene adducts have been reported until now.[20,21]

We have been studying the use of anionic functional groups pendant on the NHC to provide a "tether" by which an electropositive metal may be bound more strongly to the soft carbene center. Bisphenol-linked imidazolium salt H_3[OCO]Br (**1**) (Scheme 1), which incorporates two aryoxide anionic functional groups that act as tethers, has been designed and synthesized to stabilize IVB metal−NHC fragments after deprotonation using sodium hexamethyldisilazide (NaHMDS).[8] When the obtained sodium derivative of the dianionic aryloxide carbene at low temperature (−78 °C) was slowly warmed to room temperature, 1,2-migration occurred to give biaryloxide-substituted imidazole **2**. A similar rearrangement reaction has been observed in other carbene systems.[22] Moreover, if the Na_2[OCO] was hydrated at very low temperature, the monoaryloxy-

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(1) (a) Herrmann, W. A.; Köcher, C. *Angew. Chem., Int. Ed.* **1997**, *36*, 2162. (b) Tamm, M.; Hahn, F. E. *Coord. Chem. Rev.* **1999**, *182*, 175. (c) Bourissou, D.; Guerret, O.; Gabbaï, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39. (d) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290. (e) Hillier, A. C.; Grasa, G. A.; Viciu, M. S.; Lee, H. M.; Yang, C.; Nolan, S. P. *J. Organomet. Chem.* **2002**, *653*, 69. (f) Cavell, K. J.; McGuinness, D. S. *Coord. Chem. Rev.* **2004**, *248*, 671. (g) César, V.; Bellemin-Lapnnaz, S.; Gade, L. H. *Chem. Soc. Rev.* **2004**, *33*, 619. (h) Hahn, F. E. *Angew. Chem., Int. Ed.* **2006**, *45*, 1348.

(2) Tulloch, A. A. D.; Danopoulos, A. A.; Tooze, R. P.; Cafferkey, S. M.; Kleinhenz, S.; Hursthouse, M. B.; Tooze, R. P. *Chem. Commun*. **2000**, 1247.

(3) Wang, R.; Twamley, B.; Shreeve, J. M. *J. Org. Chem.* **2006**, *71*, 426.

(4) (a) Van Veldhuizen, J. J.; Garber, S. B.; Kingsbury, J. S.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2002**, *124*, 4954. (b) Van Veldhuizen, J. J.; Gillingham, D. G.; Garber, S. B.; Kataoka, O.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2003**, *125*, 12502.

(5) Arnold, P. L.; Rodden, M.; Davis, K. M.; Scarisbrick, A. C.; Blake A. J.; Wilson, C. *Chem. Commun.* **2004**, 1612.

(6) McGuinness, D. S.; Mueller, W.; Wasserscheid, P.; Cavell, K. J.; Skelton, B. W.; White, A. H.; Englert, U. *Organometallics* **2002**, *21*, 175.

(7) Mackinnon, A. L.; Baird, M. C. *J. Organomet. Chem.* **2003**, *683*, 114.

(8) (a) Aihara, H.; Matsuo, T.; Kawaguchi, H. *Chem. Commun.* **2003**, 2204. (b) Zhang, D.; Aihara, H.; Watanabe, T.; Matsuo, T.; Kawaguchi, H. *J. Organomet. Chem.* **2006**, in press.

(9) Wang, X.; Liu, S.; Jin, G. *Organometallics* **2004**, *23*, 6002.

(10) Ketz, B. E.; Ottenwaelder, X. G.; Waymouth, R. M. *Chem. Commun.* **2005**, 5693.

(11) Li, W.; Sun, H.; Wang, Z.; Hu, D.; Shen, Q.; Zhang, Y. *Organometallics* **2005**, *24*, 5925.

(12) Patel, D.; Liddle, S. T.; Mungur, S. A.; Rodden, M.; Blake A. J.; Arnold, P. L. *Chem. Commun.* **2006**, 1124.

(13) (a) Frøseth, M.; Dhindsa, A.; Røise, H.; Tilset, M. *Dalton Trans.* **2003**, 4516. (b) Winston, S.; Stylianides, N.; Tulloch, A. A. D.; Wright, J. A.; Danopoulos, A. A. *Polyhedron* **2004**, *23*, 2813. (c) Legault, C. Y.; Kendall C.; Charette, A. B. *Chem. Commun.* **2005**, 3826. (d) Garrison, J. C.; Youngs, W. J. *Chem. Rev.* **2005**, *105*, 3978.

