

## Expanded-Ring and Backbone-Functionalised N-Heterocyclic Carbenes

Manuel Iglesias,<sup>[a]</sup> Dirk J. Beetstra,<sup>[a]</sup> Kingsley J. Cavell,<sup>\*,[a]</sup> Athanasia Dervisi,<sup>\*,[a]</sup>  
 Ian A. Fallis,<sup>\*,[a]</sup> Benson Kariuki,<sup>[a]</sup> Ross W. Harrington,<sup>[b]</sup> William Clegg,<sup>[b]</sup>  
 Peter N. Horton,<sup>[c]</sup> Simon J. Coles,<sup>[c]</sup> and Michael B. Hursthouse<sup>[c]</sup>

**Keywords:** Carbene ligands / Cycloaddition / Rhodium / Ligand design / Isomers

An unsaturated seven-membered amidinium salt **7** decomposes in the presence of metal salts under basic conditions. However, **7** readily forms a Diels–Alder cycloadduct with CpH from which the Rh<sup>I</sup> complexes may be prepared. Thus,

structurally elaborate, sterically crowded carbene ligand complexes bearing peripheral unsaturated functionality are available in a short versatile synthesis.

### Introduction

N-Heterocyclic carbenes (NHCs) have established themselves as key ligands in organometallic chemistry and catalysis.<sup>[1]</sup> To date most work has focused on unsaturated, formally imidazolium-derived, five-membered-ring NHCs, but more recently other ring sizes have been explored, and the novel properties of these expanded-ring NHCs are currently attracting much interest.<sup>[2,3]</sup> We have recently developed a mild, efficient, functional-group-tolerant synthetic methodology, based on the method of Bertrand,<sup>[2d]</sup> which allows the synthesis of a range of structurally elaborate carbene precursors.<sup>[4]</sup> These studies highlighted large N–C–N angles for these ligands, which has the effect of pushing the N–R substituents towards the metal center, thus providing steric protection not offered by smaller-ring NHCs.<sup>[3–5]</sup> This increase in steric congestion appears to lead to enhanced performance in selected NHC-complex-catalysed reactions.<sup>[6]</sup> In this paper we examine methods of manipulating the ligand environment in NHC carbene precursors by electrophilic or Diels–Alder additions to olefinic seven-membered amidinium salts.

### Results and Discussion

To examine the possibility of incorporating further functionality into large-ring systems, we have prepared the unsaturated seven-membered-ring NHC precursors **6** and **7**

via the chloride salts **2** and **3** (Scheme 1) by the reaction of the parent amidines<sup>[4,5]</sup> **1** and (*E*)-1,4-dichlorobut-2-ene under mild conditions (see Experimental Section). Reaction temperatures below 60 °C resulted in essentially exclusive formation of seven-membered dihydrodiazepinium derivatives in moderate to good yields. Higher dilutions failed to improve the yield of this reaction, whilst increased temperatures (up to 100 °C in sealed tubes) resulted in 1:1 mixtures of the desired seven-membered products **2** or **3**, and the vinyl-substituted five-membered products **4** or **5**, presumably via competing S<sub>N</sub>2 and S<sub>N</sub>2' mechanisms.

