

# Pincer N-Heterocyclic Carbene Complexes of Ruthenium

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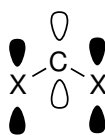
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# 1 Introduction

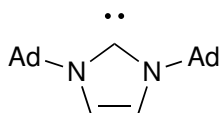
## 1.1 N-Heterocyclic carbenes

A carbene is formally defined as a neutral divalent carbon. The concept that these could be stabilised by  $\pi$  interactions with donor atoms was first developed by Wanzlick.<sup>1</sup> Whilst the triplet carbene carbon is formally divalent, stabilisation by  $\pi$ -donation means that stabilised carbenes effectively act as two electron donor ligands (Figure 1).



**Figure 1** Stabilisation of carbenes by  $\pi$  donation: filled orbitals (black) on heteroatoms donate into the empty orbital (white) on carbon.

When the donor atoms are both nitrogen and are part of a cyclic structure, the stabilised carbene system is known as an N-heterocyclic carbene or NHC. The use of N-heterocyclic carbenes as ligands for metal complexes was reported independently by Wanzlick and Schönherr<sup>2</sup> and Öfele<sup>3</sup> in 1968. However, interest in using these systems as ligands was limited until the isolation of a stable, crystalline N-heterocyclic carbene by Arduengo *et al.* in 1991 (Figure 2).<sup>4</sup>



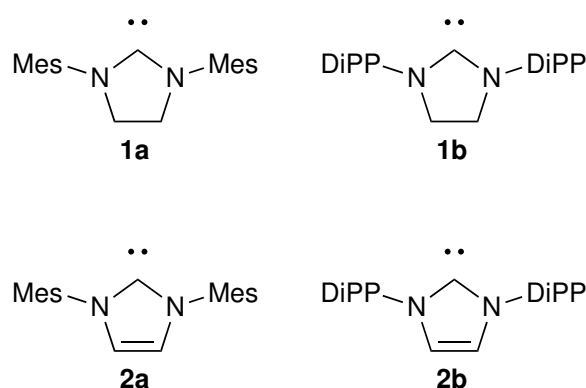
**Figure 2** The first isolated crystalline carbene (Ad = adamantyl).

The first isolated N-heterocyclic carbene features an unsaturated backbone in addition to the two nitrogen atoms (Figure 2). While it was initially believed that this was a key feature for isolation of the carbene, it is now clear that the stability of the system can be attributed mainly to the  $\pi$ -donation of the nitrogen atoms to the carbene carbon.<sup>5</sup> The stability of a variety of nitrogen-stabilised carbene systems has recently been reviewed.<sup>6</sup>

Since Arduengo's report, interest in the area has greatly intensified.<sup>5,7</sup> When bound to late transition-metals, the lability of the carbene-metal bond is often found to be

very low,<sup>7</sup> and the potential of N-heterocyclic carbenes to act as tightly-bound ligands remains an important factor in the current interest in the area. On late transition metals, the  $\sigma$ -donating ability of the ligands is high whilst the  $\pi$ -accepting ability is low. For this reason, N-heterocyclic carbenes are often regarded as being comparable to trialkylphosphanes.

While there is a growing family of N-heterocyclic ligands in the literature, the simple symmetrical NHCs continue to attract a great deal of attention. Principal amongst these are the systems bearing bulky aryl substituents (Figure 3). Both the imidazolin-2-ylidene series (**1**) and imidazol-2-ylidene series (**2**) are in widespread use. These systems are often referred to by the nature of their substituents: 'H<sub>2</sub>IMes', 'H<sub>2</sub>IPr', 'IMes' and 'IPr' for **1a**, **1b**, **2a** and **2b**, respectively.

