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'Pincer' pyridyl- and bipyridyl-*N*-heterocyclic carbene analogues of the Grubbs' metathesis catalyst

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Abstract

The 'pincer' pyridine-dicarbene and bipyridyl-carbene ruthenium benzylidene complexes, Ru(C–N–C)Cl_2(=CHPh) and Ru(C–N–N)Cl_2(=CHPh), (C–N–C) = 2,6-bis(DiPP-imidazol-2-ylidene)pyridine, (C–N–N) = (DiPP-imidazol-2-ylidene)bipyridine, have been prepared and characterised by spectroscopic and diffraction methods. They exhibit moderate metathesis activity. Non-symmetrical linear tridentate ether-functionalised *N*-heterocyclic carbene pro-ligands are also described.

Keywords: Metathesis; Grubbs' catalyst; Ruthenium; *N*-heterocyclic carbenes; Pincer complexes

1. Introduction

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. [1]. Following the initial report of Grubbs' first-generation catalyst (**1a**), many complexes have been suggested with improved activity and stability, most notably Grubbs' second- [2] and third-generation [3] systems (Fig. 1).

Whilst monodentate *N*-heterocyclic carbenes (NHC), such as H_2IMes (seen in **2** and **3**) in the presence of various co-ligands continue to attract a great deal of attention, NHC ligand design is now expanding to the study of topologies containing one or more additional functional groups [4]. One such ligand architecture is the 'pincer' system, which provides a preorganised backbone capable of blocking meridional or *pseudo*-meridional coordination sites of the metal, leaving the remaining positions available for catalysis [5].

As part of an ongoing investigation into the versatile 'pincer' 2,6-bis(arylimidazol-2-ylidene)pyridine (C–N–C) [6], we have recently reported the synthesis of Rh(I) and Rh(III) complexes supported by this ligand, and introduced the novel less robust ligand (arylimidazol-2-ylidene)bipyridine (C–N–N) [7]. We now report the synthesis of Grubbs'-type benzylidene ruthenium complexes based on (C–N–C) and (C–N–N) and compare their catalytic activity in simple metathesis with the already established systems. We also describe initial attempts directed towards the synthesis of other 'hemi-labile' tridentate ligands incorporating the NHC and pyridine functionalities.

2. Results and discussion

2.1. Symmetrical pyridine-dicarbene complex: synthesis and reactivity

Reaction of either Grubbs' first-generation metathesis catalyst **1a** or the P(*i*-Pr)$_3$ analogue **1b** with the ligand **4**

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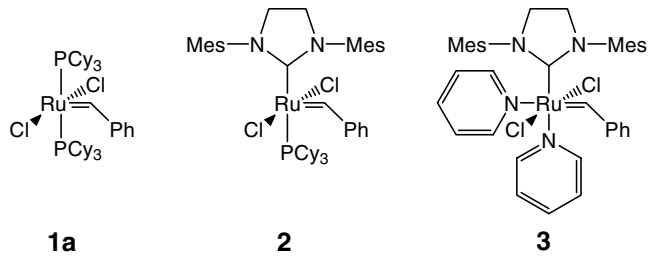


1a **2** **3**

Fig. 1. Grubbs' first-, second- and third-generation metathesis catalysts.

resulted in a rapid exchange of the phosphines for the pincer (Scheme 1).

While reaction in THF gave a mixture of products by ^{1}H NMR spectroscopy, ligand exchange in toluene proceeded cleanly [8], giving a single product as judged by the one resonance appearing in the alkylidene region (18.91 δ *cf.* 20.00 δ in **1a** [1]). After removal of the phosphine, **5** was obtained in good yields as a brown, air-stable powder. The proton spectrum in C_6D_6 showed four doublets in the range 0.92–1.53 δ (6H each), along with two septets at 2.89 and 3.62 δ (2H each), supporting the presence of inequivalent *iso*propyl groups on the aromatic "wingtips", as expected for a structure in which the benzylidene and "wingtip" groups lie in approximately parallel planes. Mass spectrometry also supported the proposed structure and demonstrated the stability of the complex. Electrospray MS in MeCN exposed to air gave a clear molecular ion at *m*/*z* 794.6 Da. Crystals of **5** were grown by slow diffusion of petrol into a toluene solution. A single-crystal X-ray diffraction study confirmed the expected molecular structure (Fig. 2).