(14) Arnold, P. L.; Mungur, S. A.; Blake A. J.; Wilson, C. *Angew. Chem., Int. Ed.* **2003**, *42*, 5981.

(15) Waltman, A. W.; Grubbs, R. H. *Organometalics* **2004**, *23*, 3105.

(16) Liddle, S. T.; Arnold, P. L. *Organometallics* **2005**, *24*, 2597.

(17) Downing, S. P.; Danopoulos, A. A. *Organometallics* **2006**, *25*, 1337.

(18) Mungur, S. A.; Blake, A. J.; Wilson, C.; McMaster, J.; Arnold, P. L. *Organometallics* **2006**, *25*, 1861.

(19) Spencer, L. P.; Winston, S.; Fryzuk, M. D. *Organometallics* **2004**, *23*, 3372.

(20) Mungur, S. A.; Liddle, S. T.; Wilson, C.; Sarsfield, M. J.; Arnold, P. L. *Chem. Commun*. **2004**, 2738.

(21) Arnold, P. L.; Rodden, M.; Wilson, C. *Chem. Commun*. **2005**, 1743.

(22) ,2-Migration of free NHCs at elevated temperature has been reported. See: (a) Alcarazo, M.; Roseblade, S. J.; Cowley, A. R.; Fernandez, R.; Brown, J. M.; Lassaletta, J. M. *J. Am. Chem. Soc.* **2005**, *127*, 3290. (b) Boehler, C.; Boehler, C.; Stein, D.; Donati, N.; Gruetzmacher, H. *New J. Chem.* **2002**, *26*, 1291. (c) Solé, S.; Gornitzka, H.; Guerret, O.; Bertrand, G. *J. Am. Chem. Soc.* **1998**, *120*, 9100. (d) Çetinkaya, B.; Çetinkaya, E.; Chamizo, J. A.; Hitchcock, P. B.; Jasim, H. A.; Küçükbay, H.; Lappert, M. F. *J. Chem. Soc., Perkin Trans. 1* **1998**, 2047.

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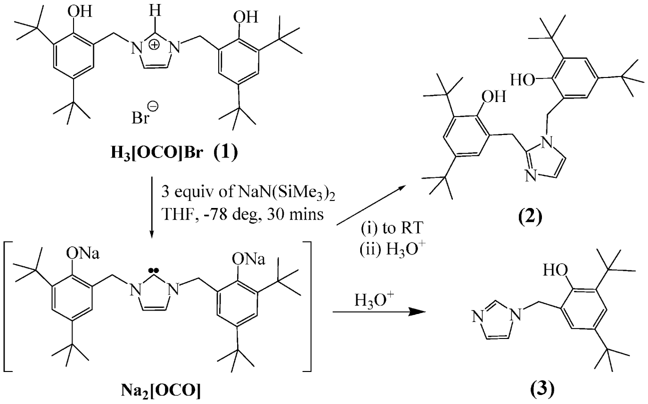
Scheme 1. Deprotonation of Bisaryloxyl Tethered Imidazolium Salt (1)



substituted imidazole **3** was observed by ^1H NMR. Herein, we wish to describe the deprotonation of imidazolium salts H_2[CO]-Br (**4**), having one aryloxy tether, and the synthesis of its magnesium complex by a transmetalation reaction (Scheme 2).

Results and Discussion

The new imidazolium salt H_2[CO]Br (**4**) is obtained as a white powder in an optimal yield of 81% by the reaction of bromomethyl-substituted phenol with methylimidazole, a route analogous to that for H_3[OCO]Br (**1**).[8] Simple deprotonation of this kind of bifunctional proligand with NaHMDS at low temperature in toluene or THF proved to be an adequate method for generation of active carbenes. Thus, treatment of **4** with 2 equiv of $NaN(SiMe_3)_2$ at −78 °C affords monoanionic free carbene ligand Na[OC], which gives a colorless sodium phenol−imidazolium complex, $\{Na[ON](THF)\}_2$ (**5**), in a high yield of 87% after its solution was slowly warmed to room temperature and continuously stirred for another 8 h.

