DOI: 10.1002/adsc.201100890

An Unexpected Synthesis of Dihydrophenazines *en Route* to Benzimidazolium Salts

Yannick Borguet,[a] Guillermo Zaragoza,[b] Albert Demonceau,[a] and Lionel Delaude[a,*]

[a] Laboratory of Macromolecular Chemistry and Organic Catalysis, Université de Liège, Institut de Chimie (B6a), Sart-Tilman par 4000 Liège, Belgium
Fax: (+32)-4-366-3497; e-mail: l.delaude@ulg.ac.be
[b] Unidade de Difracción de Raios X, Universidade de Santiago de Compostela, Edificio CACTUS, Campus Vida, 15782 Santiago de Compostela, Spain

Received: November 16, 2011; Revised: January 19, 2012; Published online: April 26, 2012

Dedicated to Dr. Christian Bruneau on the occasion of his 60th birthday.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201000890.

Abstract: The oxidation of various *N,N′*-diarylbenzene-1,2-diamines bearing bulky aromatic substituents with sodium periodate on wet silica gel afforded a series of five new dihydrophenazines instead of the expected cyclohexadiene-1,2-diimines. The reaction most likely proceeds *via* a 1,6-electrocyclic path and provides a convenient access to an important class of nitrogen heterocycles. Subsequent treatment of the mesityl derivative with chloromethyl pivalate and silver triflate led to the corresponding benzimidazolium salt.

Keywords: electrocyclic reactions; ligand design; nitrogen heterocycles; oxidation; sigmatropic rearrangement

Introduction

Stable N-heterocyclic carbenes (NHCs) have become ubiquitous ligands in organometallic chemistry and in homogeneous catalysis.[1] They have already afforded an impressive range of transition metal complexes that have found countless applications in organic synthesis and in polymer chemistry.[2] They have also acquired a place on their own as reagents and organocatalysts, since they behave as powerful nucleophiles.[3] Currently, the NHCs most commonly encountered are based on the imidazole ring system.[4] They are usually obtained by deprotonation of either imidazolium (**A**) or imidazolinium salts (**C**) with a strong base (Figure 1).[5] Various experimental and theoretical studies have shown that subtle differences between "unsaturated" and "saturated" NHCs could significantly affect their catalytic properties.[6]

Fused polycyclic NHCs, including benzimidazolylidene species derived from "aromatic" benzimidazolium salts (**B**), offer further options to fine-tune the steric and electronic properties of carbene ligands.[8] However, their synthesis is often challenging. Indeed, several research groups have reported failures to isolate benzimidazolium salts bearing bulky aromatic substituents on their nitrogen atoms.[9] This is most unfortunate because large aryl groups, such as the mesityl (2,4,6-trimethylphenyl) or 2,6-diisopropylphenyl groups, usually provide the right balance of steric protection and electronic donation to many NHC-based catalytic systems, while avoiding unwanted *ortho*-metalation side-reactions.[10]

To the best of our knowledge, the only efficient strategy developed so far for installing mesityl substituents onto polyannulated NHCs involved the condensation of *N,N′*-dimesitylformamidine with halogenated quinones to afford quinoimidazolium salts.[11]

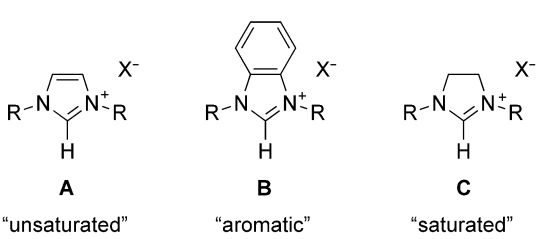


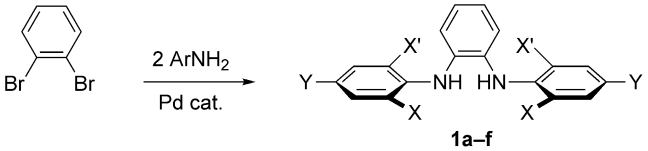
Figure 1. Structure of various azolium salts used as NHC precursors.[7]

In this article, we disclose our endeavors to isolate the up-to-now elusive 1,3-dimesitylbenzimidazolium tetrafluoroborate (**2a**) and we show that its synthesis proceeds *via* the unexpected formation of dihydrophenazines.

Results and Discussion

To begin with, we decided to reinvestigate the classical amination/cyclization path most commonly adopted to prepare 1,3-diarylbenzimidazolium salts.[12] Thus, a range of aniline derivatives substituted in *ortho* and *para* positions were coupled with 1,2-dibromobenzene in a palladium-catalyzed Buchwald–Hartwig amination reaction (Scheme 1).[13] We then tried to condense *N,N′*-bismesityl-1,2-benzenediamine (**1a**) into benzimidazolium salt **2a** using triethyl orthoformate and tetrafluoroboric acid in a microwave reactor (Scheme 2, path I). Previous work from our laboratory had shown that recourse to microwave irradiation usually provides a fast and efficient access to cyclic amidinium salts.[14] In this particular case, however, model substrate **1a** was recovered unchanged even when rather drastic conditions were applied (4 h at 200 °C).