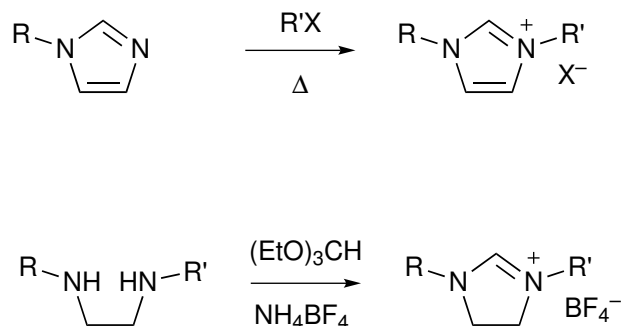


**Figure 3** Simple monodentate carbenes (Mes = 2,4,6-trimethylphenyl, DiPP = 2,6-diisopropylphenyl).

## 1.2 Synthesis of NHC metal complexes

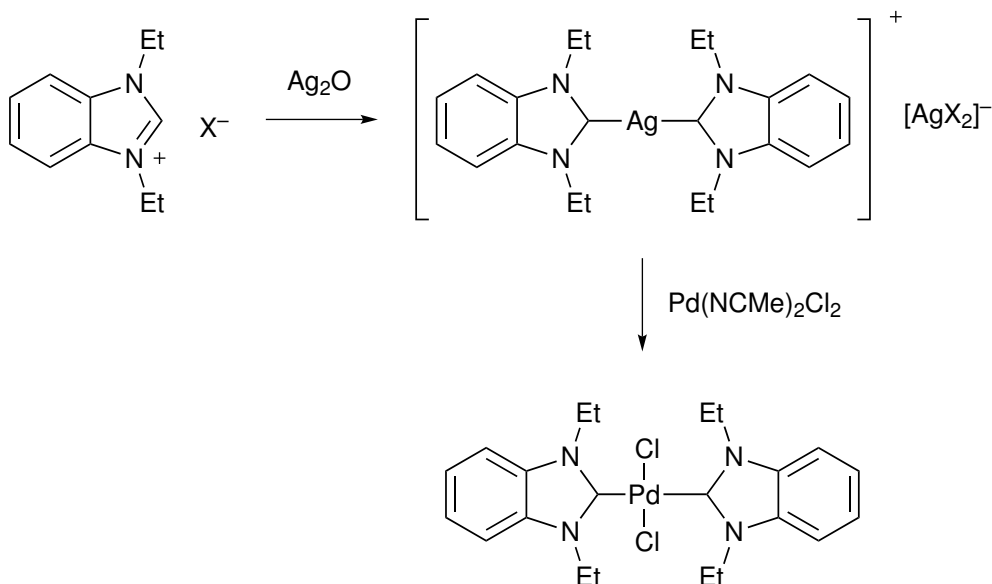
The first stage in the synthesis of NHC complexes is the construction of a suitable carbene precursor. These are usually imidazolium or imidazolinium salts (Scheme 1). Imidazolium salts can conveniently be synthesised by quaternisation of the appropriate imidazole, whereas the imidazolinium salts are usually generated by the action of triethyl orthoformate on a suitable diamine precursor.

There are two main methods for the construction of metal complexes bearing N-heterocyclic carbene ligands. The carbene may be generated in the metal binding step,



**Scheme 1** Formation of imidazolium (left) and imidazolinium (right) salts.

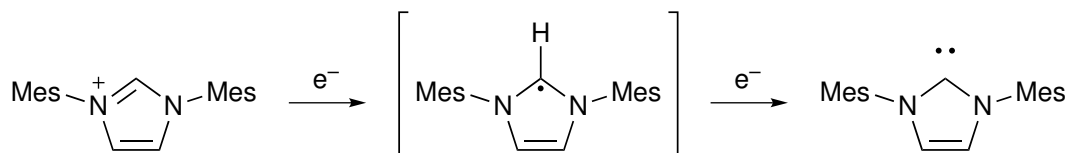
or the carbene may be prepared first in a free form prior to subsequent co-ordination in a second step. The early work by Wanzlick<sup>1,2</sup> and Öfele<sup>3</sup> involves formation of the carbene as part of the metal binding step, but these routes are rather inflexible. A much more general approach is the formation of the silver carbene complex using a basic silver salt such as  $\text{Ag}_2\text{O}$ , an approach that was pioneered by Wang and Lin.<sup>8</sup> The basic silver salt deprotonates the imidazol(in)ium salt, forming the silver carbene complex with loss of water. Subsequent transmetalation from silver can then be used to generate carbene complexes of other metals (Scheme 2).



**Scheme 2** Silver carbene transfer for complex formation.<sup>8</sup>

The alternative approach is to form the free carbene before reaction with metal starting materials. This approach is more flexible than reaction *via* the silver carbene. Carbenes are themselves strong bases, and so deprotonation requires the application of

reagents such as sodium hydride with catalytic DMSO, butyl lithium or  $K[N(SiMe_3)_2]$ . This approach was used by Arduengo in the original isolation of a free carbene,<sup>4</sup> and has subsequently been widely exploited.<sup>5,7</sup> Imidazolium salts have also been deprotonated by electrochemical or chemical reduction (Scheme 3).<sup>9</sup> Once the free carbene is available, it can be reacted with a range of metal starting materials in a similar manner to other ligand systems.