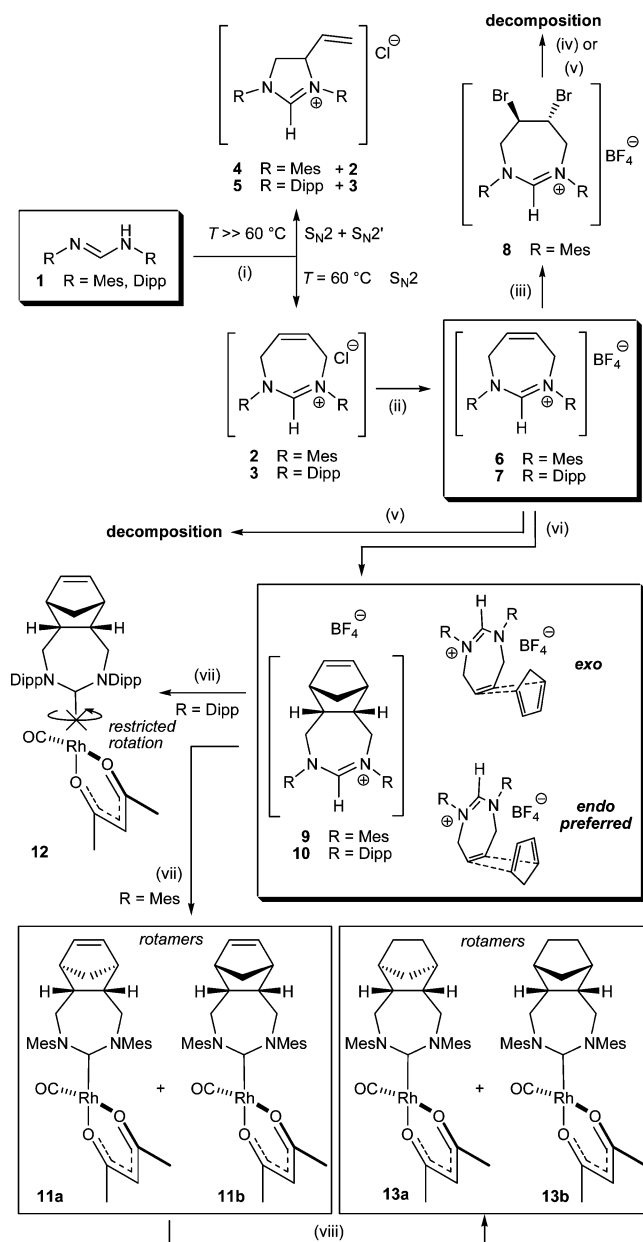
The unsaturated chloride salt **2** was structurally characterised, and the structure of the cation is shown in Figure 1(a). The unsaturated C3–C4 bond brings about an additional rigidity in the NHC ring, which results in a decrease of the C<sub>ring</sub>–N···N–C<sub>ring</sub> torsion angle and displaces the alkene carbon atoms C3 and C4 away from the NC(H)–N plane. The NC(H)N angle is similar to that of the “parent” saturated seven-membered salt (127.4°). The olefinic backbone of salts **2**, **3**, **6** and **7** offers potential for the further manipulation of the carbene ligand framework. The reactions reported here, which probe the reactivity of the alkene backbone, represent just a sample of those under study within our group. For example, electrophilic halogenation of the alkene backbone of the amidinium salt **6** in dichloromethane solution was achieved by the addition of bromine at ambient temperature to afford the amidinium dibromide **8**. Attempts to dehydrohalogenate **8** by the elimination of 2 equiv. of HBr resulted only in decomposition. This is not unexpected, as the fully unsaturated product of this reaction would be expected to be an anti-Hückel 8- $\pi$  electron system. The structure of one of the isomers of the racemate is depicted in Figure 1(b). The antiperiplanar disposition of the bromine atoms, with a Br–C–C–Br torsion angle of 178.3°, forces **8** into a twisted-chair conformation, with axial bromine atoms, resulting in a substantial increase

[a] School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff, CF10 3AT, UK  
 Fax: +44-29-20874030  
 E-mail: fallis@cardiff.ac.uk

[b] School of Chemistry, Newcastle University, Newcastle upon Tyne, UK NE1 7RU

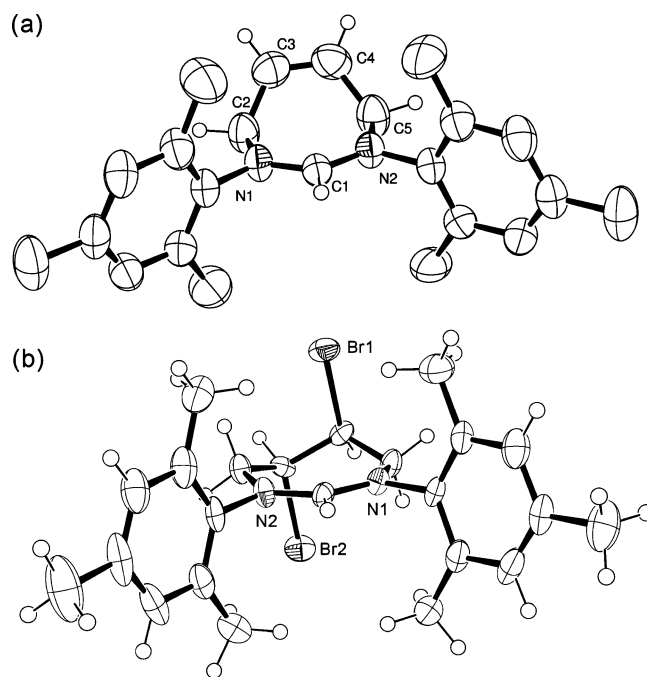
[c] University of Southampton, Highfield, Southampton, SO17 1BJ, UK

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/ejic.200901182>.



of the N–C(H)–N angle to 131.0(3)° over that of **6**. Characteristically, no (carbene)metal complexes derived from **2**, **3**, **6**, **7** and **8** could be prepared. Reaction of these amidinium salts with a range of bases and metal precursors resulted only in decomposition of the amidinium salts. These observations are in agreement with those reported by Nechaev et al.,<sup>[7a]</sup> who suggested that the decomposition of similar seven-membered materials occurred by a 1,4-Hoffman elimination to form neutral acyclic amidines. In an earlier account of 1,3-bis(1-pyrrolidino)imidazolin-2-ylidenes, Alcar-

azo et al.<sup>[7b]</sup> has also indicated that a 1,2-elimination pathway was possible in five-membered systems. Hence further ligand modifications could only be achieved by manipulations of the amidine salts themselves.



