Tetrahedron 69 (2013) 1687–1693

Contents lists available at SciVerse ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Syntheses of effectively-shielded *N*-heterocyclic carbene ligands

Shin Ando *, Hirofumi Matsunaga, Tadao Ishizuka *

Faculty of Life Sciences, Kumamoto University, 5-1 Oe-honmachi Chuo-ku, Kumamoto 862-0973, Japan

ARTICLE INFO

Article history:
Received 30 November 2012
Received in revised form 13 December 2012
Accepted 16 December 2012
Available online 21 December 2012

Keywords:
N-Heterocyclic carbene
Steric effect
Bicyclic system
Regioselective
Allylic arylation

ABSTRACT

A novel type of *N*-heterocyclic carbene ligand, with a bicyclic motif at the non-carbenic carbons of an imidazolin-2-ylidene core, has been developed. This type of ligand formed an air and moisture stable silver complex even with *N*,*N*′-dimethyl NHC. Allylic arylation with a Grignard reagent catalyzed by copper complexes of the NHC ligands proceeded preferentially at the γ-position, indicating the effective steric shielding ability of this framework.

1. Introduction

As a result of the pioneering work by Herrman et al.,[1] in which a *N*-heterocyclic carbene (NHC) was proposed as a promising alternative to phosphines as a homogeneous organometallic catalyst, extensive investigations to produce this type of novel ligand have been pursued.[2] The development of NHC ligands has generated as much activity as that of phosphine ligands.[3] This interest comes from the unique binding nature of NHC ligands,[4] such as a strong σ-donation to the bound transition metals, exceptionally strong binding toward metals, and a resultant complex with good stability against air and moisture. In addition to these remarkable properties, a more diverse structure than phosphines motivates the synthetic and organometallic chemists. Among the numerous heterocyclic core candidates that have been reported in the literature, imidazol-2-ylidene **1** (unsaturated NHC) and imidazolin-2-ylidene **2** (saturated NHC) are frequently used with ligands.[3] These heterocyclic cores have two nitrogens adjacent to a carbenic carbon, which equates to easier substitution for the heteroatom than for carbon and leads to the drastic change at the proximity of the bound transition metal. According to broad derivatization studies, the electronic effects from the substituents are relatively small,[5] which allows a wider variety of substituents with no negative impact to the binding nature.

The two cores, **1** and **2**, are often compared to one another because of their structural similarity (Fig. 1a), and each has shown a different coupling activity toward transition metal. For example, saturated NHC **2** is more active than unsaturated NHC **1** in the case of Pd mediated amination reaction.[6] On the other hand, from the viewpoint of the stability, the unsaturated NHCs **1** are generally more stable than the saturated NHCs **2** presumably by virtue of the π-delocalization of the former.[7] This trend also seems to be the case in metal-NHC complexes.[3a] To stabilize the latter core, bulky substituents, such as an aryl group, are placed on the nitrogen(s), with the intention of protecting the carbenic carbon via a steric shield. This extra requirement from the saturated NHCs should make the functionalization more difficult. Nonetheless, there has been a little

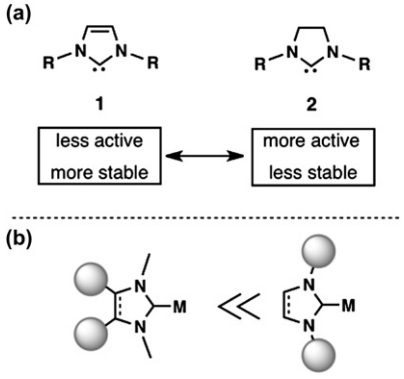


Fig. 1. (a) The opposing properties between unsaturated NHCs **1** and saturated NHCs **2**. (b) Substituents with a stronger effect on nitrogen than on non-carbenic carbon.

* Corresponding authors. E-mail addresses: ando@gpo.kumamoto-u.ac.jp (S. Ando), tstone@gpo.kumamoto-u.ac.jp (T. Ishizuka).

0040-4020/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tet.2012.12.036

use of the substituents on the non-carbenic carbons with this demand, probably because the geometry seemed unlikely to produce a strong effect toward an active site (Fig. 1b). If the stabilization from the non-carbenic carbons is possible, the substituents on nitrogen could be designed to more flexibly functionalize the saturated NHCs. Herein, we describe the synthesis and properties of a novel NHC ligand with a bicyclic structure on the non-carbenic carbons, which are effective in directly shielding the bound metal center.

2. Results and discussion

2.1. The design of a novel saturated NHC framework

Previously, we demonstrated the strong shielding effects of the bicyclic architecture between anthracene and *cis*-diamine, and a Ru complex using this diamine ligand **3** (Fig. 2) showed excellent enantio control during the hydrogenation of ketones.[8] Ideally, an NHC with this bicyclic system, which could be derived from this 'roofed' diamine, would give us a rigid shield from the non-carbenic carbon at the carbenic carbon, and the substituents on the nitrogens should be more finely tunable with less concern about stability. The asymmetric substitution on these two nitrogens provides a chiral environment, but our objectives here were the development of the synthetic strategy and an evaluation of the shielding ability of this bicyclic NHC. Therefore, we started from a synthesis of symmetric *N*,*N*′-dimethylated NHC, which should be one of the least-stable of the derivatives.