The asymmetric unit contains two molecules which have similar metrical data, along with a number of toluene molecules, of which one was successfully modelled [9]. The geometry around the ruthenium is distorted octahedral. The metrical data demonstrate that the pincer ligand is symmetrically bound, with both Ru–C_{NHC} distances equal within experimental error. The same is true for the Ru–Cl distances. The Ru=CHPh distance is approx. 0.15 Å shorter than the Ru–C_{NHC} bond, confirming the double-bond nature of the alkylidene and the single bonds between the metal and the *N*-heterocyclic carbenes.

The activity of complex **5** as a ring-opening metathesis polymerisation catalyst was examined with a range of strained alkenes (norbornadiene, norbornene, cyclooctene and cycloocta-1,5-diene) (Table 1). All of these substrates undergo ROMP in the presence of **5**, in refluxing CH_2Cl_2 or toluene. However, the activities observed were low compared with **1a** or **2**, both in terms of catalyst loading required and conversion time. Ring closing metathesis of diethyl diallylmalonate was also investigated. Again, this required high catalyst loading and long reaction times; reaction overnight in refluxing 1,2-dichloroethane with 10% of **5** led to good conversion (81%). Complex **2** quantitatively ring-closes the same substrate within 10 min (5% **2**, refluxing CH_2Cl_2) [2] (see Table 2).

Attempts to form less bulky analogues of **5** by replacement of the di-isopropylphenyl substituents of the carbene ring with the smaller mesityl or *t*-Bu were unsuccessful, yielding complex mixtures by ^{1}H NMR spectroscopy.

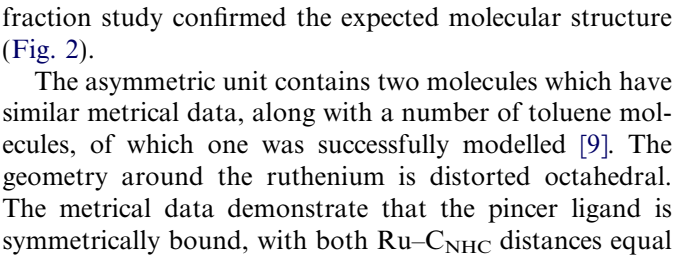
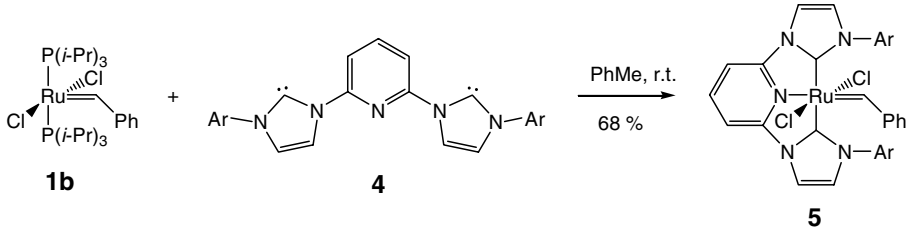


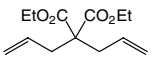
Fig. 2. ORTEP representation of the structure of **5** showing 50% probability ellipsoids; a toluene molecule and hydrogen atoms are omitted for clarity. The a.s.u. contains two independent complexes, which have similar metrical data. Selected bond lengths (Å) and angles (°) with estimated standard deviations: Ru(1)–Cl(1) 2.4154(10), Ru(2)–Cl(1) 2.4354(10), Ru(1)–C(2) 2.034(3), Ru(1)–C(21) 2.056(4), Ru(1)–N(1) 2.101(3), Ru(1)–C(36) 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).



1b **4** **5**

Scheme 1. Formation of ruthenium complex **5** [Ar = 2,6-(*i*-Pr)$_2$C$_6$H$_3$].