The ^1H and ^{13}C NMR showed that compound **5** includes an aryloxy-substituted imidazole ligand that came from an anionic carbene though a 1,2-migration rearrangement. The CH_2 resonances appear as equivalent signals at δ 4.00 ppm, and the ^{13}C resonance signal for carbon C^2 of imidazole is at δ 153.22 ppm. Colorless blocklike crystals suitable for X-ray diffraction were grown from a THF/toluene/hexane solution. The molecular structure is illustrated in Figure 1, and the crystallography data are listed in Table 1.

Arnold et al. recently reported s-block complexes of NHC ligands bearing an N-bound anionic functional group using n-BuLi for deprotonation.[20,21] However, when **4** was treated with 2.0 equiv of n-BuLi or MeLi in hexane/thf, the complex $\{Li[ON](THF)\}_2$ (**6**) was obtained. The ^1H and ^{13}C NMR spectra of lithium complex **6** are similar to those of sodium complex **5**, which indicated that they should have analogous structures. The hydrolyzates of **5** and **6** are the same as the aryloxy-substituted imidazole **7**, a compound analogous to **2**.

The formation of **5**, **6**, and **7** suggests that the aryloxy group must take precedence over other alkyl groups during the 1,2-migrations for such aryloxy-functionalized carbene compounds. This may provide another way to prepare aryloxy-substituted imidazole compounds, such as **2** and **7**. Low-temperature in-situ ^1H NMR experiments have been carried out to monitor the formation of **5** and **6**, but little information could be obtained, while the ^{13}C NMR signal in the range expected for carbene centers (δ = 199.20 ppm for sodium salt and δ = 197.85 ppm for lithium salt) was observed, which indicated that the lithium or sodium carbene salts indeed formed at lower temperature.[20]

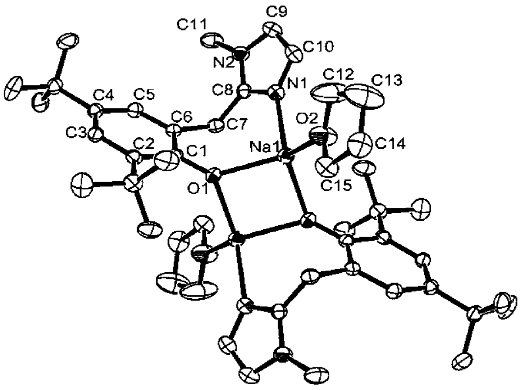


Figure 1. Molecular structures of **5**. Selected distances (Å) and angles (deg): Na(1)−O(1) = 2.226(2), Na(1)−O(2) = 2.321(2), Na(1)−N(1) = 2.389(3); O(1)−Na(1)−O(2) = 126.30(9), O(1)−Na(1)−N(1) = 93.92(8), O(2)−Na(1)−N(1) = 105.4(1).

Table 1. Summary of Data Collection and Structure Refinement Details for 5 and 8

	5	**8**
formula	$C_{46}H_{70}N_4O_4Na_2$	$C_{56}H_{78}N_4O_2Mg_2$
fw	789.06	887.87
temp, K	123	123
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/a$
a, Å	12.712(2)	12.325(4)
b, Å	14.622(3)	25.461(9)
c, Å	15.029(4)	17.227(6)
α, deg	80.20(1)	90
β, deg	65.035(9)	89.957(5)
γ, deg	64.23(1)	90
V, Å^3	2280.3(8)	5406(3)
Z	2	4
d_{calcd}, g cm^{-3}	1.149	1.091
μ, mm^{-1}	0.887	0.862
no. of rflns measd	34 794	86 820
no. of unique rflns	9620	12 590
R1/wR2	0.055/0.164	0.067/0.119
GOF	1.004	0.978
resid density, e/Å^3	−0.44/0.51	−0.45/0.45

Given that we were unable to isolate lithium or sodium carbene compounds at room temperature, we undertook the synthesis of its carbene magnesium adducts. Thus, the in situ reaction at low temperature (−78 °C) of 2.0 equiv of NaHMDS with **4**, followed by addition to 1.0 equiv of Grinard reagent MesMgBr (Mes = 2,4,6-$Me_3(C_6H_2)$) in diethyl ether/THF, was carried out (Scheme 1) with the aim of preparing the magnesium compound. Fortunately, this reaction afforded $\{Mg[OC](Mes)\}_2$ (**8**) in good yield. In *d*-chloroform, a pair of well-separated doublets signals at δ 4.48 and 5.89 ppm in the ^1H NMR spectrum suggests the existence of the bridged CH_2 group of the anionic carbene, and the two signals at 184.28 and 165.55 ppm in the $^{13}C\{1H\}$ NMR spectrum are diagnostic of Mg−carbene and Mg−C(Mes), which are comparable to the other reported mesitylmagnesium complexes.