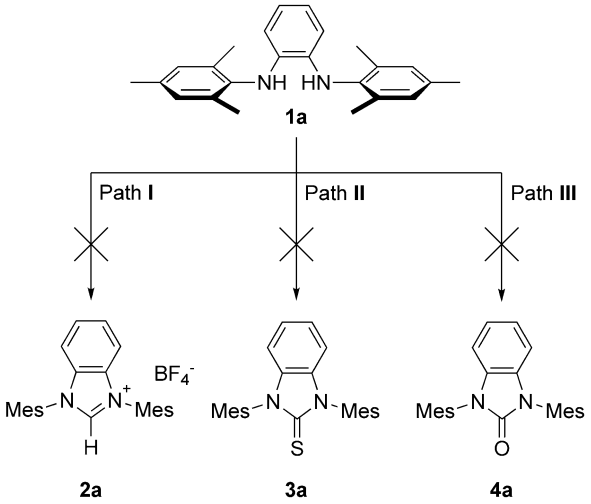
Recourse to stronger electrophilic reagents was also explored to promote the cyclization of starting material **1a** into suitable NHC precursors. A first set of experiments inspired by related work on *N,N′*-dialkylbenzimidazol-2-ylidenes was conducted with thiophosgene (Scheme 2, path II).[15] Despite several attempts to tinker with the reaction conditions by changing the nature of the base (Et_3N or Na_2CO_3) and the temperature (room temperature or 70 °C), the expected thione **3a** could not be isolated. Alternatively, we also tried to perform a cyclization of substrate **1a** with triphosgene in the presence of Na_2CO_3 in THF at 70 °C (Scheme 2, path III).[16] Once again, the desired product **4a** was not obtained.



	X	X'	Y	Yield
1a	Me	Me	Me	81%
1b	Me	Me	H	71%
1c	Me	Me	Cl	63%

	X	X'	Y	Yield
1d	Me	Cl	Me	38%
1e	*t*-Bu	H	H	83%
1f	*i*-Pr	*i*-Pr	H	60%

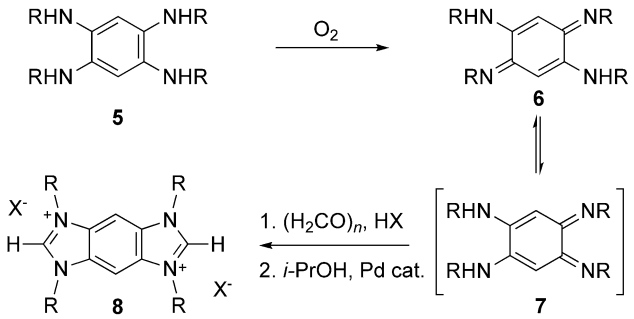
Scheme 1. Synthesis of *N,N′*-diaryl-1,2-benzenediamines **1a–f** *via* Buchwald–Hartwig amination. *Reaction conditions:* $Pd(OAc)_2$ (4 mol%), P(*t*-Bu)$_3$ (12 mol%), NaO-*t*-Bu, $PhCH_3$, 110 °C, overnight.



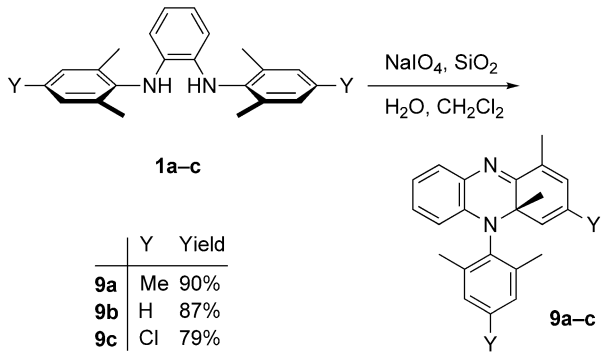
Scheme 2. Failed attempts to cyclize diamine **1a** into NHC precursors **2a**–**4a**. *Reaction conditions:* $HC(OEt)_3$, HBF_4, 200 °C (μW), 4 h (path I); $S{=}CCl_2$, THF, room temperature, 4 h (path II); $O{=}C(OCCl_3)_2$, Na_2CO_3, THF, 70 °C, 24 h (path III).