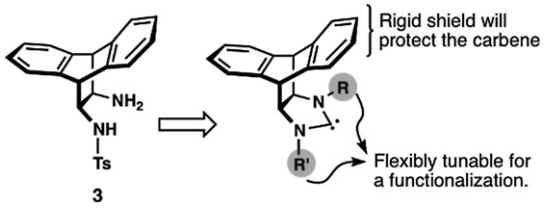


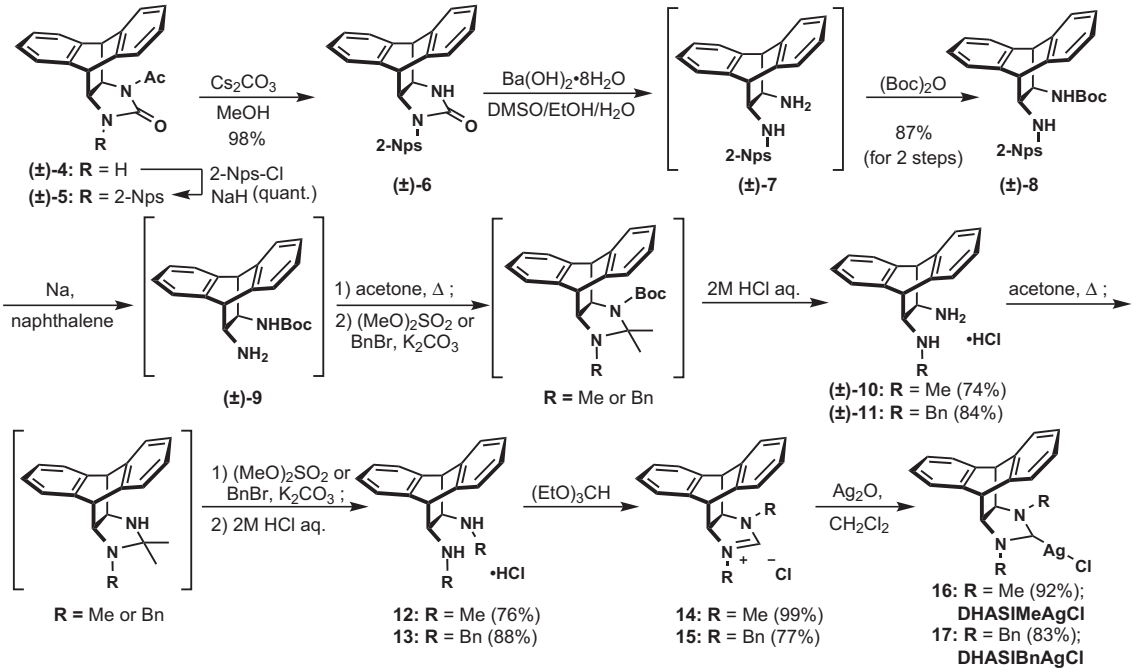
Fig. 2. The design of bicyclic saturated NHC.

2.2. Syntheses of bicyclic saturated NHC

The synthesis of a new ligand with a bicyclic ring, summarized in Scheme 1, commenced from the 'roofed' imidazolidinone **4** we previously reported.[9] A 2-naphthalenesulfonyl group (2-Nps) was placed on the *N*–H functionality in a quantitative yield not only for protection but also for activation of the carbonyl on the urea moiety, which was needed to open the imidazolidinone ring. After the methanolysis of the acetyl group in a yield of 98%, the imidazolidinone ring was opened by reflux under basic condition to obtain the free amine **7**. Since the opened diamine **7** was unstable for storage and poorly soluble in most organic solvents, a direct Boc protection from the crude mixture was performed to afford the key intermediate **8** in an 87% yield over two steps. After the deprotection of the 2-naphthalenesulfonyl group under reductive conditions, which gave **9** together with inseparable impurities, temporal aminal formation by refluxing in acetone enabled the mono alkylation of the deprotected amine. The subsequent cleavage of this aminal, and the simultaneous removal of the Boc group on the other amine, gave the mono methylated diamine as an HCl salt **10** in a 74% yield overall. The same sequential mono alkylation of the free amine resulted in *N*,*N*′-dimethylated diamine **12** in a 76% yield (over two steps). This HCl salt was treated with refluxed triethyl orthoformate to achieve the synthesis of the carbene precursor **14** in 99% yield. Dibenzylated derivative **15** was also prepared under the similar conditions with use of BnBr for alkylations. Although the imidazolidinone **4** used for these syntheses was a racemic mixture, it should be noted that we have the synthetic methodology for the optically active form, which will allow us to synthesize chiral NHC ligands in the future.[9]

2.3. Synthesis and properties of *N*,*N*′-dimethylated bicyclic NHC–Ag complex

The dimethylated carbene precursor **14** was applied to the syntheses of an Ag–carbene complex under the condition reported by Lin et al.[10a] NHC–Ag complexes are generally accepted as good NHC transfer agents, and a transmetalation to another transition metal is easily accomplished by a simple mix in a reaction solution



Scheme 1. The syntheses of bicyclic NHC precursors and NHC–Ag complexes; 2-Nps=2-naphthalenesulfonyl.

prior to use as a catalyst.[10] Gratifyingly, bicyclic imidazolinium salt **14** reacted smoothly with Ag_2O in CH_2Cl_2, and we obtained carbene complex **16** wherein the ^1H NMR showed a disappearance of the imidazolinium proton signal. This complex was isolated as a colorless solid and was stable enough to store on a bench at ambient temperature. We named this bicyclic NHC motif DHASI (4,5-(9,10-**di**hydro**a**nthraceno)-imidazolin-2-ylidene. Based on the abbreviation on the past reports about NHCs,[3] the imidazolin-2-ylidene core was named **SI**). The dibenzylated precursor **15** was also reacted with Ag_2O in CH_2Cl_2 and gave the stable complex **17** as a colorless solid. It was somewhat surprising that there were no signals indicating the carbenic carbon on the ^{13}C NMR spectrum, which also was the case in reports by other groups.[11] The MS spectrum (FAB^+) showed the *m*/*z* L_2Ag^+ as the parent peak (the structures of NHC–Ag complexes in the gas phase are often inaccurate[10b]). Because the structures of NHC–silver complexes with a halogen counter anion are varied,[10b,c] finally, the X-ray studies of the crystal were accepted as confirmation of their structure.[12]

Single crystals of complex **16** were grown by the slow vapor diffusion of Et_2O into a CH_2Cl_2 solution. The silver complex of *N*,*N*′-dimethylated NHC **16** was a 1:1 complex between NHC and Ag (Fig. 3), which is relatively rare among the saturated NHC ligands. The degree (171.64°) of the angle of C(1)–Ag(1)–Cl(1) and the packing system indicated that there was a weak interaction between the two silver atoms, however, the distances between Ag(1)–Ag(1)′ (3.650 Å) and Ag(1)–Cl(1)′ (3.717 Å) were longer than the sum of van der Waals radii. The selected bond lengths and angles are shown in the caption of Fig. 3. These geometric characters around the carbenic carbon were within the range of the general NHC species, and the distances between the silver and the carbons on the bicyclic motif ranged from 5.0 to 5.5 Å, which was three times longer than the van der Waals radius for silver.

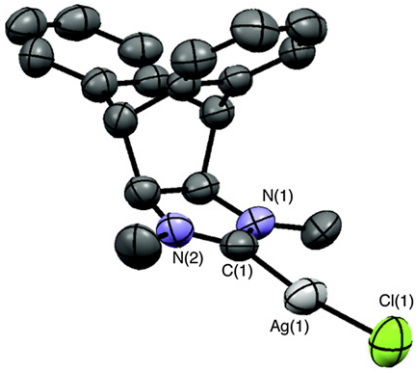
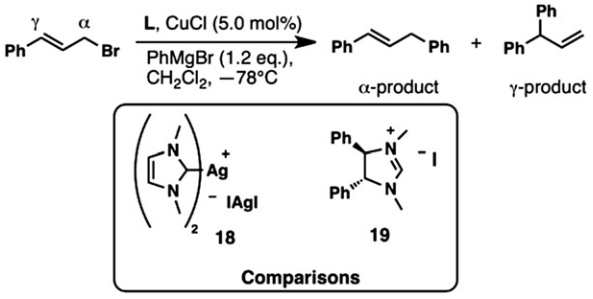


Fig. 3. ORTEP diagram of complex **16**, thermal ellipsoids are shown at 50% probability level. Selected bond length (Å) and angles (°): Cl(1)–Ag(1), 2.326; Ag(1)–C(1), 2.100; C(1)–N(1), 1.323; C(1)–N(2), 1.328; Cl(1)–Ag(1)–C(1), 171.64; Ag(1)–C(1)–N(1), 125.14; Ag(1)–C(1)–N(2), 126.00; N(1)–C(1)–N(2), 108.86.