Magnesium carbene complexes are very rare.[20,23−25] Arnold et al. just reported the amido N-heterocyclic carbene Mg(II) complex $[MgL_2]$ (L = $^tBu-N-CH_2CH_2-C_3N_2H_2-^tBu$) with a bent metal carbene geometry.[20] Complex **8** is the first reported s-block complex with an aryloxy-bound NHC anionic functional

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(23) Schumann, H.; Gottfriedsen, J.; Glanz, M.; Dechert, S.; Demtschuk, J. *J. Organomet. Chem.* **2001**, *617−618*, 588.

(24) Arduengo, A. J., III; Davidson, F.; Krafczyk, R.; Marshall, W. J.; Tamm, M. *Organometallics* **1998**, *17*, 3375.

(25) Arduengo, A. J., III; Dias, H. V. R.; Davidson, F.; Harlow, R. L. *J. Organomet. Chem.* **1993**, *462*, 13.

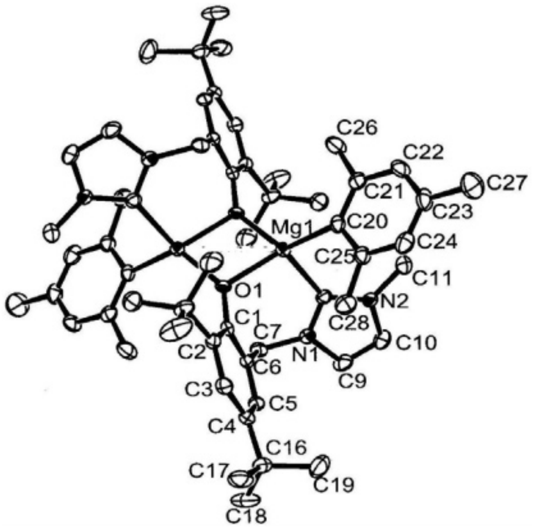


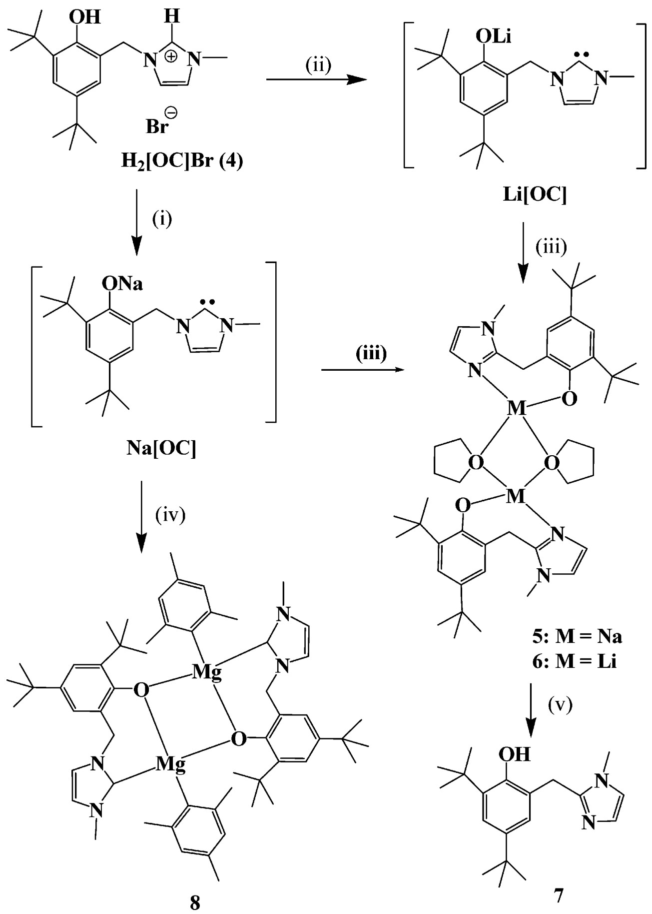
Figure 2. Molecular structures of **8**. Selected distances (Å) and angles (deg): Mg(1)−O(1) = 2.042(3), Mg(1)−C(8) = 2.224(4), Mg(1)−C(20) = 2.179(4); O(1)−Mg(1)−C(8) = 99.7(1), O(1)−Mg(1)−C(20) = 128.7(1), C(8)−Mg(1)−C(20) = 102.7(2)

ligand. X-ray diffraction quality crystals were obtained by storing the THF/toluene/hexane solutions at −30 °C for a week. The molecular structure is illustrated in Figure 2, and the crystallography data are listed in Table 1.