**Figure 1.** (a) Displacement ellipsoid (30%) plots of the amidinium cation of the chloride salt **2**; selected bond lengths [Å] and angles [°]: N1–C1 1.318(3), C1–N2 1.319(3), N1–C2 1.482(3), N2–C5 1.485(3), C2–C3 1.486(4), C4–C5 1.486(4), C3–C4 1.328(4); N1–C1–N2 127.4(2), C1–N2–C15 117.49(19), C1–N1–C6 117.41(19); C2–N1...N2–C5 1.3. (b) Displacement ellipsoid (30%) plots of the amidinium salt **8**; selected bond lengths [Å] and angles [°]: N1–C1 1.317(5), C1–N2 1.304(5), N1–C2 1.475(5), N2–C5 1.457(5), C3–Br1 1.964(6), C4–Br2 1.980(6); N1–C1–N2 133.7(4), C1–N2–C15 114.1(4), C1–N1–C6 113.0(3); C2–N1...N2–C5 8.7.

As a means of further functionalizing the system we reasoned that the salts **6** and **7**, as electron-deficient (i.e. cationic) alkenes, should readily undergo Diels–Alder additions with suitable dienes.

Thus, for example, reaction of methanol solutions of **6** or **7** with an excess of cyclopentadiene in a sealed tube at 60 °C afforded the Diels–Alder cycloaddition products **9** and **10**, respectively, as the *endo* products in high yields. <sup>1</sup>H NMR spectroscopy confirmed the formation of only one of the two possible isomers (*endo* or *exo*), and X-ray data (Figure 2) confirmed the formation of the *endo* isomers for both salts **9** and **10**. The *cis* substitution on the backbone in **9** and **10** does not significantly change the geometry of the salt, which is in contrast to our previously reported seven-membered *trans*-substituted 5,6-dioxolane salt.<sup>[3]</sup> The N–C–N angles obtained for **9** (128.2°) and **10** (127.7°) are comparable to that of **2** (127.4°).

The Rh<sup>I</sup> complexes, **11** and **12**, were prepared in good yields by in situ reaction of the amidinium salts **9** and **10**, respectively, with KN(SiMe<sub>3</sub>)<sub>2</sub> in the presence of the metal precursor [Rh(acac)(CO)<sub>2</sub>]. Compound **11** was isolated as a 50:50 mixture of rotamers (**11a**/**11b**) (Scheme 1), as defined