At this stage, we turned our attention to the cyclization of diimine precursors into imidazolium salts using a combination of chloromethyl pivalate and silver triflate. Since it was first reported by Glorius et al. in 2002,[17] this method has been widely used for the synthesis of strained and sterically encumbered imidazolium salts.[18] Because its application to the synthesis of **2a** would require the preliminary conversion of diamine **1a** into the corresponding 3,5-cyclohexadiene-1,2-diimine, we searched for a suitable oxidizing agent to perform this additional reaction. Reports from the literature dealing with the oxidation of *ortho*-phenylenediamines are scarce,[19] but we felt encouraged by related work from the groups of Harlan[20] and Bielawski[21] who showed that 1,2,4,5-tetraaminobenzene derivatives **5** had a high propensity to oxidize into the corresponding 2,5-diamino-1,4-benzoquinonediimines **6** under aerobic conditions (Scheme 3). An equilibrium between these azophenazines and their *ortho*-quinoid tautomers **7** was then postulated to expose the vicinal diamino and diimino fragments that ultimately led to the benzobis(imidazolium) salts **8** in a one-pot cyclization/oxidation reaction sequence.[21]

Attempts to oxidize diamine **1a** under aerobic conditions showed that the reaction was very sluggish, most likely because this substrate is not as electron-rich as the analogous tetraamine derivative **5**. Thus, we decided to use a stronger oxidizing agent. Sodium periodate on wet silica gel was chosen, because it is an efficient, easy to handle reagent for the oxidation of hydroquinones into quinones.[22] Indeed, a complete conversion of substrate **1a** occurred within 24 h using a heterogeneous system based on $NaIO_4/SiO_2$ and



Scheme 3. Synthesis of benzobis(imidazolium) salts *via* an oxidation/cyclization route.



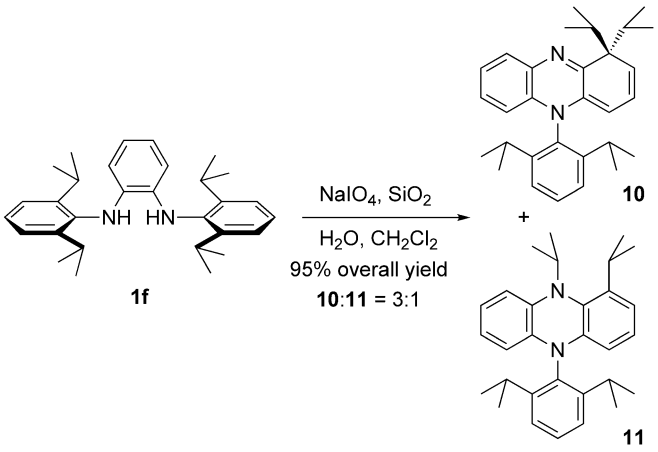
	Y	Yield
9a	Me	90%
9b	H	87%
9c	Cl	79%

Scheme 4. Synthesis of dihydrophenazines **9a–c**.

a single product was isolated in 90% yield after chromatographic purification (Scheme 4). NMR analysis of this compound revealed, however, that it possessed a much more unsymmetrical structure than expected. Indeed, there were no less than 24 different carbon atoms and 14 peaks for hydrogen atoms visible on ^{13}C and ^{1}H NMR spectra, respectively. Recourse to DEPT, HMBC, and HSQC sequences helped us assign these various signals to racemic dihydrophenazine **9a**, whose structure was unambiguously confirmed by X-ray diffraction analysis (Figure 2).[23]

To probe the generality of this new oxidative cyclization path, we carried out additional reactions starting from diamines **1b–f** instead of the mesityl derivative **1a**. These experiments showed that the presence of methyl groups on both *ortho* positions of the remote aryl substituents was mandatory to achieve the clean formation of a single product. Indeed, dihydrophenazines **9b** and **9c** were isolated in high yields when substrates **1b** or **1c** were treated with the periodate reagent (Scheme 4 and Figure 2).[23] Structural variations on the *para*-position of the 2,6-dimethylphenyl ring (**1a**: Me, **1b**: H, **1c**: Cl) did not seem to have any significant influence on the outcome of the reaction. Besides, the spectral properties and molecular structures of compounds **9a–c** were very similar (see the Supporting Information for details). Conversely, substrates **1d** and **1e** that were obtained from 2-chloro-4,6-dimethylaniline and 2-*tert*-butylaniline, respectively, afforded only complex mixtures of unidentified products.

We also examined the reactivity of diamine **1f** bearing 2,6-diisopropylphenyl substituents on its nitrogen atoms. In this case, the reaction with $NaIO_4/SiO_2$ took



Scheme 5. Synthesis of dihydrophenazines **10** and **11**.