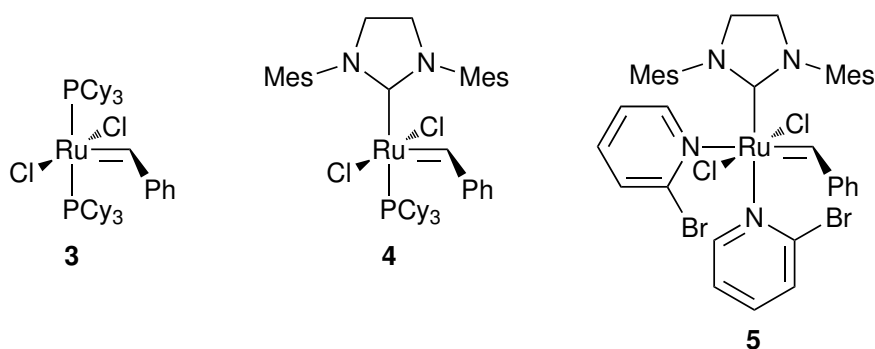
**Scheme 3** Reductive route for carbene formation.<sup>9</sup>

A number of workers have demonstrated the utility of monodentate N-heterocyclic carbenes in forming catalytically useful complexes; the most notable example is the second generation metathesis system reported by Grubbs.<sup>10</sup> More generally, many very active catalysts contain only monodentate ligands. However, the use of bi- or tridentate ligands has been found to be generally successful in complexation chemistry. The potential for higher levels of control at the metal centre means that multidentate ligands form the majority of newly-developed ligand architectures.

### 1.3 Ruthenium-based metathesis catalysts

Olefin metathesis as a route to the synthesis of small molecule targets has seen a vast expansion of interest following the introduction of air- and moisture-stable ruthenium-alkylidene catalysts by Grubbs *et al.*<sup>11</sup> Following the initial report of Grubbs' first-generation catalyst (**3**), many complexes have been suggested with improved activity and stability, most notably Grubbs' second- (**4**)<sup>10,12</sup> and third-generation (**5**)<sup>13,14</sup> systems (Figure 4).

The first generation catalyst (**3**) does not feature a carbene at all, utilising instead two phosphane groups. Replacement of a single phosphane by a carbene increases the activity of the catalyst markedly,<sup>10,12</sup> while using two carbene groups does not lead to



**Figure 4** Grubbs' catalysts: first-, second- and third-generation catalysts from left to right.

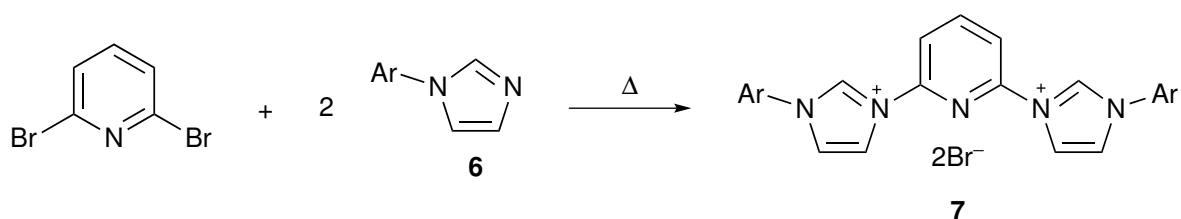
the same improvement.<sup>15</sup> This has been attributed to the need for a dissociation of a single phosphane to take place prior to catalytic turn-over. The third generation catalyst (5) replaces the second phosphane with a pyridine group to allow faster dissociation, whilst retaining the H<sub>2</sub>IMes group for catalyst

The Grubbs' family of catalysts show good tolerance of both water and functional groups within the substrate. This allows the ruthenium-based systems to be used in a range of metathesis reactions with a variety of substrates. However, loadings of catalyst tend to be high (10 mol% is a typical figure), and improving catalyst stability to allow lower loadings remains an important target.