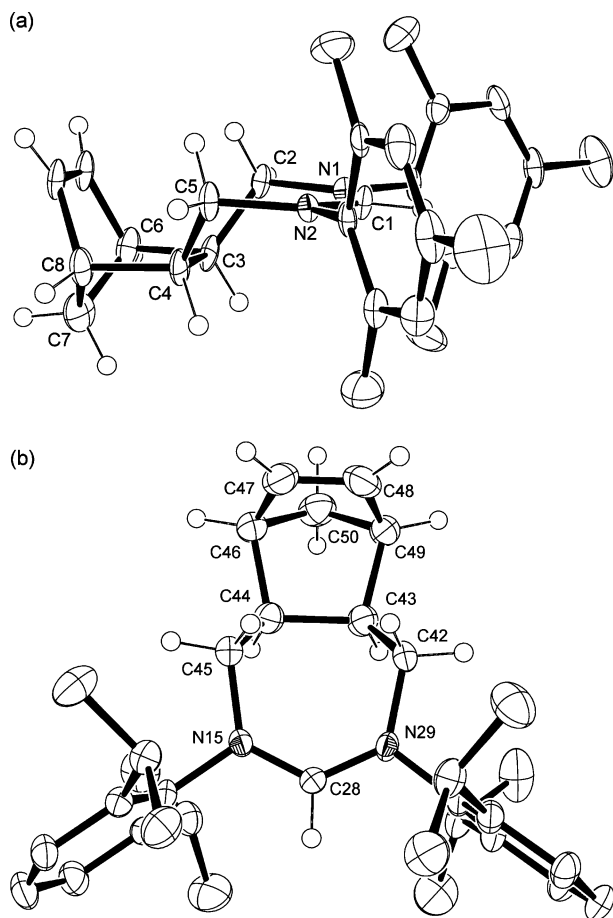


Figure 2. Displacement ellipsoid plots (30%) of the amidinium salts **9** (a) and **10** (b). Selected bond lengths [Å] and angles [°] for **9**: C1–N1 1.287(15), C1–N2 1.358(14), C2–C3 1.489(14), C2–N1 1.519(11), C3–C4 1.582(12), C4–C5 1.485(15), C5–N2 1.519(11); N1–C1–N2 128.2(5), C3–C2–N1 110.4(10), C2–C3–C4 115.4(11), C6–C3–C4 102.6(8), C8–C4–C3 101.3(8); selected H atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°] for **10**: N29–C28 1.317(3), N15–C28 1.316(3), C43–C44 1.568(4), C47–C48 1.322(5); N15–C28–N29 127.7(2), C28–N29–C30 116.8(2), C16–N15–C28 117.8(2), C42–C43–C49 112.9(3), C45–C44–C46 112.7(3).

by the relative orientation of the carbene alkene; the  $^{13}\text{C}$  NMR spectrum shows two carbene resonances at  $\delta = 206.9$  ( $^1J_{\text{RhC}} = 53.6$  Hz) and  $206.7$  ( $^1J_{\text{RhC}} = 54.3$  Hz) ppm, and two carbonyl doublet resonances at  $\delta = 190.5$  ( $^1J_{\text{RhC}} = 49.5$  Hz) and  $189.6$  ( $^1J_{\text{RhC}} = 49.4$  Hz) ppm. In the  $^1\text{H}$  NMR spectrum two peaks of equal intensity are observed for the methine group of the acac ligand. Assuming that the carbene ligand is perpendicular to the coordination plane, in isomer **11a** the alkene would be pointing towards the acac ligand and in **11b** towards the carbonyl ligand. On heating, the  $^1\text{H}$  NMR spectrum no broadening of the acac CH peaks of **11** was observed, suggesting no interconversion between the two isomers at temperatures up to 353 K. However, in a spin saturation transfer experiment, the irradiation of the CH proton of the acac ligand in one isomer resulted in the expected disappearance of this peak and a 17% decrease in the intensity of the corresponding CH resonance in the other isomer, indicating slow interconversion

of the isomers. In contrast, for complex **12** the increased bulk of the Dipp groups results in the formation of only one of the two possible isomers in solution, as evidenced by a single resonance for the acac methine group at  $\delta = 5.18$  ppm in the  $^1\text{H}$  NMR spectrum, and two acac methyl resonances in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra. In addition, four signals are observed for the isopropyl methyl groups, indicating a static structure at room temperature, with no rotation about the Rh–NHC or N–Ar bonds observed. Figure 3(a) illustrates the structure of **11a**, the isomer in which the carbene double bond resides on the “acac side”; for **12** the sole “carbonyl side” isomer is shown [Figure 3(b)]. In both cases the carbene ring adopts a conformation, which