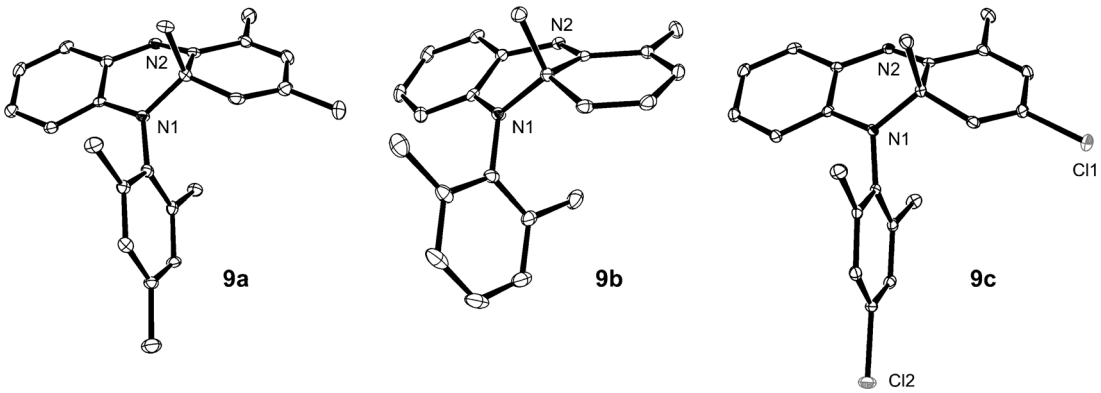


Figure 2. Molecular structures of dihydrophenazines **9a–c** in the solid state (hydrogen atoms were omitted for clarity).

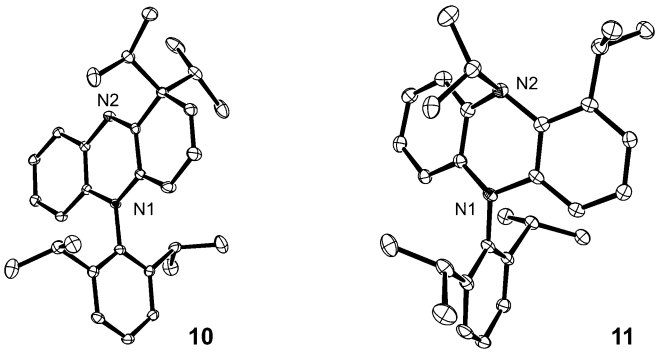
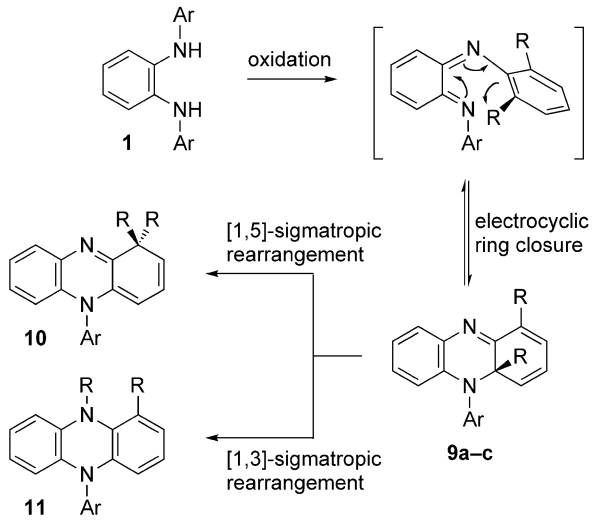


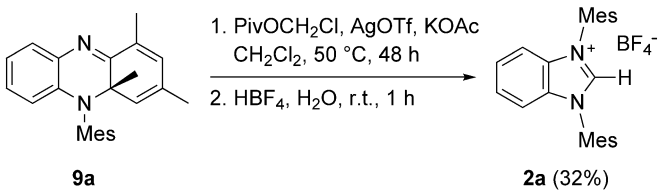
Figure 3. Molecular structures of dihydrophenazines **10** and **11** in the solid state (hydrogen atoms were omitted for clarity).[24]

a different course and afforded a mixture of 1,5-dihydrophenazine **10** and its 5,10-isomer **11** in a 3:1 molar ratio (Scheme 5). The structures of these two products were established by ^{1}H and ^{13}C NMR spectroscopy and further confirmed by X-ray diffraction analysis (Figure 3).[23,24]

The formation of 4a,5-dihydrophenazines **9a–c** probably begins with the oxidation of the *N,N′*-diarylbenzene-1,2-diamines **1a–c** into the corresponding diimines. However, these intermediates were not detected in the reaction media. We tentatively propose that they further react *via* a 6 e^- electrocyclic process involving the diimine moiety and a neighboring aryl substituent to afford ring closure (Scheme 6). Although the nitrogen atom bearing the remaining aryl group featured an almost planar geometry indicative of a substantial sp^2 character, an anticlinal conformation between the 5-aryl group and the angular 4a-methyl substituent was clearly visible in the X-ray crystal structures of compounds **9a–c** (cf. Figure 2, see



Scheme 6. Possible mechanism for the formation of dihydrophenazines **9a–c**, **10** and **11**.



Scheme 7. Synthesis of benzimidazolium salt **2a**.

also Table S2 in the Supporting Information). This stereochemistry is in good agreement with the disrotatory cyclization path expected for a thermal π^6s electrocyclic process.[25] When the diamine **1f** served as starting material, an additional sigmatropic rearrangement may be invoked to explain the migration of the angular isopropyl group onto its final position in products **10** and **11**. This would release the steric pressure exerted by the bulky 2,6-diisopropylphenyl substituent located on the proximal 5-N heterocyclic position. The formation of the major 1,5-dihydrophenazine **10** may be explained by a [1,5]-shift, whereas the minor 5,10-isomer **11** would result from a thermally less favored [1,3]-migration of the alkyl substituent.