Table 1
Metathesis activity of complex **5**

Substrate[a]	CD_2Cl_2, 45 °C		d_8-toluene, 115 °C	
	1% **5**[b]	10% **5**[c]	1% **5**[b]	10% **5**[c]
	>95%	–[d]	–[d]	–[d]
	>95%	–[d]	–[d]	–[d]
	<10%	>95%	NR	>95%
	NR	>95%	NR	>95%
	NR	81%[e]	–[d]	–[d]

NR, no reaction observed.
[a] 0.75 mL solvent in sealed NMR tubes, reaction success measured by NMR.
[b] 4 mg **5**, 0.50 mmol substrate.
[c] 21 mg **5**, 0.25 mmol substrate.
[d] not attempted.
[e] 1.0 mL CH_2ClCH_2Cl, 21 mg **5**, 0.25 mmol substrate, 18 h, reflux under N_2 stream, product isolated and crude analysed by NMR.

2.2. Carbene-bipyridyl complex

The low metathesis activity of **5** pointed to a limitation of the C–N–C ligand design, especially on late 4d and 5d transition-metals. This may originate from combination of the low lability of the metal–NHC bond and the blocking of three co-ordination sites by the rigid ligand. In order to test this hypothesis, we have started the study of other tridentate ligands comprising one pyridine donor flanked by one NHC and one 'classical' donor. As part of this effort, we have recently introduced an alternative 'pincer' architecture, C–N–N, in which the NHC is covalently attached to a bipyridyl system **7** as shown in Scheme 2 [7].

We have already noted [7] that, in contrast to the symmetrical **4**, the synthesis of the ligand **7** is susceptible to low isolated yields mainly due to poor solubility of the product in compatible organic solvents. Therefore, we chose to generate **7** *in situ* and react it directly with **1b**. Deprotonation of the salt **6** with $KN(SiMe_3)_2$, followed by addition of **1b** gave brown solution containing more than one species (Scheme 2). Whilst the ^1H NMR spectrum of the reaction mixture indicated the presence of at least two benzylidene-containing products, it was possible to isolate only small amounts of **8** by fractional crystallisation from THF/petrol. This led to the formation of crystals suitable for X-ray diffraction studies (Fig. 3).

The structure shows the benzyl group displaced to one side of the complex, as with the pincer complex **5**. The two $Ru–N_{pyr}$ bonds differ in length by ~0.05 Å, with the longer bond to the terminal N_{pyr}. The $C_{NHC}–Ru–N_{pyr}$ (terminal) angle of 152.7(3)° demonstrates the distorted nature of the co-ordination sphere at the metal, caused by the geometric restrains inherent in ligand **7**.

Table 2
Crystallographic data for **5** and **8**

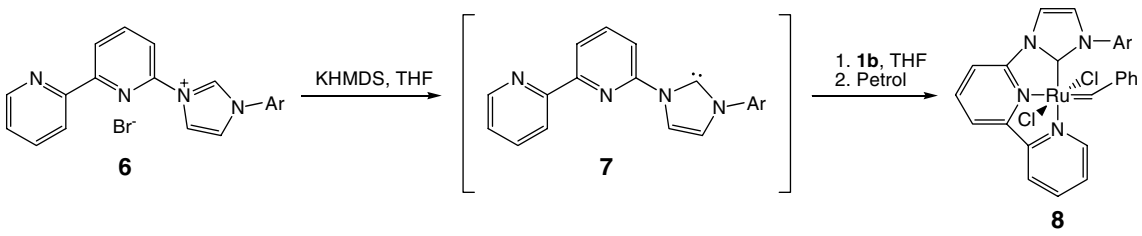
Compound	**5**	**8**
Formula	$2(C_{42}H_{47}Cl_2N_5Ru)\cdot C_7H_8$	$C_{32}H_{32}Cl_2N_4Ru\cdot C_4H_8O$
Formula weight	1679.77	716.69
Crystal description	Orange plate	Dark red plate
Crystal dimensions (mm)	$0.02\times0.16\times0.18$	$0.04\times0.10\times0.14$
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
Unit cell dimensions		
a (Å)	13.8497(16)	17.408(8)
b (Å)	17.604(2)	13.3097(19)
c (Å)	19.809(3)	15.761(9)
α (°)	76.133(12)	90
β (°)	69.945(11)	114.02(3)
γ (°)	85.262(13)	90
V (Å^3)	4404.6(10)	3336(3)
Z	2	4
T (K)	120(2)	120(2)
μ (mm^{-1})	0.513	0.665
Number of data collected	91,656	24,795
Number of unique data	20,252	7594
R_{int}	0.0736	0.1267
R_1 ($I>2\sigma(I)$)	0.0567	0.0954
wR_2 (all data)	0.1376	0.2263