The magnesium salt forms a dimer via bridging aryloxy groups, and the open coordination site was occupied by a mesityl group. Two bridged oxygen and two carbon atoms coordinated with the Mg(II) center to form a tetrahedral geometry. The closest C−Mg interaction is actually with the carbene center (2.224(2) Å), which is similar to those in $[L\cdot Mg(C_5Me_5)_2]$ (L = tetramethylimidazol-2-ylidene) [C−Mg = 2.194(2) Å][23] and $[(C_5Me_4H)_2Mg\cdot L]$ (L = 1,3-di-isopropyl-4,5-dimethylimidazol-2-ylidene) [C−Mg = 2.2260(13) Å],[24] with neutral monodentate carbene ligands, but shorter than that in $[MgL_2]$ (L = $^tBu-N-CH_2CH_2-C_3N_2H_2-{}^tBu$) [Mg(1)−C(1) = 2.263(2) Å, Mg(1)−C(14) = 2.2697(16) Å],[25] with an anionic amido-NHC ligand. The Mg−C (mestyl) bond distance [2.179(4) Å] is comparable with other analogous compounds.

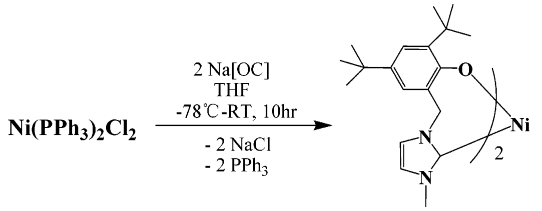
Titanium complex $Ti[OCO]X_2$ ($H_3[OCO]Br \equiv$ **1**; X = Cl), bearing a bisphenol-linked carbene ligand, has been prepared and proved to be a highly active precatalyst (10^5 g PE/mol Ni h) for polymerization of ethylene under methylaluminoxane (MAO) activation. [8] We therefore turned to the preparation of metal complexes that are likely catalysts for olefin polymerization. For example, reaction of in-situ-generated Na[OC] ($H_2[OC] \equiv$ **4**) with 0.5 equiv of $[Ni(PPh_3)_2Cl_2]$ affords nickel complex $Ni[OC]_2$ (**9**) (Scheme 3). The formation of complex **9** was confirmed by ^1H NMR spectroscopy, which shows the absence of the ArOH and NCHN protons. Furthermore, the ^{13}C NMR spectrum shows the $C_{carbene}$ resonance at δ 168.5 ppm, which is comparable to those of other reported nickel carbene adducts.[6] The formation of **9** is due to the NHC's strong donor properties that make it possible to replace phosphine ligands to generate nickel carbene complexes more stable than their phosphine congeners. Complex **9** is much less sensitive to air and moisture and can be stored in open air for several days. Previously, polymerization experiments showed that **9** revealed high activity (10^5g PNBE/mol Ni h) toward the addition polymerization of norbornene with MAO as cocatalyst. We are currently working on the mechanism of such 1,2-migration rearrangements and are investigating the metathesis chemistry to isolate IVB metal carbene complexes and study their catalytic behaviors.

Scheme 2. Deprotonation of 4 and Synthesis of Its Carbene Complexes[a]



[a] Reagent and conditions: (i) 2 $NaN[SiMe_3]_2$/THF, −78 °C, 30 min; (ii) 2 equiv of n-BuLi/ THF, −78 °C, 30 min; (iii) to rt, 8 h; (iv) 1 equiv of $(2,4,6\text{-}Me_3C_6H_2)MgBr$, to rt, 8 h; (v) H_3O^+.