2.4. The application to a copper-catalyzed allylic arylation with PhMgBr

With these bicyclic NHC ligands in hand, we tested the regioselective allylic arylation for proof of our concept. Copper-catalyzed γ-selective allylic substitution with a Grignard reagent is one of the most well-established reactions and a synthetic chemist would be expected to design a ligand theoretically on the basis of two important factors: steric bulkiness and electron deficiency.[13] More bulky and electron-deficient ligands accelerate the reductive elimination step, which produces the γ-substituted product preferentially.[14] To test the efficiency of the steric shielding by the framework, we set the ligands **18** and **19** for the comparisons shown in Table 1. As the comparison with DHASIMe (entries 3 and 5) obviously indicates, our rigid framework overcame the electron deficiency of the unsaturated NHC (ligand **18**, entry 2) and the steric effect of the DPEN framework (ligand **19**, entry 4), which has been the most widely used of chiral NHC ligands.[3] In the case of the reaction catalyzed by the copper complex with DHASIBn (entry 6), which is more bulky ligand than DHASIMe, the substitution with the resultant copper complex gave a product that was almost completely γ-selective. These results suggest that our bicyclic motif on non-carbenic carbons induces the appropriate shielding effect for the metal center. Despite the fact that the buried volume ($\%V_{bur}$) of complex **16**, which is the quantity of the steric demand of the NHC ligands represented by Nolan and Cavallo et al.,[15] was only 26.1%,[16] the rigidity of the bicyclic framework seemed to amplify the 'steric bulkiness'.

Table 1
Copper-catalyzed allylic arylation with PhMgBr



Entry	**L** (mol %)	Combined yield[a] (%)	Ratio (α:γ)[a]
1	None	95	96:4
2	**18** (2.5)[b]	98	49:51
3	DHASIMe **16** (5.0)[b]	98	20:80
4	**19** (5.0)[c]	99	80:20
5	**14** (5.0)[c]	98	21:79
6	DHASIBn **17** (5.0)[b]	95	5:95

[a] Determined by ^1H NMR.
[b] NHC–Ag complex was used as NHC transfer agent.
[c] Carbene was generated in situ.

3. Conclusion

In conclusion, we synthesized NHC ligands with a bicyclic framework on the non-carbenic carbons, and used them to construct silver complexes. The structure of the silver complex was confirmed by X-ray crystallographic analysis. This novel type of NHC ligand has successfully been applied to a copper-catalyzed regioselective allylic arylation with a Grignard reagent, and the selectivity suggested that the bound copper was effectively shielded from the backbone framework of these NHC ligands. Further investigation into the synthesis of chiral and functionalized NHC ligands with this bicyclic motif and their applications to stereoselective reactions are underway in our laboratory.

4. Experimental section

4.1. General remarks

All reactions were carried out under an argon atmosphere with freshly distilled solvents under anhydrous conditions, unless otherwise noted. Anhydrous CH_2Cl_2 and THF were purchased from KANTO CHEMICAL CO. INC. and used without further distillation. Dimethoxyethane (DME) was distilled from Na. Reagents were used without further purification. Yields refer to chromatography and spectroscopically (^1H NMR) homogeneous materials, unless

otherwise stated. All reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25-mm E. Merck silica gel plates (60F–254) using UV-light (254 nm) for visualization or using 5% ninhydrin in *n*-BuOH for developing agents and heat for visualization. Fuji silysia silica gel (PSQ60B) was used for flash chromatography. Melting points were measured using Yanako micro melting point apparatus and are uncorrected. NMR spectra were recorded on JEOL JNM-AL300 (300 MHz) or JEOL JNM-ECX-400 (400 MHz) instruments and calibrated using solvent and TMS peaks as internal references. The following abbreviations are used to indicate the multiplicities; s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, br=broad, app=apparent. MS and HRMS (EI or FAB) were obtained with a JEOL JMS-700 mass spectrometer. High-resolution mass spectra were obtained using EBE geometry. IR spectra were recorded on a JEOL JIR-6500W FT-IR spectrometer. Optical rotation was measured at 27 °C in a 5.0 cm cell on JASCO DIP-360; $[\alpha]_D$ value was given in 10^{-1} deg cm^2 g^{-1} (concentration given as g/100 mL). X-ray crystallography was recorded on a Rigaku AFC/RASA7R single-crystal diffractometer with sealed-tube Molybdenum radiation.

4.2. Syntheses of the bicyclic NHC ligand precursors and NHC–Ag complexes

*4.2.1. (±)-N-Ac, N′-2-Naphthalenesulfonyl-4,5-(9,10-dihydroanthraceno)-imidazolidinone **5**.* A solution of imidazolidinone **4**[9] (61 mg, 0.2 mmol) in THF (2.0 mL) was cooled to 0 °C in an ice bath. NaH (60% in mineral oil, 16 mg, 0.4 mmol) was added to the solution at 0 °C, followed by 2-naphthalenesulfonyl chloride (68 mg, 0.3 mmol). The resulting reaction mixture was warmed to 25 °C by a removal of the ice bath and stirred at the same temperature for 1 h. After the confirmation of the accomplishment of the reaction by TLC monitoring, the reaction mixture was cooled in an ice bath and then quenched by addition of saturated NH_4Cl aq (4.0 mL) at 0 °C. The resulting solution was extracted with EtOAc (3×4.0 mL), and the combined organic extracts were washed with brine (1×2.0 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was purified by flash chromatography (10–30% EtOAc in *n*-hexane) on silica gel (10 mL) to afford the titled compound **5** (97 mg, quantitative) as a colorless amorphous solid; mp >200 °C; R_f=0.33 (30% EtOAc in *n*-hexane); IR (KBr pellet): ν_{max}=3035, 2962, 1753 (C=O), 1701 (C=O), 1470, 1369, 1288, 1236, 1171, 1132, 1099, 1072, 860, 731 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ=8.63 (s, 1H), 8.02–7.90 (m, 4H), 7.70–7.60 (m, 2H), 7.46–7.37 (m, 2H), 7.24–7.04 (m, 4H), 6.95–6.90 (m, 2H), 5.05 (d, *J*=2.9 Hz, 1H), 5.03 (d, *J*=2.9 Hz, 1H), 4.58 (dd, *J*=9.9, 2.9 Hz, 1H), 4.47 (dd, *J*=9.9, 2.9 Hz, 1H), 2.25 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ=170.4, 150.8, 139.1, 138.9, 138.0, 137.1, 135.3, 131.8, 130.2, 129.6, 129.3, 127.9, 127.8, 127.3, 127.2, 127.1, 126.5, 125.5, 125.3, 125.2, 122.7, 57.0, 55.8, 48.1, 45.1, 24.4 ppm; HRMS (FAB$^+$) calcd for $C_{29}H_{23}N_2O_4S$ $[M+H]^+$ 495.1379, found 495.1404.