2.3. Trimethylsilyloxy functionalised pyridine imidazolium salts and carbenes

The very low yield of **8** from the *in situ* method used above, coupled with the difficulties of obtaining the free carbene **7**, have to date prevented the detailed study of **8** as a metathesis catalyst. We have therefore investigated the synthesis of other potentially hemi-labile ligands based on the NHC–pyridine core. With this aim in mind, we have targeted C–N–O ligands, where O is an ether group. The synthetic strategy followed is outlined in Scheme 3.

The alcohol **9** is readily available from commercial starting materials. Quaternisation with imidazole **10** at 140 °C proceeded smoothly to give **11** in high yields. Electrospray mass spectroscopy confirms the formation of the desired material, with the molecular ion observed at 336.3 Da.

Conversion of the alcohol to an ether under standard conditions was attempted. Reaction with sodium hydride (1 equiv.), followed by the addition of iodomethane gave a mixture of products. A number of other conditions using basic reagents (such as alkali metal carbonates) were also unsuccessful. The presence of two acidic functionalities in the substrate (the alcohol and the imidazolium salt) could well be responsible for the failure of this transformation [10]. As an alternative to deprotonation using bases, the reaction of **11** with hexamethyldisilazane (HMDS) was explored [11]. Refluxing **11** and HMDS in 1,4-dioxane in the presence of a catalytic amount of TMSCl led to clean conversion to the desired ether **12**, as seen by NMR spectroscopy. The key change in the spectra is the appearance



Scheme 2. *In situ* formation of C–N–N ligand **7** and reaction to give ruthenium complex **8** [Ar = 2,6-(*i*–Pr)$_2$C$_6$H$_3$].

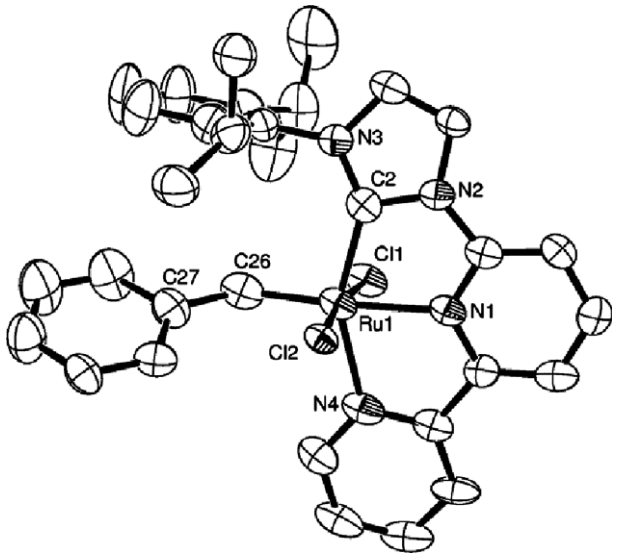
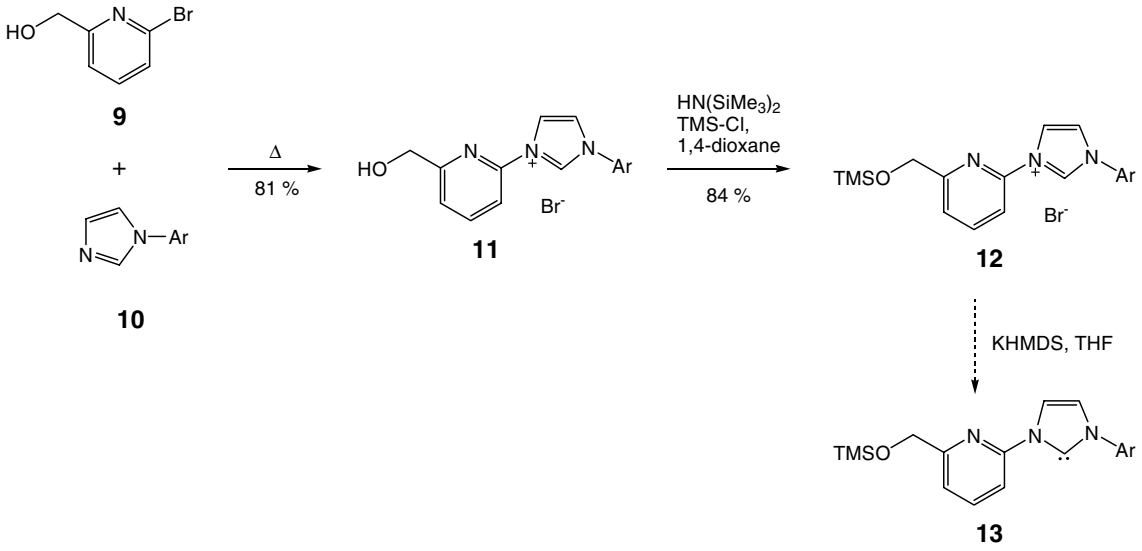