## 2 Results and discussion

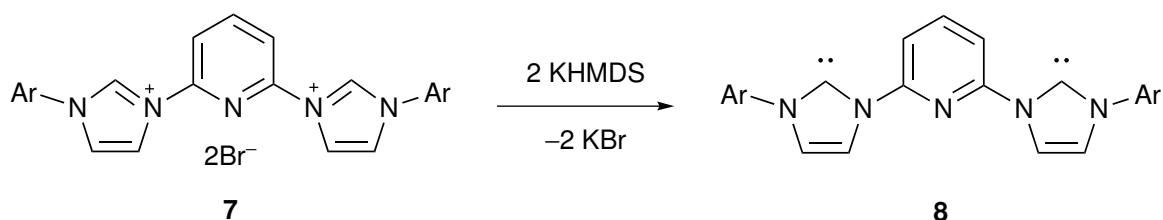
### 2.1 Ligand synthesis

The Danopoulos group have previously developed a high-yielding route to the pincer N-heterocyclic salts **7a** (R = Mes) and **7b** (R = *i*-Pr) (Scheme 4).<sup>16</sup> Heating the appropriate imidazole **6** with 2,6-dibromopyridine for a number of days in a melt gives the imidazolium salts **7**.



**Scheme 4** Formation of pincer salts (**a**: R = Mes, **b**: R = *i*-Pr).

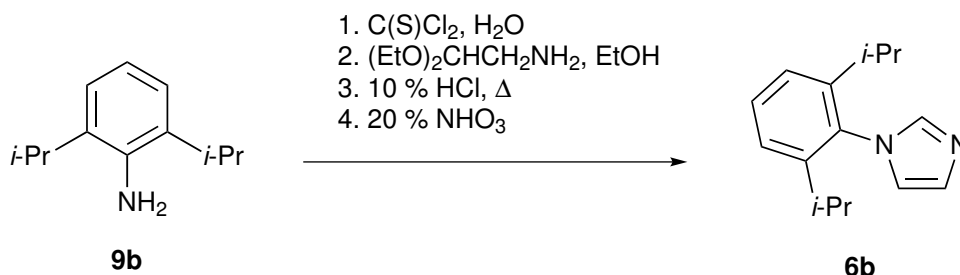
The salts can then be deprotonated using potassium bis(trimethylsilyl)amide (KHMDs) to give the free carbenes. This hindered strong base is known to work efficiently for this class of imidazole salts.<sup>16</sup>



**Scheme 5** Formation of pincer carbenes (**a**: R = Mes, **b**: R = *i*-Pr).

Efforts have been made to define the scalability and efficiency of this route to the pincer ligands. A limitation on the route as a whole is the availability of the imidazoles. Imidazole **6a** can be prepared on a large scale by the method of Arduengo.<sup>17</sup> This is a one-pot procedure using only readily available starting materials, and when run large scale can produce over 100 g of material in one run (in a yield of approximately 50%).<sup>18</sup> However, imidazole **6b** cannot be formed *via* the Arduengo route; reaction of aniline **9b** under the one-pot conditions gave only intractable tarry oils. This imidazole must therefore be produced by a multi-step route (Scheme 6).<sup>19</sup> This reaction reliably

proceeds in overall yields of 50 % to 70 %, and was carried out to give large amounts of material (up to 105 g of isolated product). The key disadvantages of this route are the greater cost of the starting materials, and the more labour-intensive nature of the method compared with the one-pot procedure.



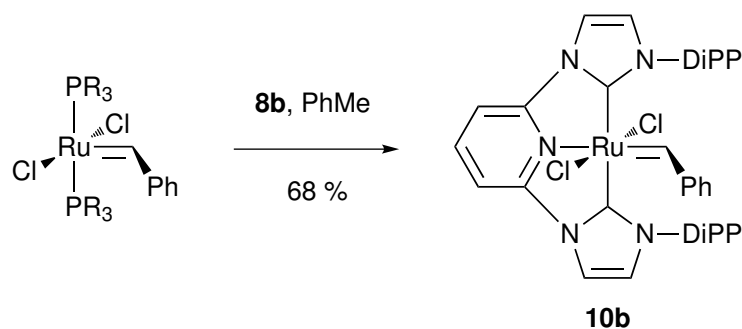
**Scheme 6** Synthesis of imidazole **6b**.

Formation of the pincer imidazolium salt **7b** (Scheme 4) was carried out on a scale of up to 100 g. The reaction proceeded successfully at this scale, and gave the desired product in yields of 80 % to 95 %. Attempts to generate the imidazolium salt using microwave heating proved to be unsuccessful, with no conversion occurring over extended periods (up to two hours irradiation time). The salt was routinely dried azeotropically with toluene before use. This removes water from the hygroscopic salt, but also improves purity as byproducts are effectively dissolved by extended heating in toluene.

Formation of the free pincer carbene has been carried out starting from up to 15 g of the salt. Formation of **8b** proceeds well, with the carbene showing good solubility in toluene (used to separate the carbene from KBr): in most runs the yield exceeded 70 %.