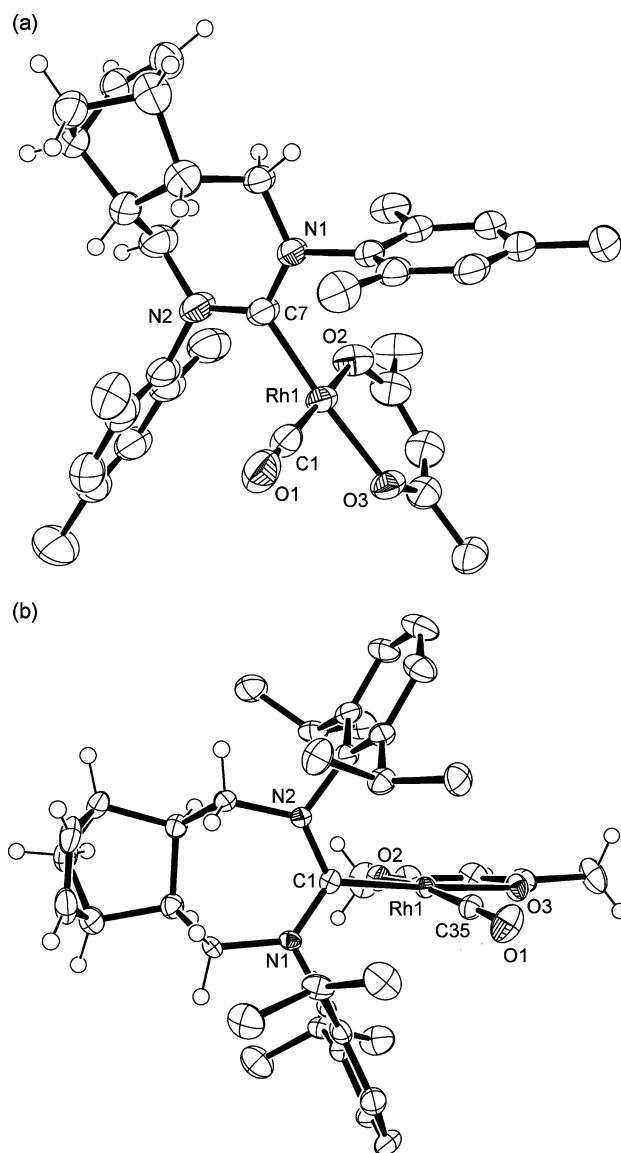


Figure 3. Displacement ellipsoid plots (30%) of (a) **11a** (one of two independent but essentially identical molecules) and (b) **12**. Selected bond lengths [Å] and angles [°] for **11**: Rh1–O2 2.076(3), Rh1–O3 2.076(2), Rh1–C1 1.785(4), Rh1–C7 2.003(3); N1–C7–N2 118.8(3), O2–Rh1–O3 87.52(10). Selected bond lengths [Å] and angles [°] for **12**: Rh1–O2 2.067(2), Rh1–O3 2.064(2), Rh1–C1 2.000(3), Rh1–C35 1.798(3); N1–C1–N2 120.0(3), O2–Rh1–O3 89.10(8).

forces the ligand aryl rings to be closer together over one face of the NCN core. Thus, in **12** the distance between the *i*Pr groups on the double bond side is shorter (3.8 Å) than for the pair on the opposite side (5.9 Å), permitting the less hindered face to tilt over the *cis* ligand. This allows weak H-bonding between the methine *i*Pr protons and the acac oxygen donors and the *i*Pr methyl protons on the other face of the carbene with the oxygen atom of the carbonyl ligand. The asymmetry of the aryl groups results from a large ArCN...NCAr torsion angle of 14.5° in **12**, due to pyramidalisation of the nitrogen atoms on coordination to the rhodium atom (0.07 and 0.08 Å from N to the C<sub>NHC</sub>–C<sub>Dipp</sub>–C<sub>ring</sub> plane in **12**). Stirring of a chloroform solution of **11** at ambient temperature under hydrogen (2 bar) for 48 h (Scheme 1) resulted in auto-hydrogenation of the backbone olefin to afford **13** as a mixture of rotamers (salt **7**, without metal present, is of course inert under similar conditions). Other self-catalytic hydrogenation reactions have been reported by Hahn and co-workers.<sup>[8]</sup> The hydrogenation of the alkene has the benefit of preventing the breakdown of the carbene structure, by retro-Diels–Alder reaction, thus affording a more robust ligand.<sup>[9]</sup>

## Conclusions

Unsaturated amidinium salts such as **6** and **7**, although incompatible with direct carbene formation or complexation, do lend themselves to Diels–Alder adduct formation and hence permit the formation of structurally elaborate, sterically hindered ligands. These amidinium salts are in turn suitable for complex formation which facilitates the incorporation of synthetically versatile functionality into the ligand backbone. In essence an intermediate Diels–Alder step has been used to “decouple” the ligand backbone alkene reactivity from the NCN carbene core. This study also highlights the potential value of large-ring NHCs as ligands in catalytic hydrogenation. Their application in this area has recently been reported.<sup>[10]</sup> Other catalytic applications, and further ligand modifications will be reported shortly.

## Experimental Section

Refer to the Supporting Information for all synthetic and characterisation details. CCDC-723035 (**2**), -7233036 (**8**), -725799 (**9**), -723033 (**10**), -725798 (**11**) and -723034 (**12**) 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](http://www.ccdc.cam.ac.uk/data_request/cif).

**Supporting Information** (see footnote on the first page of this article): Full experimental details for the synthesis and characterisation of all materials.

## Acknowledgments

We thank the Engineering and Physical Sciences Research Council (EPSRC) for support (EP/C528638/1, EP/C53090X/1, GR/S86105/

01, GR/R06458/01) and for funding the National Crystallography Service and the Science and Technology Facilities Council (STFC) for access to synchrotron facilities. We thank the Cardiff Institute of Tissue Engineering and Repair (CITER) for MS instrumentation.

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Received: December 7, 2009

Published Online: March 11, 2010