Last but not least, we were very pleased to find that dihydrophenazine **9a** reacted with chloromethyl pivalate and silver triflate as initially planned to afford the desired 1,3-dimesitylbenzimidazolium salt **2a** in 32% isolated yield (Scheme 7). This result is in accordance with the reversible nature of an electrocyclic process and is reminiscent of the equilibrium postulated by Bielawski between structures **6** and **7**, although the latter one was never observed.[21] It should be pointed out that the modest yield obtained for product **2a** is due in part to its tedious purification from tarry ionomer by-products.[10c,26]

Conclusion and Perspectives

Altogether, the synthetic path that we have devised paves the way to benzimidazol-2-ylidene species bearing bulky aromatic substituents on their nitrogen atoms, and we are currently investigating the ligand properties of these new NHCs. This study also opens new vistas in the chemistry of dihydrophenazines. The recognition that pericyclic reactions occur readily on these planar, highly conjugated nitrogen heterocycles could ease the access to this important family of biologically active compounds.[27] Furthermore, the presence of a quaternary chiral center in products **9a–c** is an attractive feature for future developments in asymmetric organic synthesis.

Experimental Section

General Information

Toluene was distilled from sodium under N_2. Aniline derivatives were stirred over KOH and distilled under vacuum prior to use. *N,N′*-Diaryl-1,2-benzenediamines **1a–f** were synthesized according to literature procedures.[20] Palladium(II) acetate, tri-*tert*-butylphosphine (1 M solution in toluene), 1,2-dibromobenzene, sodium *tert*-butoxide, sodium periodate, silver(I) triflate, chloromethyl pivalate, potassium acetate and tetrafluoroboric acid (48% solution in water) were purchased from Aldrich and used as received. Petroleum ether refers to the hydrocarbon fraction of bp 40–60 °C and was purchased from Labotec. Column chromatography was performed on silica gel 60 (60 Å nominal pore diameter, 0.063–0.200 mm particle size) supplied by Biosolve. Preparative TLC was performed on PLC aluminum oxide 60 F_{254} glass plates (20×20 cm, 1.5 mm thickness) supplied by Merck. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX 400 or a Bruker Avance 250 spectrometer at 298 K unless otherwise specified. Chemical shifts are listed in parts per million downfield from TMS and are referenced from the solvent peaks or TMS. IR spectra were recorded with a Perkin–Elmer Spectrum One FT-IR spectrometer. Mass spectral analyses were performed on a Bruker Daltonics microTOF-Q spectrometer at the Plateforme d'Analyses Chimiques et de Synthèse Moléculaire of the University of Bourgogne.

Typical Procedure for the Oxidation of Benzene-1,2-diamines into Dihydrophenazines

A 0.65 M aqueous solution of $NaIO_4$ (8.70 mL, 5.65 mmol) was added dropwise to a vigorously stirred suspension of chromatographic grade silica gel (8.70 g) in CH_2Cl_2 (70 mL), whereupon a flaky suspension was obtained. A solution of **1a** (1.50 g, 4.35 mmol) in CH_2Cl_2 (15 mL) was then added slowly. The reaction mixture was vigorously stirred at room temperature until ^{1}H NMR showed a complete disappearance of the starting diamine (*ca.* 24 h). The dark suspension was filtered with suction and the filtrate was evaporated. The residue was purified by column chromatography on silica gel with CH_2Cl_2 as eluent. The eluate was dried on Na_2SO_4 and evaporated under vacuum to afford dihydrophenazine **9a** as a bright yellow solid; yield: 1.40 g (90%); (see the Supporting Information for characterization details).

Synthesis of *N,N′*-Bis(2,4,6-trimethylphenyl)benzimidazolium Tetrafluoroborate (2a)