## 2.2 Co-ordination to ruthenium

Reaction of either Grubbs' first generation metathesis catalyst **3**<sup>11</sup> or the P(*i*-Pr)<sub>3</sub> analogue<sup>20</sup> with the free carbene **8b** gives a rapid exchange of the phosphane ligands for the pincer (Scheme 7). While reaction in thf gives a mixture of products, ligand exchange in toluene proceeds cleanly. After crystallisation to remove the phosphane, the complex **10b** was obtained in good yields as a brown, air-stable powder.

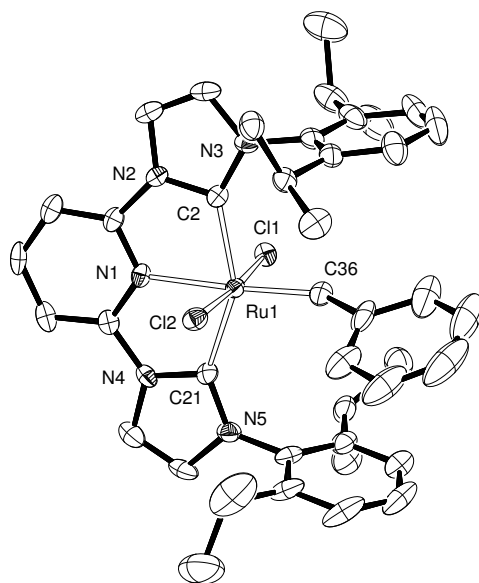


**Scheme 7** Formation of the pincer Grubbs' complex (R = *i*-Pr, Cy).

Crystals of the complex were grown by slow diffusion of petrol into a toluene solution of the complex. As expected, a single-crystal X-ray diffraction study showed a six-coordinate ruthenium(IV) centre, in which the benzylidene is coplanar with the aromatic 'wingtips' (Figure 5). The asymmetric unit contains two molecules of **10b** which have similar metrical data, along with a number of toluene molecules, of which only one was successfully modelled. The diffraction data supports the symmetrical nature of the metal environment, with all of the metal-chloride and metal-carbene distances equal within experimental error. The metal-alkylidene distance is 0.15 Å shorter than the metal-N-heterocyclic carbene bond; this confirms the double-bond nature of the alkylidene and the single bond between the metal and the N-heterocyclic carbene.

## 2.3 Catalysis

The activity of complex **10b** in a variety metathesis reactions has been examined (Tables 1 and 2). Both norbornadiene and norbornene undergo ring-opening metathesis polymerisation (ROMP) in the presence of **10b**; this is expected as both systems are highly-strained and react readily with many potential metathesis catalysts. The less-strained substrates cyclo-octene (coe) and cyclo-octa-1,5-diene (cod) also undergo ROMP with **10b**, but require higher catalyst loadings. The reaction rates in both CD<sub>2</sub>Cl<sub>2</sub> and *d*<sub>8</sub>-toluene were similar, despite the much higher temperature of the reactions in the later solvent. In both cases, complete reaction required refluxing for two days. Ring-closing metathesis (RCM) of the standard test substrate substrate diethyl


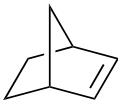
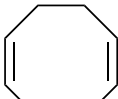
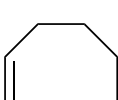
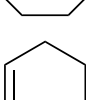
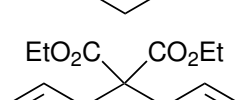


**Figure 5** ORTEP representation of the structure of one of the two independent molecules of **10b** in asymmetric unit showing 50 % probability ellipsoids. Selected bond lengths (Å) and angles (°) with estimated standard deviations: Cl(1)–Ru(1) 2.4154(10), Cl(2)–Ru(1) 2.4354(10), C(2)–Ru(1) 2.034(3), C(21)–Ru(1) 2.056(4), N(1)–Ru(1) 2.101(3), C(36)–Ru(1) 1.889(4); C(37)–C(36)–Ru(1) 142.7(3), Cl(1)–Ru(1)–Cl(2) 175.06(3), C(36)–Ru(1)–N(1) 175.54(14), C(36)–Ru(1)–C(2) 101.28(15), C(36)–Ru(1)–C(21) 107.76(14).