Scheme 3



Experimental Section

All manipulations were carried out under a dry oxygen-free argon atmosphere using standard Schlenk techniques. Solvents were dried by refluxing with appropriate drying agents (sodium/benzophenone for toluene, diethyl ether, THF, and hexane; CaH_2 for dichloromethane) and distilled under argon prior to use. d_1-Chloroform was distilled from CaH_2 and degassed by three freeze−pump−thaw cycles prior to use. The chemicals $NaN(SiMe_3)_2$ (1.1 M solution in THF), LiMe (1.4 M solution in diethyl ether), and n-BuLi (1.59 M solution in hexane) were obtained commercially and used as received. ^1H and ^{13}C NMR spectra were recorded on a JEOL Lambda-500 spectrometer. Chemical shifts are reported in parts per million. Elemental analyses were measured using Yanaco MT-6 and MSU-32 microanalyzers.

Synthesis of H_2[OC]Br (4). A 500 mL three-necked round-bottom flask, containing a magnetic stirring bar and *N*-1-methylimidazole (2.8 mL, 35 mmol), was fitted with serum cup, a dropping funnel, and a reflux condenser connected to a three-way stopcock with a balloon filled with nitrogen. After THF (25 mL) was added, the mixture was refluxed with stirring. To the suspension was slowly added from a dropping funnel a solution of 2-bromomethyl-4,6-di-*tert*-butylphenol (9.0 g, 30 mmol) in THF (50 mL), and then the mixture was stirred for 12 h. After being cooled to room temperature, the solvent was evaporated to dryness to give the crude product. Washing of the crude by *n*-hexane gave a fine, colorless powder of H_2[OC]Br (81.3%, 9.3 g, 24.4 mmol). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.27 (s, 9H, C*Me*$_3$), 1.38 (s,9H, C*Me*$_3$), 3.99 (s, 3H, C*H*$_3$-N), 5.73 (s, 2H, N-CH_2-N), 6.95 (brs, 2H, OH), 7.16 (d, *J* = 2.5 Hz, 1H), 7.27 (d, *J* = 2.5 Hz, 2H), 7.34 (m, *J* = 2.5 Hz, 2H), 9.81 (brs, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 30.1 (*C*H_3), 31.5 (*C*H_3), 34.3(*C*HMe_3), 35.1 (*C*HMe_3), 36.7 (N-*C*H_3), 51.3 (*C*H_2), 121.9, 122.2, 122.7 (*C*H), 125.5, 125.9 (*C*H), 136.9, 139.8 (*C*H, imidazolium), 143.7, 151.8 (O-*C*), 168.5 ($C_{carbene}$). Anal. Calcd for $C_{19}H_{29}BrN_2O$: C, 59.84; H, 7.66; N, 7.35. Found: C, 59.79; H, 7.81; N, 7.34.

Synthesis of {Na[ON](THF)}$_2$ (5). To a suspension of imidazolium salt [H_2OC]Br (**4**) (1.0 g, 2.6 mmol) in THF (30 mL) was slowly added a 1.1 M solution of $NaN(SiMe_3)_2$ in THF (5.2 mmol, 4.8 mL) at −78 °C. The solution was allowed to warm slowly to room temperature and stirred for 8 h. Volatiles were removed in vacuo to give a sticky red solid. The product was dissolved in THF (10 mL)/toluene (20 mL)/hexane (5 mL) and stored at −30 °C overnight to afford 0.89 g (1.13 mmol) of $Na_2[OC]_2(THF)_2$ as a crop of colorless block crystals suitable for an X-ray diffraction study. Yield: 87%. ^{1}H NMR (500 MHz, $CDCl_3$ at rt): δ 1.26 (s, 18H, ^{t}Bu), 1.41 (s, 18H, ^{t}Bu), 1.78 (m, 8H, OCH_2CH_2), 3.63 (m, 8H, OCH_2CH_2), 3.74 (s, 6H, N-CH_3), 4.00 (brs, 4H, C*H*$_2$), 6.55 (brs, 2H, CH), 6.61 (brs, 2H, CH), 7.01 (d, 2H, J_{H-H} = 2.2 Hz, CH), 7.12 (d, 2H, J_{H-H} = 2.65 Hz, CH). ^{13}C NMR (126 MHz, $CDCl_3$): δ 153.22 (C^2 imidazol), 147.84, 141.42, 138.44, 126.04, 124.26, 123.87, 123.19, 122.53, 120.30, 120.19 (CH), 67.92 (OCH_2-CH_2), 35.27 (N-*C*H_3), 32.87 (CH_2), 31.96, 31.60 (*C*$(CH_3)_3$), 29.99, 29.77 (C(*C*H_3)$_3$), 25.53 (d, *J* = 7.8 Hz, OCH_2CH_2). Anal. Calcd for $C_{46}H_{70}N_4Na_2O_4$: C, 70.02; H, 8.94; N, 7.10. Found: C, 70.01; H, 8.96; N, 7.14.