*4.2.2. (±)-N–H, N′-2-Naphthalenesulfonyl-4,5-(9,10-dihydroanthraceno)-imidazolidinone **6**.* Cs_2CO_3 (652 mg, 2.0 mmol) was added to a solution of imidazolidinone (±)-**5** (9.89 g, 20 mmol) in MeOH/CH_2Cl_2 (130 mL, 1:1 mixture) at 25 °C. The reaction solution was stirred at the same temperature until TLC monitoring showed the accomplishment of the reaction (normally within 30 min). The reaction was quenched by an addition of citric acid (4.0 g) and subsequent 15 min stirring at 25 °C. The resulting mixture was concentrated under reduced pressure, and the residue was dissolved in CH_2Cl_2 (200 mL). The mixture was then washed with brine (1×200 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was purified by chromatography (0–5% EtOAc in CH_2Cl_2) on silica gel (600 mL) to afford the titled compound (±)-**6** (8.86 g, 98%) as a white powder; mp >200 °C; R_f=0.26 (CH_2Cl_2); IR (KBr pellet): ν_{max}=3356, 3054, 2927, 1743 (C=O), 1470, 1348, 1246, 1169, 1134, 1076, 1032, 931, 860, 818, 748 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6, 298 K): δ=8.59 (s, 1H), 8.01–7.90 (m, 4H), 7.68–7.58 (m, 2H), 7.46–7.43 (m, 1H), 7.29–7.21 (m, 4H), 7.20–7.07 (m, 1H), 6.97–6.90 (m, 2H), 4.98 (d, *J*=3.1 Hz, 1H), 4.65 (dd, *J*=9.5, 3.1 Hz, 1H), 4.32 (d, *J*=3.1 Hz, 1H), 4.01 (dd, *J*=9.5, 3.1 Hz, 1H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6, 298 K): δ=154.1, 140.4, 139.6, 139.0, 138.4, 136.1, 134.7, 131.5, 129.5, 129.3, 129.0, 129.0, 127.8, 127.6, 126.8, 126.7, 126.3, 126.20, 126.16, 126.0, 125.2, 124.9, 122.8, 59.4, 52.5, 48.3, 47.8 ppm; HRMS (FAB$^+$) calcd for $C_{27}H_{21}N_2O_3S$ $[M+H]^+$ 453.1273, found 453.1289.

*4.2.3. (±)-N-Boc, N′-2-naphthalenesulfonyl-1,2-(9,10-dihydroanthraceno)-ethylenediamine **8**.* $Ba(OH)_2\cdot 8H_2O$ (31.5 g, 100 mmol) was added to a suspension of imidazolidinone (±)-**6** (9.05 g, 20 mmol) in EtOH/DMSO/H_2O (280 mL, 5:1:1 mixture) at 25 °C. The reaction solution was heated at reflux until TLC monitoring showed the accomplishment of the reaction (normally 24–48 h). The reaction was cooled to 25 °C and then poured to H_2O (1.0 L) at the same temperature to precipitate the diamine product (±)-**7**. The white precipitate was filtered and suspended into CH_2Cl_2 (200 mL). $(Boc)_2O$ (5.52 mL, 24 mmol) was added to the resulting mixture and stirred at 25 °C for 17 h. The reaction mixture was filtered through Celite® pad, washed with CH_2Cl_2. The combined filtrate and washings were washed with brine (1×200 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was purified by chromatography (0–10% EtOAc in CH_2Cl_2) on silica gel (600 mL) to afford the titled compound (±)-**8** (9.14 g, 87%) as a pale yellow foam; R_f=0.30 (30% EtOAc in *n*-hexane); IR (KBr pellet): ν_{max}=3381, 3184, 2976, 2943, 1693 (C=O), 1468, 1361, 1331, 1169, 1099, 1072, 1022, 957, 818, 760 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$+1% CD_3OD, 323 K): δ=8.43 (s, 1H), 7.98 (d, *J*=8.80 Hz, 2H), 7.91 (d, *J*=7.3 Hz, 1H), 7.79 (d, *J*=8.80 Hz, 1H), 7.67–7.61 (m, 2H), 7.30–7.20 (m, 5H), 7.10–7.08 (m, 3H), 4.28 (d, *J*=2.2 Hz, 1H), 4.14 (br s, 1H), 4.11 (dd, *J*=9.2, 2.2 Hz, 1H), 3.90 (dd, *J*=9.2, 2.2 Hz, 1H), 1.34 (s, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$, 323 K): δ=155.1, 140.5, 139.9, 139.1, 138.6, 135.0, 132.3, 129.5, 129.3, 128.8, 128.3, 127.9, 127.6, 127.1, 126.8, 126.7, 126.5, 125.9, 124.4, 122.4, 80.1, 53.4, 51.2, 50.0, 49.4, 28.2 ppm; HRMS (FAB$^+$) calcd for $C_{31}H_{30}N_2O_4SNa$ $[M+Na]^+$ 549.1824, found 549.1843.