2,2-diallylmalonate with **10b** was also attempted. Again, this required high catalyst loading and long reaction times; reaction overnight in refluxing 1,2-dichloroethane with 10 mol% **10b** led to good conversion (81 %). This reaction rate compare very poorly with **4**, which quantitatively converts diethyl 2,2-diallylmalonate within ten minutes to the ring-closed product.<sup>10</sup>

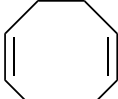
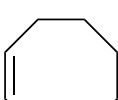
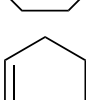
One possible explanations were considered for the low level of metathesis activity. The complex **10b** is formally  $18e^-$ , and co-ordinatively saturated. Thus co-ordination of an alkene, in order to begin a catalytic cycle, may be impossible. Of course, in solution there may be equilibria, in which one or more ligands dissociate from the metal centre, enabling co-ordination of other species. The the chloride-abstracting agent trimethylsilyl trifluoromethylsulphonate (TMS-OTf) was used to probe this possibility. Addition of TMS-OTf to a 1 % solution of **10b** in  $CD_2Cl_2$  gave a rapid colour change from orange-brown to light yellow. This solution showed no metathesis activity with cod, coe or cyclohexene. Both the cod and coe solutions became very dark over time, and gave complex NMR spectra, whereas no change was observed with cyclohexene.

**Table 1** Metathesis reactions in  $\text{CD}_2\text{Cl}_2$ .<sup>a</sup>

Substrate	Catalyst loading	
	1 %	10 %
	✓	—
	✓	—
	No reaction	✓
	Trace	✓
	No reaction	No reaction
	No reaction	✓ <sup>b</sup>

<sup>a</sup> Reactions in sealed NMR tubes at 40 °C; <sup>b</sup> Reaction in 1,2-dichloroethane in an open vessel at 70 °C.

**Table 2** Metathesis reactions in *d*<sub>8</sub>-toluene.<sup>a</sup>

Substrate	Catalyst loading	
	1 %	10 %
	No reaction	✓
	No reaction	✓
	No reaction	No reaction

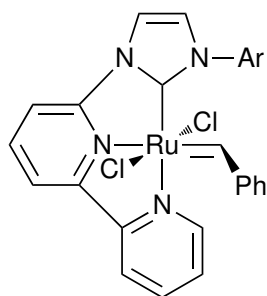
<sup>a</sup> Reactions in sealed NMR tubes at 120 °C.

Attempts to characterise the product of the reaction of TMS-OTf with **10b** were not successful.

## 2.4 Conclusions and outlook

An improved synthesis of the 'pincer' carbene ligand **8b** has been developed. This can be used to produce high yields of the ligand on a multi-gram scale. Reaction of the ligand with Grubbs' first-generation metathesis catalyst leads to the formation of a novel ruthenium complex. This has been fully characterised, including the collection of an X-ray structure of the new compound. Attempts to use this complex as a catalyst in a range of simple metathesis reactions showed only limited success, with low activities observed. This may be due to overly tight binding of the metal by the ligand.

There are three areas for further work. Firstly, the ligand synthesis should be extended to include a wider range of aryl 'wingtip' groups on the pincer ligand. For example, simple phenyl groups would provide a less sterically-crowded ligand system. Secondly, these ligands should be reacted with Grubbs' first-generation metathesis catalyst. This may generate more active catalytic systems. Thirdly, a modified ligand system could be investigated. By replacing one carbene by a pyridine ring, it may be possible to generate a complex similar to **5**, as illustrated in Figure 6. This features a potentially-labile pyridine ligand, and so may have higher metathesis activity than structure **10**. However, the pyridine unit must remain in close proximity to the metal at all times. This may give this modified system higher stability than the parent molecule **5**.



**Figure 6** Potential target complex.

## 3 Experimental

### 3.1 General

Chemicals were obtained from Aldrich, Avocado or Lancaster, and were used as received unless noted otherwise. Solvents were dried by standard methods prior to use.<sup>21</sup> Petroleum ethers refers to the fraction with b.p. 40 °C to 60 °C. All air- or moisture-sensitive reactions were carried out using standard Schlenk techniques or in an M. Braun glovebox (O<sub>2</sub> concentration < 2 ppm). NMR spectra were recorded at 25 °C in 5 mm tubes, at 300.1 MHz (<sup>1</sup>H) or 66.7 MHz (<sup>13</sup>C) on a Bruker Avance 300. Chemical shifts are given in parts per million ( $\delta$ ) and quoted relative to the residual solvent peak (7.15  $\delta$  for <sup>1</sup>H and 128.02  $\delta$  for C<sub>6</sub>D<sub>6</sub>). Coupling constants (*J*) are given in hertz.