Fig. 3. ORTEP representation of the structure of **8** showing 50% probability ellipsoids; hydrogen atoms and one molecule of THF have been omitted for clarity. Selected bond lengths (Å) and angles (°) with estimated standard deviations: Ru(1)–Cl(1) 2.430(3), Ru(1)–Cl(2) 2.460(2), Ru(1)–N(1) 2.087(7), Ru(1)–N(4) 2.134(6), Ru(1)–C(2) 1.995(7), Ru(1)–C(26) 1.885(9); Cl(1)–Ru(1)–Cl(2) 172.59(7), C(27)–C(26)–Ru(1) 139.0(7), C(26)–Ru(1)–C(2) 99.4(3), C(26)–Ru(1)–N(4) 107.7(3), C(2)–Ru(1)–N(4) 152.7(3).

of signals for the TMS group (new signals at 0.19 δ in the ^{1}H and −0.55 δ in the ^{13}C), whilst the rest of the spectrum is only slightly perturbed.

Conversion of **12** to the free carbene was hindered by the high solubility imparted by the TMS group. In contrast to the very low solubility of the majority of the imidazolium salts in non-chlorinated solvents, **12** is highly soluble in THF and 1,4-dioxane. Reaction of **12** with KHMDS gave a very soluble product; after removal of potassium bromide (by filtration of a toluene solution), the remaining material freely dissolved in petrol. Proton NMR spectroscopy indicated that the majority (>80%) of this material was the desired carbene, but this could not be successfully separated from byproducts.

Given the NMR evidence for the existence of carbene **13**, *in situ* formation of the carbene followed by reaction with **1b** was attempted. On addition of the carbene solution to the metal source, the reaction medium became lighter in colour (from purple to pink). However, attempts to crystallise the desired product from the reaction mixture were again hindered by the solubility of the ligand system. Layering of the reaction mixture with petrol or cooling the reaction solution to −30 °C led to the preferential crystallisation of unreacted **1b**.



Scheme 3. Quaternisation to **11**, conversion to the TMS ether **12** and route toward carbene **13** [Ar = 2,6-(*i*-Pr)$_2$C$_6$H$_3$].

3. Conclusions

'Pincer' carbene analogues of Grubbs' catalysts have been prepared for the first time. Whilst the C–N–C complex shows limited metathesis activity, the catalytic potential of the C–N–N system is yet to be tested. The synthesis of tridentate 'designer' complexes of ruthenium based around a non-symmetrical ligand architecture remains a challenge.