Chloromethyl pivalate (0.29 mL, 1.35 equiv.) was added to a suspension of silver triflate (506.4 mg, 1.35 equiv.) in CH_2Cl_2 (10 mL) under argon. The resulting suspension was stirred for 45 min at room temperature. The supernatant solution was then transferred with a syringe onto a suspension of dihydrophenazine **9a** (500 mg, 1 equiv.) and potassium acetate (157.6 mg, 1.1 equiv.) in CH_2Cl_2 (10 mL). The resulting suspension was stirred for 48 h at 50 °C under an inert atmosphere in the dark. Next, a further 0.5 equiv. of the pivalate/silver salt solution were added at room temperature and the resulting suspension was further stirred for 24 h at 50 °C under an inert atmosphere in the dark. After cooling to room temperature, the reaction mixture was quenched with methanol and the solvents were evaporated under vacuum. The resulting black oil was purified by preparative TLC on alumina using H_2O/MeOH (6/4 v/v) as eluents. The product (R_f = 0.4) was desorbed with methanol to afford a light-yellow oil, which was taken up with water (10 mL) and diethyl ether (2 mL). 48% Aqueous HBF_4 (0.5 mL) was added and the biphasic mixture was stirred for 1 h at room temperature. Upon evaporation of diethyl ether, a light-yellow precipitate was obtained. It was filtered and water was removed by azeotropic distillation with benzene. The precipitate was further dried for one night under high vacuum to afford the title compound as a light-yellow solid; yield: 205 mg (32%); mp 231 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3116 (m), 3053 (m), 2912 (m), 1811 (w), 1613 (m), 1542 (m), 1484 (m), 1467 (m), 1384 (w), 1319 (w), 1288 (w), 1225 (m), 1060 (s), 909 (w), 861 (m), 758 cm^{-1} (m); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.59 (s, 1H, Im C2), 7.68 (dd, J = 6.3 and 3.1 Hz, 2H), 7.33 (dd, J = 6.3 and 3.1 Hz, 2H), 7.06 (s, 4H, Mes *m*-CH), 2.33 (s, 6H, Mes *p*-CH_3), 1.98 (s, 12H, Mes *o*-CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 142.8, 141.6, 134.8, 131.4, 130.0, 128.8, 127.6, 113.4, 21.0, 17.0; HR-MS (ESI): m/z = 355.21653, calcd. for $C_{25}H_{27}N_2$: 355.21688 [$(M-BF_4)^+$].

References

[1] For monographs, see: a) *Carbene Chemistry: From Fleeting Intermediates to Powerful Reagents*, (Ed.: G. Bertrand), Marcel Dekker, New York, **2002**; b) *N-Heterocyclic Carbenes in Synthesis*, (Ed.: S. P. Nolan), Wiley-VCH, Weinheim, **2006**; c) *N-Heterocyclic Carbenes in Transition Metal Catalysis,* (Ed.: F. Glorius), in: *Topics in Organometallic Chemistry*, Vol. 21, Springer, Berlin, **2007**; d) *N-Heterocyclic Carbenes: From Laboratory Curiosities to Efficient Synthetic Tools*, (Ed.: S. Díez-González), RSC Catalysis Series, Vol. 6, Royal Society of Chemistry, Cambridge, **2010**; e) *N-Heterocyclic Carbenes in Transition Metal Catalysis and Organocatalysis,* (Ed.: C. S. J. Cazin), in: *Catalysis by Metal Complexes*, Vol. 32, Springer, Dordrecht, **2011**.

[2] For selected, recent reviews, see: a) N. Marion, S. P. Nolan, *Chem. Soc. Rev.* **2008**, *37*, 1776–1782; b) F. E. Hahn, M. C. Jahnke, *Angew. Chem.* **2008**, *120*, 3166–3216; *Angew. Chem. Int. Ed.* **2008**, *47*, 3122–3172; c) J. C. Y. Lin, R. T. W. Huang, C. S. Lee, A. Bhattacharyya, W. S. Hwang, I. J. B. Lin, *Chem. Rev.* **2009**, *109*, 3561–3598; d) S. Díez-González, N. Marion, S. P. Nolan, *Chem. Rev.* **2009**, *109*, 3612–3676; e) M. Poyatos, J. A. Mata, E. Peris, *Chem. Rev.* **2009**, *109*, 3677–3707; f) C. Samojłowicz, M. Bieniek, K. Grela, *Chem. Rev.* **2009**, *109*, 3708–3742; g) G. C. Vougioukalakis, R. H. Grubbs, *Chem. Rev.* **2010**, *110*, 1746–1787.

[3] a) V. César, S. Bellemin-Laponnaz, L. H. Gade, *Chem. Soc. Rev.* **2004**, *33*, 619–636; b) D. Enders, O. Niemeier, A. Henseler, *Chem. Rev.* **2007**, *107*, 5606–5655; c) N. Marion, S. Díez-González, S. P. Nolan, *Angew. Chem.* **2007**, *119*, 3046–3058; *Angew. Chem. Int. Ed.* **2007**, *46*, 2988–3000; d) V. Nair, S. Vellalath, B. P. Babu, *Chem. Soc. Rev.* **2008**, *37*, 2691–2698; e) J. Moore, T. Rovis, in: *Asymmetric Organocatalysis*, in: *Topics in Current*

Chemistry, Vol. 291, (Ed.: B. List), Springer, Berlin, **2009**, pp 77–144; f) A. T. Biju, N. Kuhl, F. Glorius, *Acc. Chem. Res.* **2011**, *44*, 1182–1195; g) V. Nair, R. S. Menon, A. T. Biju, C. R. Sinu, R. R. Paul, A. Jose, V. Sreekumar, *Chem. Soc. Rev.* **2011**, *40*, 5336–5346.

[4] a) A. J. Arduengo III, *Acc. Chem. Res.* **1999**, *32*, 913–921; b) D. Bourrisou, O. Guerret, F. P. Gabbaï, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39–91; c) P. de Frémont, N. Marion, S. P. Nolan, *Coord. Chem. Rev.* **2009**, *253*, 862–892; d) T. Dröge, F. Glorius, *Angew. Chem.* **2010**, *122*, 7094–7107; *Angew. Chem. Int. Ed.* **2010**, *49*, 6940–6952.