The following materials were prepared by literature methods: 1-(2,6-diisopropylphenyl)-3*H*-imidazole **6b**,<sup>19</sup> 2,6-bis[3-(2,6-diisopropylphenyl)imidazolium]pyridine dibromide **7b**<sup>16</sup> and [(*i*-Pr<sub>3</sub>P)<sub>2</sub>RuCl<sub>2</sub>(=CHPh)] **3**.<sup>20</sup>

### 3.2 Potassium bis(trimethylsilyl)amide (KHMDS)

Hexamethyldisiazane (HMDS) (12.5 cm<sup>3</sup>, 60 mmol) was added to a suspension of potassium hydride (2.00 g, 49.8 mmol) in toluene (250 cm<sup>3</sup>). The mixture was refluxed for 2 h, after which time all of the solid has dissolved. The reaction mixture was cooled to room temperature, filtered through Celite and the solvent removed at reduced pressure. The resulting white solid was washed with petrol to removed excess HMDS, giving a white powder (9.90 g, 99%).

### 3.3 2,6-Bis-[3-(2,6-diisopropylphenyl)imidazol-2-ylidene]pyridine **8b**

The imidazolium salt **7b** (6.86 g, 9.93 mmol) was suspended in thf (100 cm<sup>3</sup>) and cooled to -78 °C. A solution of KHMDS (4.32 g, 21.6 mmol) in thf (100 cm<sup>3</sup>) was cooled to

–78 °C, and added to the vigorously stirred reaction solution. This was allowed to warm slowly to room temperature over 16 h. After evaporation of the solvent at reduced pressure, the residue was dissolved in toluene (100 cm<sup>3</sup>) and filtered through Celite. The solvent volume was reduced to 20 cm<sup>3</sup>, and petrol (40 cm<sup>3</sup>) was added. Cooling to 0 °C overnight gave a cream solid and a red solution. The solution was filtered and the solid washed with petrol (20 cm<sup>3</sup>). The product was obtained as a cream solid (4.06 g, 77%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C, 300.1 MHz): δ 1.09 (d, 12H, *J* = 6.9 Hz, Me), 1.18 (d, 12H, *J* = 6.8 Hz, Me), 2.90 (sept., 4H, *J* = 6.9 Hz, CHMe<sub>2</sub>), 6.62 (d, 2H, *J* = 1.8 Hz, imidazole backbone CH), 7.05 (t, 1H, *J* = 8.0 Hz, central pyridine CH), 7.14 (d, 4H, *J* = 7.4 Hz, aromatic CH), 7.25 (dd, 2H, *J* = 6.9 Hz, 8.4 Hz; central aromatic CH), 8.06 (d, 2H, *J* = 1.7 Hz, imidazole backbone CH), 8.43 (d, 2H, *J* = 8.0 Hz, pyridine CH). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C, 66.7 MHz): δ 24.03 (Me), 24.42 (Me), 28.60 [CH(CH<sub>3</sub>)<sub>2</sub>], 111.70 (aromatic CH), 116.25 (aromatic CH), 122.82 (aromatic CH), 128.53 (aromatic CH), 129.29 (aromatic CH), 138.72 (aromatic C), 140.69 (aromatic C), 146.20 (aromatic CH), 152.62 (aromatic C), 220.34 (carbene C).

### 3.4 Benzylidene{2,6-bis-[3-(2,6-diisopropylphenyl)imidazol-2-ylidene]pyridine}dichlororuthenium(IV) 10b

The carbene **8b** (384 mg, 0.72 mmol) was dissolved in toluene (40 cm<sup>3</sup>), and added to **3** (420 mg, 0.72 mmol) in toluene (10 cm<sup>3</sup>). The brown solution was stirred for 90 min, before the solvent was removed at reduced pressure. The solid was redissolved in toluene (5 cm<sup>3</sup>) and precipitated with petrol (30 cm<sup>3</sup>). Filtration gave the product as a brown solid (390 mg, 68%). Single crystals of the complex were grown by slow diffusion of petrol into a toluene solution of the complex. Found C 63.42, H 5.98, N 8.70%; C<sub>42</sub>H<sub>49</sub>Cl<sub>2</sub>N<sub>5</sub>Ru requires C 63.39, H 6.21, N 8.80%. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C, 300.1 MHz): δ 0.92 (d, 6H, *J* = 6.8 Hz, Me), 0.98 (d, 6H, *J* = 6.8 Hz, Me), 1.18 (d, 6H, *J* = 6.5 Hz, Me), 1.53 (d, 1H, *J* = 6.4 Hz, Me), 2.89 (sept., 2H, *J* = 6.8 Hz, CHMe<sub>2</sub>), 3.62 (sept., 2H, *J* = 6.5 Hz, CHMe<sub>2</sub>), 6.48 to 6.52 (m, 4H, aromatic CH), 6.84 (m, 2H, aromatic CH), 6.95 to 7.02 (m, 4H, aromatic CH), 7.22 to 7.25 (m, 1H, aromatic CH), 7.79