*4.2.4. (±)-N–H, N′-Methyl-1,2-(9,10-dihydroanthraceno)-ethylenediamine hydrochloride **10**.* Na metal (1.29 g, 56 mmol) was added to a solution of naphthalene (1.54 g, 24 mmol) in DME (40 mL) at 25 °C. The resulting mixture was sonicated at 25 °C for 10 min and then cooled to −30 °C. A solution of protected-diamine (±)-**8** (2.11 g, 4.0 mmol) in DME (15 mL) was dropwise to the reaction mixture, and an additional DME (5.0 mL) was used to rinse the vessel and complete the addition of the compound (±)-**8**. The reaction solution was stirred at the same temperature until TLC monitoring showed the accomplishment of the reaction (normally 1.5–2 h). The reaction mixture was then poured to H_2O (500 mL), which had been prechilled in an ice bath, by pipette (CAUTION!! Extra amount of Na still be in the reaction mixture. Pour the supernatant carefully and kill the residual Na appropriately). Brine (100 mL) was added to the resulting mixture, and the resulting mixture was extracted with Et_2O (3×200 mL). The combined organic extracts were washed with brine (1 ×200 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was purified by flash chromatography (50–100% EtOAc in CH_2Cl_2) on silica gel (50 mL) to afford *N*-Boc, *N′*–H diamine product (±)-**9** (1.18 g; R_f=0.29 (EtOAc)) together with inseparable impurities. The deprotected diamine (±)-**9** was dissolved in acetone (20 mL) and heated at reflux until TLC monitoring indicated the complete formation of aminal protected compound (normally ca. 2 h). The reaction solution was cooled to 25 °C, and K_2CO_3 (1.66 g, 12 mmol) and $(MeO)_2SO_2$ (0.38 mL, 6 mmol) were added. The resulting mixture was then heated at reflux for 12 h. The

mixture was cooled to 25 °C, diluted with EtOAc (20 mL), and filtered through Celite® pad. The filtrate was concentrated under reduced pressure to afford the methylated aminal product as a crude mixture. Because of its instability against light, this crude mixture was used for the next step directly. The crude residue was dissolved in MeOH (10 mL), and 2 M HCl aq (10 mL) was added to the solution. The reaction mixture was then heated at reflux until TLC monitoring indicated the complete consumption of methylated aminal compound (normally 2–3 h). The resulting solution was concentrated under reduced pressure, and the residue was dissolved in EtOH. CH_2Cl_2 was added to the solution to precipitate the product as HCl salt. The salt was filtered and washed with CH_2Cl_2 to afford the titled compound (±)-**10** (849 mg, 74% over three steps) as a white powder; mp >200 °C; IR (KBr pellet): ν_{max}=3570, 3496, 2841, 1430, 2050, 1556, 1508, 1470, 1174, 1149, 1028, 769, 744 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 333 K): δ=7.57–7.40 (m, 4H), 7.27–7.19 (m, 4H), 5.05 (d, J=2.4 Hz, 1H), 4.89 (d, J=2.4 Hz, 1H), 3.96 (dd, J=8.8, 2.4 Hz, 1H), 3.84 (dd, J=8.8, 2.4 Hz, 1H), 2.80 (s, 3H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6, 333 K): δ=139.7, 139.4, 137.2, 136.9, 127.42, 127.38, 126.9, 126.8, 126.4, 126.2, 124.5, 124.3, 58.1, 50.2, 46.1, 43.8, 31.6 ppm; HRMS (FAB^+) calcd for $C_{17}H_{19}N_2$ $[M+H]^+$ 251.1548, found 251.1546.

*4.2.5. (±)-N–H, N′-Benzyl-1,2-(9,10-dihydroanthraceno)-ethylenediamine hydrochloride **11**.* The preparation of *N*–H, *N*′-Bn diamine **11** was accomplished by the same procedure as the method used for *N*–H, *N*′-Me diamine **10** except for the following differences. One was the usage of BnBr instead of $(MeO)_2SO_2$ as an alkylating reagent, and the other one was the usage of Et_2O instead of CH_2Cl_2 to precipitate the HCl salt. The titled compound **11** was obtained in 70% yield (455 mg from 603 mg of **8**) over three steps as a white powder; mp >200 °C; IR (KBr pellet): ν_{max}=3442, 2740, 2428, 1620, 1556, 1516, 1500, 1460, 1427, 1201, 1171, 1024, 746 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 353 K): δ=7.57–7.55 (m, 3H), 7.45–7.33 (m, 6H), 7.26–7.17 (m, 4H), 4.94 (br s, 1H), 4.76 (d, J=2.6 Hz, 1H), 4.28 (d, J=13.4 Hz, 1H), 4.20 (d, J=13.4 Hz, 1H), 3.81 (dd, J=8.8, 2.6 Hz, 1H), 3.62 (br d, J=8.8 Hz, 1H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6, 353 K): δ=139.8, 139.7, 137.4, 129.6, 128.5, 128.3, 127.4, 127.3, 126.8, 126.5, 126.2, 124.42, 124.36, 56.6, 50.3, 49.8, 46.2, 43.8, ppm; HRMS (FAB^+) calcd for $C_{23}H_{23}N_2$ $[M+H]^+$ 327.1861, found 327.1884.

*4.2.6. N,N′-Dimethyl-1,2-(9,10-dihydroanthraceno)-ethylenediamine hydrochloride **12**.* Excess amount of Et_3N was added to the suspension of mono methylated-diamine hydrochloride (±)-**10** (143 mg, 0.5 mmol) in CH_2Cl_2, and the resulting solution was concentrated under reduced pressure to desalt. The desalted diamine was dissolved in acetone (20 mL) and heated at reflux until TLC monitoring indicated the complete formation of the aminal protected compound (normally ca. 2 h). The reaction solution was cooled to 25 °C, and K_2CO_3 (207 mg, 1.5 mmol) and $(MeO)_2SO_2$ (71 μL, 750 μmol) were added. The resulting mixture was then heated at reflux for 12 h. The mixture was cooled to 25 °C, diluted with EtOAc (20 mL), and filtered through Celite® pad. The filtrate was concentrated under reduced pressure to afford the methylated aminal product as crude mixture. This crude mixture was used for the next step directly. The crude residue was dissolved in MeOH (1 mL), and 2 M HCl aq (1 mL) was added to the solution. The reaction mixture was then heated at reflux until TLC monitoring indicated the complete consumption of methylated aminal compound (normally 2–3 h). The resulting solution was concentrated under reduced pressure, and the residue was dissolved in EtOH. CH_2Cl_2 was added to the solution to precipitate the product as HCl salt. The salt was filtered and washed with CH_2Cl_2 to afford the titled compound **12** (115 mg, 76% over two steps) as a white powder; mp >200 °C; IR (KBr pellet): ν_{max}=3442, 2725, 2428, 1628, 1562, 1460, 1161, 1022, 768, 748 cm^{-1}; ^1H NMR (300 MHz, D_2O, 298 K): δ=7.50 (dd, J=5.5, 3.3 Hz, 2H), 7.37 (dd, J=5.5, 3.3 Hz, 2H), 7.27 (dd, J=5.5, 3.3 Hz, 2H), 7.17 (dd, J=5.5, 3.3 Hz, 2H), 4.91 (s, 2H), 3.89 (s, 2H), 2.90 (s, 6H) ppm; ^{13}C NMR (75 MHz, D_2O+10% DMSO-d_6, 298 K): δ=140.5, 138.3, 129.3, 128.4, 126.5, 60.3, 45.1, 34.6 ppm; HRMS (FAB^+) calcd for $C_{18}H_{21}N_2$ $[M+H]^+$ 265.1705, found 265.1709.