[5] L. Benhamou, E. Chardon, G. Lavigne, S. Bellemin-Laponnaz, V. César, *Chem. Rev.* **2011**, *111*, 2705–2733.

[6] a) A. C. Hillier, W. J. Sommer, B. S. Yong, J. L. Petersen, L. Cavallo, S. P. Nolan, *Organometallics* **2003**, *22*, 4322–4326; b) M. Süßner, H. Plenio, *Chem. Commun.* **2005**, 5417–5419; c) R. L. Lord, H. Wang, M. Vieweger, M.-H. Baik, *J. Organomet. Chem.* **2006**, *691*, 5505–5512; d) S. Díez-González, S. P. Nolan, *Coord. Chem. Rev.* **2007**, *251*, 874–883; e) M. Bieniek, A. Michrowska, D. L. Usanov, K. Grela, *Chem. Eur. J.* **2008**, *14*, 806–818.

[7] The terms "unsaturated", "aromatic", and "saturated" used to describe imidazolium, benzimidazolium, and imidazolinium salts, respectively, were originally proposed by Cavallo et al., see: A. Poater, B. Cosenza, A. Correa, S. Giudice, F. Ragone, V. Scarano, L. Cavallo, *Eur. J. Inorg. Chem.* **2009**, 1759–1766.

[8] A. J. Arduengo III, L. I. Iconaru, *Dalton Trans.* **2009**, 6903–6914.

[9] a) C. J. O'Brien, E. A. B. Kantchev, G. A. Chass, N. Hadei, A. C. Hopkinson, M. G. Organ, D. H. Setiadi, T.-H. Tang, D.-C. Fang, *Tetrahedron* **2005**, *61*, 9723–9735; b) D. M. Khramov, A. J. Boydston, C. W. Bielawski, *Org. Lett.* **2006**, *8*, 1831–1834; c) D. M. Khramov, E. L. Rosen, V. M. Lynch, C. W. Bielawski, *Angew. Chem.* **2008**, *120*, 2299–2302; *Angew. Chem. Int. Ed.* **2008**, *47*, 2267–2270; d) J. A. V. Er, A. G. Tennyson, J. W. Kamplain, V. M. Lynch, C. W. Bielawski, *Eur. J. Inorg. Chem.* **2009**, 1729–1738.

[10] For a few examples, see: a) C. W. Bielawski, R. H. Grubbs, *Angew. Chem.* **2000**, *112*, 3025–3028; *Angew. Chem. Int. Ed.* **2000**, *39*, 2903–2906; b) A. Fürstner, L. Ackermann, B. Gabor, R. Goddard, C. W. Lehmann, R. Mynott, F. Stelzer, O. R. Thiel, *Chem. Eur. J.* **2001**, *7*, 3236–3253; c) L. Delaude, M. Szypa, A. Demonceau, A. F. Noels, *Adv. Synth. Catal.* **2002**, *344*, 749–756; d) G. A. Grasa, T. Güveli, R. Singh, S. P. Nolan, *J. Org. Chem.* **2003**, *68*, 2812–2819; e) N. Ledoux, B. Allaert, F. Verpoort, *Eur. J. Org. Chem.* **2007**, 5578–5583; f) H. Clavier, C. A. Urbina-Blanco, S. P. Nolan, *Organometallics* **2009**, *28*, 2848–2854.

[11] a) M. D. Sanderson, J. W. Kamplain, C. W. Bielawski, *J. Am. Chem. Soc.* **2006**, *128*, 16514–16515; b) A. G. Tennyson, R. J. Ono, T. W. Hudnall, D. M. Khramov, J. A. V. Er, J. W. Kamplain, V. M. Lynch, J. L. Sessler, C. W. Bielawski, *Chem. Eur. J.* **2010**, *16*, 304–315.

[12] a) F. M. Rivas, U. Riaz, A. Giessert, J. A. Smulik, S. T. Diver, *Org. Lett.* **2001**, *3*, 2673–2676; b) N. Hadei, E. A. B. Kantchev, C. J. O'Brien, M. G. Organ, *Org. Lett.* **2005**, *7*, 1991–1994; c) A. R. Chianese, A. Mo, D. Datta, *Organometallics* **2009**, *28*, 465–472; d) A. R. Chianese, P. T. Bremer, C. Wong, R. J. Reynes, *Organometallics* **2009**, *28*, 5244–5252.

[13] a) J. P. Wolfe, S. Wagaw, S. L. Buchwald, *J. Am. Chem. Soc.* **1996**, *118*, 7215–7216; b) M. S. Driver, J. F. Hartwig, *J. Am. Chem. Soc.* **1996**, *118*, 7217–7218; c) J. P. Wolfe, S. Wagaw, J.-F. Marcoux, S. L. Buchwald, *Acc. Chem. Res.* **1998**, *31*, 805–818; d) J. F. Hartwig, *Angew. Chem.* **1998**, *110*, 2154–2177; *Angew. Chem. Int. Ed.* **1998**, *37*, 2046–2067; e) B. H. Yang, S. L. Buchwald, *J. Organomet. Chem.* **1999**, *576*, 125–146.