(d, 2H,  $J = 7.2$  Hz, aromatic CH), 18.91 (s, 1H, alkylidene CH).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C, 66.7 MHz):  $\delta$  22.78 (Me), 22.94 (Me), 26.28 (Me), 26.48 (Me), 27.86 [ $\text{CH}(\text{CH}_3)_2$ ], 28.11 [ $\text{CH}(\text{CH}_3)_2$ ], 104.57 (aromatic CH), 115.80 (aromatic CH), 123.62 (aromatic CH), 124.16 (aromatic CH), 125.66 (aromatic C), 126.30 (aromatic CH), 127.30 (aromatic CH), 127.81 (aromatic CH), 129.30 (aromatic C), 129.91 (aromatic CH), 131.84 (aromatic CH), 136.54 (aromatic C), 139.25 (aromatic CH), 146.46 (aromatic C), 148.50 (aromatic C), 153.10 (aromatic C), 211.17 (alkylidene CH).  $m/z$  (ES+) 794.6 ( $\text{M}^+$ ).

### 3.5 X-Ray crystallography

From a sample **10b** of under polyether oil, a crystal *ca.* 0.02 mm  $\times$  0.16 mm  $\times$  0.18 mm was mounted on a glass fibre and fixed in the cold nitrogen stream of a Bruker–Nonius  $\kappa$ -CCD instrument, equipped with a FR591 rotating anode source (Mo  $k_\alpha$  wavelength 0.71073 Å). Data collection and refinement were controlled by the programs COLLECT<sup>22</sup> and DENZO<sup>23</sup> programs. The structure was determined by direct methods in SIR-92<sup>24</sup> and refined by full-matrix least-squares methods on  $F^2$  in SHELXL.<sup>25</sup> The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in idealised positions and their  $U_{\text{iso}}$  values were set to ride on the  $U_{\text{eq}}$  values of the parent carbon atoms. The crystal structure contained a highly disordered molecule of toluene, which could not be successfully modelled, and was handled using the SQUEEZE procedure.<sup>26</sup>

*Crystal data:*  $2(\text{C}_{42}\text{H}_{47}\text{Cl}_2\text{N}_5\text{Ru}) \cdot \text{C}_7\text{H}_8$ ,  $M = 1679.77$ , triclinic, space group  $P\bar{1}$ ,  $a = 13.8497(16)$  Å,  $b = 17.604(2)$  Å,  $c = 19.809(3)$  Å,  $\alpha = 76.133(12)^\circ$ ,  $\beta = 69.945(11)^\circ$ ,  $\gamma = 85.262(13)^\circ$ ,  $V = 3740.2(7)$  Å<sup>3</sup>,  $Z = 2$ ,  $T = 120(2)$  K. At the conclusion of the refinement,  $R_1 = 0.057$  for  $I > 2\sigma(I)$  and  $wR_2 = 0.138$  for all data.

### 3.6 Metathesis of diethyl 2,2-diallylmalonate

Complex **10b** (21 mg, 30  $\mu\text{mol}$ ) was dissolved in 1,2-dichloroethane (1.0 cm<sup>3</sup>), and diethyl 2,2-diallylmalonate (64 mg, 0.27 mmol) was added. The solution was refluxed overnight under a slow stream of nitrogen, then cooled to room temperature and the

solvent removed *in vacuo*.

### 3.7 NMR scale metathesis reactions

The following general procedure was used for the metathesis reactions. Complex **10b** (4 mg for 10 % loading, 21 mg for 10 % loading) was dissolved in the appropriate solvent ( $\text{CD}_2\text{Cl}_2$  or  $d_8$ -toluene) ( $0.75 \text{ cm}^3$ ) in a Youngs' tap NMR tube. The substrate (0.50 mmol for 1 % loading or 0.25 mmol for 10 %) was added under nitrogen, and the tube heated to the boiling point of the solvent. After heating overnight, the system was examined by NMR.

For reactions in the presence of trimethylsilyl trifluoromethanesulfonate (TMS-OTf), a drop of TMS-OTf was added to the catalyst solution prior to addition of the substrate.

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