*4.2.7. N,N′-Dibenzyl-1,2-(9,10-dihydroanthraceno)-ethylenediamine hydrochloride **13**.* The preparation of *N*,*N*′-dibenzylated diamine **13** was accomplished by the same procedure as the method used for *N*,*N*′-dimethylated diamine **12** except for the following differences. One was the usage of BnBr instead of $(MeO)_2SO_2$ as an alkylating reagent, and the other one was the usage of Et_2O instead of CH_2Cl_2 to precipitate the HCl salt. The titled compound **13** was obtained in 88% (547 mg from 499 mg, 1.1 mmol of (±)-**11**) yield over two steps as a white powder; mp 143–145 °C; IR (KBr pellet): ν_{max}=3421, 2964, 2696, 1585, 1460, 1209, 1174, 1014, 962, 920, 748, 698 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 353 K): δ=7.57–7.51 (m, 6H), 7.39–7.32 (m, 8H), 7.25–7.16 (m, 4H), 5.01 (br s, 2H), 4.40 (d, J=13.0 Hz, 2H), 4.23 (d, J=13.0 Hz, 2H), 3.69 (br s, 2H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6, 353 K): δ=140.1, 137.8, 129.3, 128.0, 127.9, 126.8, 126.4, 126.1, 124.0, 56.7, 50.2, 44.3 ppm; HRMS (FAB^+) calcd for $C_{30}H_{29}N_2$ $[M+H]^+$ 417.2331, found 417.2322.

*4.2.8. N,N′-Dimethyl-4,5-(9,10-dihydroanthraceno)-imidazolinium chloride **14**.* $(EtO)_3CH$ (6.8 mL) was added to a flask charged with *N*,*N*′-dimethyldiamine hydrochloride **12** (460 mg, 1.38 mmol), and the resulting suspension was heated at 100 °C in an oil bath for 16 h. The white precipitate was filtered and washed with Et_2O to afford the titled compound **14** (420 mg, 99%) as a white powder; mp >200 °C; IR (KBr pellet): ν_{max}=3020, 2954, 1659, 1529, 1458, 1311, 1279, 1153, 1034, 771 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K): δ=8.23 (s, 1H), 7.55 (dd, J=5.3, 3.3 Hz, 2H), 7.45 (dd, J=5.3, 3.3 Hz, 2H), 7.24 (dd, J=5.3, 3.3 Hz, 4H), 5.06 (s, 2H), 4.65 (s, 2H), 3.06 (s, 6H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6, 298 K): δ=158.1, 139.1, 137.8, 127.0, 126.9, 125.7, 125.2, 66.1, 43.2, 31.8 ppm; HRMS (FAB^+) calcd for $C_{19}H_{19}N_2$ $[M]^+$ 275.1548, found 275.1534.

*4.2.9. N,N′-Dibenzyl-4,5-(9,10-dihydroanthraceno)-imidazolinium chloride **15**.* $(EtO)_3CH$ (3.0 mL) was added to a flask charged with *N*,*N*′-dibenzylated diamine hydrochloride **13** (136 mg, 0.30 mmol), and the resulting suspension was heated to a 100 °C in an oil bath for 16 h. The white precipitate was filtered and washed with Et_2O to afford the titled compound **15** (107 mg, 77%) as a white powder; mp >200 °C; IR (KBr pellet): ν_{max}=3039, 2999, 2881, 2837, 1633, 1458, 1435, 1362, 1308, 1279, 1215, 1173, 1105, 1043, 758, 704 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K): δ=8.36 (s, 1H), 7.46–7.34 (m, 14H), 7.23–7.17 (m, 4H), 5.05 (s, 2H), 4.71 (d, J=14.8 Hz, 2H), 4.59 (d, J=14.8 Hz, 2H), 4.55 (s, 2H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6, 298 K): δ=158.7, 139.6, 138.4, 133.8, 129.7, 129.5, 129.2, 127.6, 127.4, 126.4, 125.8, 65.5, 49.2, 43.9 ppm; HRMS (FAB^+) calcd for $C_{31}H_{27}N_2$ $[M]^+$ 427.2174, found 427.2193.

*4.2.10. N,N′-Dimethyl-4,5-(9,10-dihydroanthraceno)-imidazolin-2-ylidene silver chloride (DHASIMeAgCl) **16**.* Ag_2O (25.3 mg, 0.11 mmol) was added to a suspension of *N*,*N*′-dimethyl imidazolinium salt **14** (62 mg, 0.2 mmol) in CH_2Cl_2 (2.0 mL), and the reaction mixture was stirred for 1 h with cover of aluminum foil to darken. The resulting mixture was filtered through Celite® pad, washed with CH_2Cl_2. The combined filtrate and washings were concentrated under reduced pressure to make the total volume ca. 2.0 mL. Hexane (ca. 4 mL) was added to the resulting solution to precipitate the titled complex **16** (77 mg, 92%) as a white powder. The single crystalline for X-ray diffraction analysis was grown by the slow vapor diffusion of Et_2O into a CH_2Cl_2 solution; mp 179–182 °C (decomp.); IR (KBr pellet): ν_{max}=3039, 2914, 2860, 2789, 1520, 1468, 1400, 1315, 1273, 1207, 1034, 960, 926, 758 cm^{-1}; ^1H NMR (300 MHz, CD_2Cl_2, 298 K): δ=7.37 (dd, J=5.5, 3.3 Hz, 2H),

7.35 (dd, J=5.5, 3.3 Hz, 2H), 7.24–7.19 (m, 4H), 4.68 (s, 2H), 4.32 (dd, J=1.5, 1.5 Hz, 2H), 3.09 (s, 6H) ppm; ^{13}C NMR (75 MHz, CD_2Cl_2, 298 K): δ=139.6, 138.0, 127.3, 127.2, 125.6, 125.1, 68.8, 45.7, 35.8 ppm; LRMS (FAB$^+$) m/z 655 $[(C_{19}H_{18}N_2)_2{}^{107}Ag]^+$, 657 $[(C_{19}H_{18}N_2)_2{}^{109}Ag]^+$. Anal. Calcd for $C_{19}H_{18}AgClN_2\cdot H_2O$ (434.0315): C, 52.38; H, 4.63; N, 6.43. Found: C, 52.32; H, 4.28; N, 6.19. (Removal of H_2O could not be accomplished by a heating under reduced pressure.)