[14] a) A. Aidouni, A. Demonceau, L. Delaude, *Synlett* **2006**, 493–495; b) A. Aidouni, S. Bendahou, A. Demonceau, L. Delaude, *J. Comb. Chem.* **2008**, *10*, 886–892; c) M. Hans, L. Delaude, *Org. Synth.* **2010**, *87*, 77–87.

[15] F. E. Hahn, L. Wittenbecher, R. Boese, D. Bläser, *Chem. Eur. J.* **1999**, *5*, 1931–1935.

[16] R. T. Lum, M. Cheng, C. P. Cristobal, I. D. Goldfine, J. L. Evans, J. G. Keck, R. W. Macsata, V. P. Manchem, Y. Matsumoto, S. J. Park, S. S. Rao, L. Robinson, S. Shi, W. R. Spevak, S. R. Schow, *J. Med. Chem.* **2008**, *51*, 6173–6187.

[17] F. Glorius, G. Altenhoff, R. Goddard, C. Lehmann, *Chem. Commun.* **2002**, 2704–2705.

[18] a) G. Altenhoff, R. Goddard, C. W. Lehmann, F. Glorius, *Angew. Chem.* **2003**, *115*, 3818–3821; *Angew. Chem. Int. Ed.* **2003**, *42*, 3690–3693; b) G. Altenhoff, R. Goddard, C. W. Lehmann, F. Glorius, *J. Am. Chem. Soc.* **2004**, *126*, 15195–15201; c) S. Saravanakumar, M. K. Kindermann, J. Heinicke, M. Knöckerling, *Chem. Commun.* **2006**, 640–642; d) A. P. Dove, H. Li, R. C. Pratt, B. G. G. Lohmeijer, D. A. Culkin, R. M. Waymouth, J. L. Hedrick, *Chem. Commun.* **2006**, 2881–2883; e) J.-M. Suisse, L. Douce, S. Bellemin-Laponnaz, A. Maisse-François, R. Welter, Y. Miyake, Y. Shimizu, *Eur. J. Inorg. Chem.* **2007**, *2007*, 3899–3905; f) E. P. Kündig, T. M. Seidel, Y.-X. Jia, G. Bernardinelli, *Angew. Chem.* **2007**, *119*, 8636–8639; *Angew. Chem. Int. Ed.* **2007**, *46*, 8484–8487; g) S. Würtz, C. Lohre, R. Fröhlich, K. Bergander, F. Glorius, *J. Am. Chem. Soc.* **2009**, *131*, 8344–8345.

[19] a) A. Nicolaides, T. Nakayama, K. Yamazaki, H. Tomioka, S. Koseki, L. L. Stracener, R. J. McMahon, *J. Am. Chem. Soc.* **1999**, *121*, 10563–10572; b) K. Ujike, N. Akai, S. Kudoh, M. Nakata, *J. Mol. Struct.* **2005**, *735–736*, 335–342; c) V. N. Telvekar, B. S. Takale, *Tetrahedron Lett.* **2010**, *51*, 3940–3943.

[20] T. Wenderski, K. M. Light, D. Ogrin, S. G. Bott, C. J. Harlan, *Tetrahedron Lett.* **2004**, *45*, 6851–6853.

[21] A. J. Boydston, D. M. Khramov, C. W. Bielawski, *Tetrahedron Lett.* **2006**, *47*, 5123–5125.

[22] M. Daumas, Y. Vo-Quang, L. Vo-Quang, F. Le Goffic, *Synthesis* **1989**, 64–65.

[23] CCDC 848965 (**9a**), CCDC 848966 (**9b**), CCDC 848967 (**9c**), CCDC 848968 (**10**), and CCDC 848969 (**11**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

[24] Compound **11** crystallized with two molecules in the asymmetric unit. For the sake of clarity, only one of them is depicted in Figure 3.
[25] a) V. A. Bakulev, *Russ. Chem. Rev.* **1995**, *64*, 99–124; b) I. Fleming, *Pericyclic Reactions*, Oxford University Press, Oxford, **1999**; c) S. Sankararaman, *Pericyclic Reactions: A Textbook*, Wiley-VCH, Weinheim, **2005**; d) I. Fleming, *Molecular Orbitals and Organic Chemical Reactions*, Wiley, Chichester, **2009**.
[26] A. J. Arduengo III, R. Krafczyk, R. Schmutzler, H. A. Craig, J. R. Goerlich, W. J. Marshall, M. Unverzagt, *Tetrahedron* **1999**, *55*, 14523–14534.
[27] J. B. Laursen, J. Nielsen, *Chem. Rev.* **2004**, *104*, 1663–1686.