Preparation of {Li[ON](THF)}$_2$ (6). To a suspension of **4** (1.0 g, 2.6 mmol) in THF (30 mL) was slowly added a 1.56 M solution of Li^{n}Bu in THF (5.2 mmol, 3.3 mL) at −78 °C. The mixture was slowly warmed to room temperature to give a colorless solution, which was stirred overnight, and then the solvent was evaporated to dryness in a vacuum. The white crude was recrystallized from THF/toluene/hexane to afford colorless plates. ^{1}H NMR (500 MHz, $CDCl_3$ at rt): δ 1.30 (s, 18H, ^{t}Bu), 1.47 (s, 18H, ^{t}Bu), 1.84 (m, 8H, OCH_2CH_2), 3.74 (s, 6H, N-CH_3), 3.76 (m, 8H, OCH_2CH_2), 3.99 (brs, 4H, Ar-C*H*$_2$-N), 6.61 (s, 2H, CH), 6.63 (s, 2H, CH), 7.23 (d, 2H, J_{H-H} = 2.4 Hz, CH). ^{13}C NMR (126 MHz, $CDCl_3$): δ 149.84 (C^2 imidazole), 125.83, 124.67, 124.21, 123.02 120.22, 118.38 (Ar), 67.98 (OCH_2CH_2), 34.85 (N-CH_3), 33.80, 33.21 (*C*$(CH_3)_3$), 31.87 (*C*H_2), 30.27, 29.60 (C(*C*H_3)$_3$), 25.59 (OCH_2CH_2). Anal. Calcd for $C_{46}H_{70}$ N_4 Li_2O_4: C, 72.99; H, 9.32; N, 7.40. Found: C, 72.81; H, 9.26; N, 7.44.

Hydrolysis of 5 and 6. Complex **5** or **6** was hydrolyzed with diethyl ether/H_3O^+ solution at room temperature to give 1-methyl-2-[2-hydroxyl-3,5-^{t}Bu$_2$(C_6H_2)CH_2]($C_3N_2H_2$) (**7**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.25 (s, 9H, C*Me*$_3$), 1.236 (s, 9H, C*Me*$_3$), 3.78 (s, 3H, C*H*$_3$), 4.65 (s, 2H, CH_2) 7.04 (s, 1H, CH), 7.16 (s, 2H, CH), 7.23 (s, 2H, CH). ^{13}C NMR (126 MHz, $CDCl_3$): δ 29.92, 31.45 (*C*H_3), 34.18, 34.95 (*C*Me_3), 35.14 (N-*C*H_2), 46.09 (*C*H_2), 117.57, 121.02, 122.54, 123.92, 124.86, 139.34, 143.45, 146.30, 150.98 (Ar). Anal. Calcd for $C_{19}H_{28}N_2O$: C, 75.96; H, 9.34; N, 9.32. Found: C, 75.99; H, 9.41; N, 9.54.