4.2.11. N,N′-Dibenzyl-4,5-(9,10-dihydroanthraceno)-imidazolin-2-ylidene silver chloride (DHASIBnAgCl) ***17****.* Ag_2O (18.7 mg, 81 μmol) was added to a suspension of *N,N′*-dibenzyl imidazolinium salt **15** (62 mg, 134 μmol) in CH_2Cl_2 (2.6 mL), and the reaction mixture was stirred for 17 h with cover of aluminum foil to darken. The resulting mixture was filtered through Celite® pad, washed with CH_2Cl_2. The combined filtrate and washings were concentrated under reduced pressure. The residue was treated with a mixture of CH_2Cl_2 and Et_2O (ca. 1: 10) and sonicated for 5 min. The filtration of the white precipitate yielded the titled complex **17** (63 mg, 83%) as a white powder; mp 168–171 °C (decomp.); IR (KBr pellet): ν_{max}=3026, 2914, 1485, 1452, 1354, 1311, 1248, 1169, 1047, 1028, 945, 928, 754, 706 cm^{-1}; ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ=7.46–7.22 (m, 16H), 7.12–7.09 (m, 2H), 4.93 (d, J=15.2 Hz, 2H), 4.63 (s, 2H), 4.44 (d, J=15.2 Hz, 2H), 4.19 (dd, J=1.6, 1.6 Hz, 2H) ppm; ^{13}C NMR (75 MHz, CD_2Cl_2, 298 K): δ=139.5, 138.1, 135.0, 129.2, 128.6, 128.2, 127.3, 127.2, 125.7, 125.1, 65.9, 53.1, 45.4 ppm; LRMS (FAB$^+$) 959 $[(C_{31}H_{26}N_2)_2{}^{107}Ag]^+$, 961 $[(C_{31}H_{26}N_2)_2{}^{109}Ag]^+$. Anal. Calcd for $C_{31}H_{26}AgCl\,N_2\cdot H_2O$ (586.0941): C, 63.33; H, 4.80; N, 4.77. Found: C, 63.41; H, 4.45; N, 4.63. (Removal of H_2O could not be accomplished by a heating under reduced pressure.)

4.3. Copper-catalyzed allylic arylation with PhMgBr

4.3.1. General procedure for an allylic arylation via a transmetalation process. CH_2Cl_2 (0.50 mL) was added to a flask charged with CuCl (2.5 mg, 25 μmol), silver–carbene complex (25 μmol for **16** or **17**, 12.5 μmol for $[Ag(IMe)_2][AgI_2]$**18**), and magnetic stir bar at 25 °C. The resulting suspension was stirred at the same temperature for 10 min, and a solution of cinnamyl bromide (99 mg, 0.50 mmol) in CH_2Cl_2 (0.50 mL) was added to the resulting mixture, followed by cooling in a dry-ice/EtOH bath. A solution of PhMgBr (0.20 mL of 3.0 M solution in Et_2O diluted with 0.25 mL of CH_2Cl_2) was added to the reaction mixture by a syringe pump over 15 min. Once the addition was complete, the resulting mixture was stirred for another 1 h at the same temperature. The reaction mixture was then diluted with Et_2O (2.0 mL) and quenched with 2 M HCl aq (2.0 mL) at −78 °C. The resulting mixture was allowed to warm to 25 °C and extracted with Et_2O (3×4 mL). The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was dissolved in CH_2Cl_2, and anthracene (89 mg, 0.5 mmol) was added to the solution as an external standard to calculate the yield based on the crude ^{1}H NMR. After the removal of the solvent, the ratios of the products were calculated based on the crude ^{1}H NMR.

4.3.2. General procedure for an allylic arylation via a carbene generation in situ. CH_2Cl_2 (0.50 mL) was added to a flask charged with CuCl (2.5 mg, 25 μmol), imidazolinium salt (25 μmol of **14** or **19**), and magnetic stir bar at 25 °C. The resulting suspension was cooled in a dry-ice/EtOH bath, and *n*-BuLi (2.69 M in hexane, 19 μL) was added to the mixture. After being stirred at the same temperature for 30 min, a solution of cinnamyl bromide (99 mg, 0.50 mmol) in CH_2Cl_2 (0.50 mL) was added to the resulting mixture. A solution of PhMgBr (0.20 mL of 3.0 M solution in Et_2O diluted with 0.25 mL of CH_2Cl_2) was added to the reaction mixture by a syringe pump over 15 min. Once the addition was complete, the resulting mixture was stirred for another 1 h at the same temperature. The reaction mixture was then diluted with Et_2O (2.0 mL) and quenched with 2 M HCl aq (2.0 mL) at −78 °C. The resulting mixture was allowed to warm to 25 °C and extracted with Et_2O (3×4 mL). The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was dissolved in CH_2Cl_2, and anthracene (89 mg, 0.5 mmol) was added to the solution as an external standard to calculate the yield based on the crude ^{1}H NMR. After the removal of the solvent, the ratios of the products were calculated based on the crude ^{1}H NMR.

4.3.3. The preparation of the comparison, (4R),(5R)-N,N′-dimethyl-4,5-diphenyl-4,5-dihydro-imidazolinium iodide ***19****.* CH_2Cl_2 (3.9 mL) was added to a flask charged with (*R*),(*R*)-4,5-diphenyl-4,5-dihydro-1-*H*-imidazoline[17] (172 mg, 0.77 mmol), K_2CO_3 (107 mg, 0.77 mmol), and magnetic stir bar at 25 °C. MeI (145 μL, 2.33 mmol) was added to the resulting mixture, and the reaction mixture was stirred at 25 °C for 21 h. The resulting mixture was then filtered through Celite® pad, washed with CH_2Cl_2. The combined filtrate and washings were concentrated under reduced pressure, and the residue was washed with Et_2O to afford the titled compound **19** (102 mg, quantitative) as a white powder; mp 185–187 °C (decomp.); IR (KBr pellet): ν_{max}=3487, 3444, 3008, 2941, 1641, 1495, 1458, 1284, 1223, 1151, 1101, 978, 827, 758, 700 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 293 K): δ=7.47–7.45 (m, 6H), 7.40–7.38 (m, 4H), 4.91 (s, 2H), 3.23 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$, 293 K): δ=159.4, 133.9, 130.0, 129.8, 127.8, 75.8, 33.9 ppm; HRMS (FAB$^+$) calcd for $C_{17}H_{19}N_2$ $[M]^+$ 251.1548, found 251.1553. $[\alpha]_D^{27}$ 210.4 (*c* 0.10, $CHCl_3$).

Acknowledgements

This research was financially supported in part by JSPS KAKENHI (NO. 23590011 to H.M.) and by the Hoansha Foundation (to T.I.). We greatly thank Dr. Akihito Yamano (Rigaku Corporation) for assistance with the X-ray analysis.

Supplementary data

Supplementary data related to this article can be found online at http://dx.doi.org/10.1016/j.tet.2012.12.036.

References and notes

1. Herrmann, W. A.; Elison, M.; Fischer, J.; Köcher, C.; Artus, G. R. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2371–2374.
2. (a) *N-Heterocyclic Carbenes in Synthesis*; Nolan, S. P., Ed.; WILEY-VCH GmbH: KGaA, Weinheim, 2001; (b) *N-Heterocyclic Carbenes: From Laboratory Curiosities to Efficient Synthetic Tools*; Díez-González, S., Ed.; the Royal Society of Chemistry: 2011.
3. (a) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290–1309; (b) Díez-González, S.; Marion, N.; Nolan, S. P. *Chem. Rev.* **2009**, *109*, 3612–3676; (c) Perry, M. C.; Burgess, K. *Tetrahedron: Asymmetry* **2003**, *14*, 951–961; (d) Wang, F.; Liu, L.-j.; Wang, W.; Li, S.; Shi, M. *Coord. Chem. Rev.* **2012**, *256*, 804–853; (e) Cesar, V.; Bellemin-Laponnaz, S.; Gade, L. H. *Chem. Soc. Rev.* **2004**, *33*, 619–636.
4. (a) Cavallo, L.; Correa, A.; Costabile, C.; Jacobsen, H. *J. Organomet. Chem.* **2005**, *690*, 5407–5413; (b) Jacobsen, H.; Correa, A.; Poater, A.; Costabile, C.; Cavallo, L. *Coord. Chem. Rev.* **2009**, *253*, 687–703.
5. (a) Chianese, A. R.; Li, X.; Janzen, M. C.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2003**, *22*, 1663–1667; (b) Dorta, R.; Stevens, E. D.; Scott, N. M.; Costabile, C.; Cavallo, L.; Hoff, C. D.; Nolan, S. P. *J. Am. Chem. Soc.* **2005**, *127*, 2485–2495.
6. Marion, N.; Navarro, O.; Mei, J.; Stevens, E. D.; Scott, N. M.; Nolan, S. P. *J. Am. Chem. Soc.* **2006**, *128*, 4101–4111.
7. (a) Heinemann, C.; Müller, T.; Apeloig, Y.; Schwarz, H. *J. Am. Chem. Soc.* **1996**, *118*, 2023–2038; (b) Boehme, C.; Frenking, G. *J. Am. Chem. Soc.* **1996**, *118*, 2039–2046; (c) Denk, M. K.; Rodezno, J. M.; Gupta, S.; Lough, A. J. *J. Organomet. Chem.* **2001**, *617–618*, 242–253.
8. Matsunaga, H.; Ishizuka, T.; Kunieda, T. *Tetrahedron Lett.* **2005**, *46*, 3645–3648.
9. Yokoyama, K.; Ishizuka, T.; Ohmachi, N.; Kunieda, T. *Tetrahedron Lett.* **1998**, *39*, 4847–4850.
10. (a) Wang, H. M. J.; Lin, I. J. B. *Organometallics* **1998**, *17*, 972–975 For review of NHC–Ag complexes, see; (b) Garrison, J. C.; Youngs, W. J. *Chem. Rev.* **2005**, *105*, 3978–4008; (c) Lin, I. J. B.; Vasam, C. S. *Coord. Chem. Rev.* **2007**, *251*, 642–670.

11. (a) Ramnial, T.; Abernethy, C. D.; Spicer, M. D.; McKenzie, I. D.; Gay, I. D.; Clyburne, J. A. C. *Inorg. Chem.* **2003**, *42*, 1391–1393; (b) Tominaga, S.; Oi, Y.; Kato, T.; An, D. K.; Okamoto, S. *Tetrahedron Lett.* **2004**, *45*, 5585–5588; (c) de Frémont, P.; Scott, N. M.; Stevens, E. D.; Ramnial, T.; Lightbody, O. C.; Macdonald, C. L. B.; Clyburne, J. A. C.; Abernethy, C. D.; Nolan, S. P. *Organometallics* **2005**, *24*, 6301–6309; (d) Sentman, A. C.; Csihony, S. r.; Waymouth, R. M.; Hedrick, J. L. *J. Org. Chem.* **2005**, *70*, 2391–2393.
12. CCDC reference number is 900527. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
13. (a) López, F.; Minnaard, A. J.; Feringa, B. L. *Acc. Chem. Res.* **2006**, *40*, 179–188; (b) Alexakis, A.; Bäckvall, J. E.; Krause, N.; Pàmies, O.; Diéguez, M. *Chem. Rev.* **2008**, *108*, 2796–2823; (c) Harutyunyan, S. R.; den Hartog, T.; Geurts, K.; Minnaard, A. J.; Feringa, B. L. *Chem. Rev.* **2008**, *108*, 2824–2852.
14. For leading references, see; (a) Goering, H. L.; Singleton, V. D. *J. Am. Chem. Soc.* **1976**, *98*, 7854–7855; (b) Goering, H. L.; Singleton, V. D. *J. Org. Chem.* **1983**, *48*, 1531–1533; (c) Corey, E. J.; Boaz, N. W. *Tetrahedron Lett.* **1984**, *25*, 3063–3066; (d) Goering, H. L.; Kantner, S. S. *J. Org. Chem.* **1984**, *49*, 422–426; (e) Baeckvall, J. E.; Sellen, M.; Grant, B. *J. Am. Chem. Soc.* **1990**, *112*, 6615–6621; (f) Selim, K. B.; Nakanishi, H.; Matsumoto, Y.; Yamamoto, Y.; Yamada, K.-i.; Tomioka, K. *J. Org. Chem.* **2011**, *76*, 1398–1408.
15. (a) Hillier, A. C.; Sommer, W. J.; Yong, B. S.; Petersen, J. L.; Cavallo, L.; Nolan, S. P. *Organometallics* **2003**, *22*, 4322–4326; (b) Clavier, H.; Nolan, S. P. *Chem. Commun.* **2010**, 841–861; (c) Poater, A.; Cosenza, B.; Correa, A.; Giudice, S.; Ragone, F.; Scarano, V.; Cavallo, L. *Eur. J. Inorg. Chem.* **2009**, *2009*, 1759–1766; (d) www.molnac.unisa.it/OMtools.php.
16. A radius of 3.5 Å for the sphere, a distance of 2.1 Å between the metal and coordinating carbene atom, and a mesh spacing of 0.05 Å were used for the calculation. This $\%V_{bur}$ value was almost identical to that of the *N*,*N*′-diethyl imidazolinylidene ligand without substituents on non-carbenic carbons, indicating that almost no effect of our framework was detected based on this calculation.
17. Murai, K.; Morishita, M.; Nakatani, R.; Fujioka, H.; Kita, Y. *Chem. Commun.* **2008**, 4498–4500.