Synthesis of {Mg[OC](Mes)}$_2$ (8). To a suspension of **4** (1.0 g, 2.6 mmol) in THF (30 mL) was slowly added 2.0 equiv of $NaN(SiMe_3)_2$ (5.2 mmol) in THF (1.0 M, 5.2 mL) or a 1.56 M solution of Li^{n}Bu in hexane (5.2 mmol, 3.3 mL) at −78 °C. The reaction mixture was kept at −78 °C, and stirring for 30 min afforded the suspended solution of the sodium or lithium salt of the ligand. The in-situ-generated salt was slowly transferred to a flask containing (1,3,5-$Me_3C_6H_2$)MgBr (2.8 mL, 0.92 M in THF, 2.6 mmol). The reaction was slowly warmed to room temperature and stirred for another 12 h. The solvent was removed under reduced pressure to give a white crude, which was purified by recrystallization from THF/toluene/hexane to afford colorless prism crystals. ^{1}H NMR (500 MHz, $CDCl_3$ at rt): δ 1.30 (s, 18H, ^{t}Bu), 1.40 (s, 18H, ^{t}Bu), 2.12 (s, 12H, *o*-C*H*$_3$), 2.28 (s, 6H, *p*-C*H*$_3$), 3.83 (s, 6H, N-CH_3), 4.48 (d, 2H, J_{H-H} = 13.9 Hz, CH_2), 5.89 (d, 2H, J_{H-H} = 13.9 Hz, CH_2), 6.76 (s, 2H, CH), 6.99−7.09 (m, 8H, CH), 7.29 (s, 2H, CH). ^{13}C NMR (126 MHz, $CDCl_3$): δ 184.28 (NCN), 165.55 (Mg-C), 156.24 (*C*-O-Mg), 147.90, 146.65, 140.40, 138.91, 133.54, 128.58, 126.90, 125.71, 124.82, 124.43, 123.85, 121.08, 121.31 (Ar), 120.36 (=CH-N of carbene), 52.67 (*C*H_2), 35.51 (N-*C*H_3), 31.82, 31.57 (*C*$(CH_3)_3$), 29.92, 29.73 (C(*C*H_3)$_3$). Anal. Calcd for $C_{56}H_{76}Mg_2N_4O_2$: C, 75.93; H, 8.65; N, 6.32. Found: C, 75.86; H, 8.56; N, 6.44.

Synthesis of Ni[OC]$_2$ (9). To a suspension of **4** (0.385 g, 1.0 mmol) in THF (30 mL) was slowly added 2.0 mL of a solution of $NaN(SiMe_3)_2$ in THF (1.0 M, 2.0 mmol) at −78 °C. The reaction was continuously stirred for 30 min and then slowly transferred to a suspension of $Ni(PPh_3)_2Cl_2$ (0.327 g, 0.5 mmol) in THF at −78 °C by stainless steel canula. The resulting solution was gradually warmed to room temperature and then stirred overnight. The mixture was centrifuged, and the super clear solution was evaporated to dryness to afford the crude product, which was purified by recrystallization. Yield: 63%. ^{1}H NMR (500 MHz, C_6D_6): δ 7.64 (1H, s, Ph-H), 7.60 (1H, s, Ph-H), 7.47 (1H, s, Ph-H), 6.99 (1H, s, Ph- H), 6.17 (2H, s, NCH), 5.72 (2H, s, NCH), 4.30 (2H, s, CH_2), 4.27 (2H, s, CH_2), 3.97 (CH_3-N), 1.87 (18H, s, $C(CH_3)_3$), 1.45-(18H, s, $C(CH_3)_3$). ^{13}C NMR (126 MHz, $CDCl_3$): δ 30.1 (*C*H_3), 31.5 (*C*H_3), 34.3 (*C*HMe_3), 35.1(*C*HMe_3), 36.7 (N-*C*H_3), 51.3 (*C*H_2), 121.9, 122.2, 122.7 (*C*H), 125.5, 125.9 (*C*H), 136.9, 139.8 (*C*H), 143.7, 151.8 (O-*C*), 168.5 ($C_{carbene}$). Anal. Calcd for $C_{38}H_{54}N_4NiO_2$: C, 69.20; H, 8.56; N, 8.49. Found: C, 69.43; H, 8.81; N, 8.25.

X-ray Crystal Structure Determination of 5 and 8. A suitable crystal was immersed in mineral oil and mounted on a nylon loop in a random orientation under a cold stream of dry nitrogen (Rigaku GNNP low-temperature device). Diffraction experiments were performed with Mo Kα radiation (λ = 0.710 70 Å) on a Rigaku CCD diffractometer. The data were collected in a hemisphere of data in 720 frames with 20−40 s exposure times. The data sets were collected (4.0° < 2θ < 45−55°). The data were processed using CrystalClear (Rigaku) processing packages.[26] Crystal data and data collection parameters are contained in Table 1, and the crystallographic information file is available as Supporting Information.

Supporting Information Available: Crystallographic data for **5** and **8** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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[26] (a) *CrystalClear* software package; Rigaku and Molecular Structure Corp., 1999. (b) Pflugrath, J. W. *Acta Crystallogr.* **1999**, *D55*, 1718−1725.