4. Experimental

4.1. General methods

Solvents were dried by standard methods [12] and either used directly or stored in ampoules over 4 Å molecular sieves. All air- or moisture-sensitive reactions were carried out under dry nitrogen using standard Schlenk techniques or in a M. Braun glove box. NMR data were recorded on Bruker AMX-300 and DPX-400 spectrometers, operating at 300 and 400 MHz (^{1}H), respectively. The spectra were referenced internally using the signal from the residual *protio*-solvent (^{1}H) or the signals of the solvent (^{13}C). Mass spectra (electrospray ionization) were obtained from acetonitrile solutions on a VG Biotec platform. The calculated isotopic envelopes agree well with the experimentally observed patterns. Commercial chemicals were from Acros, Aldrich, Lancaster and Avocado; the light petroleum had T_b 40–60 °C. The following starting materials were prepared as described in the literature: [(*i*-Pr$_3$P)$_2$RuCl$_2$(=CHPh)] (**1b**) [13], 3-(2,6-di*iso*propylphenyl)-1*H*-imidazole [14], 2,6-bis[(2,6-di*iso*propylphenyl)imidazol-1-yl-2-idene]pyridine (**4**) [7], 1-(2,2′-bipyridinyl-6-yl)-3-(2,6-di*iso*propylphenyl)-3*H*-imidazol-1-ium bromide (**6**) [7].

4.2. Benzylidene{2,6-bis-[3-(2,6-diisopropylphenyl)imidazol-2-ylidene]pyridine}dichlororuthenium(IV) (5)

The carbene **4** was dissolved in toluene (40 mL), and added to **1b** (420 mg, 0.721 mmol) in toluene (10 mL). The brown solution was stirred for 11/2 h, before the solvent was removed under reduced pressure. The solid residue was redissolved in toluene (5 mL) and precipitated with petrol (30 mL). 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. ^{1}H (C$_6$D$_6$, 300 MHz) δ (ppm): 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, C*H*(CH$_3$)$_2$], 3.62 [sept., 2H, $J = 6.5$ Hz, C*H*(CH$_3$)$_2$], 6.48–6.52 (m, 4H, aromatic), 6.84 (m, 2H, aromatic), 6.95–7.02 (m, 4H, aromatic), 7.22–7.25 (m, 1H, aromatic), 7.79 (d, 2H, $J = 7.2$ Hz, aromatic), 18.91 (s, 1H, alkylidene CH). ^{13}C (C$_6$D$_6$, 75.45 MHz) δ (ppm): 22.78 (Me), 22.94 (Me), 26.28 (Me), 26.48 (Me), 27.86 [CH(*C*H$_3$)$_2$], 28.11 [CH(*C*H$_3$)$_2$], 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* (ESI) 794.6 (M$^+$). Anal. calc. for C$_{42}$H$_{49}$Cl$_2$N$_5$Ru: C 63.39, H 6.21, N 8.80%; found C 63.42, H 5.98, N 8.70%.

4.3. Ring-opening metathesis polymerisation of cyclic alkenes

The following general procedure was used for the metathesis reaction. The catalyst **5** (21 mg, 0.03 mmol, 10 mol%) was dissolved in the appropriate solvent (CD_2Cl_2 or d_8-toluene, 0.75 mL) in a Youngs tap NMR tube. The substrate (0.25 mmol) was added under nitrogen, and the tube heated to the boiling point of the solvent. After heating overnight, the system was examined by NMR.

4.4. Ring-closing metathesis of diethyl diallylmalonate

Complex **5** (21 mg, 0.03 mmol) was dissolved in 1,2-dichloroethane (1.0 mL), and diethyl 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*. The residue was examined by NMR.

4.5. Benzylidene[1-(2,2-bipyridin-6-yl)-3-(2,6-diisopropylphenyl)imidazol-2-ylidene]dichlororuthenium(IV) (8)

A suspension of **7** (46 mg, 0.10 mmol) in THF (4 mL) was cooled to −78 °C, and KHMDS (22 mg, 0.11 mmol) in THF (4 mL) was added. The solution was allowed to warm to r.t., giving a clear solution. After cooling to −78 °C, **1b** (58 mg, 0.10 mmol) in THF (4 mL) was added, and the solution stirred overnight at r.t. The solvent was removed at reduced pressure, the residue dissolved in toluene (50 mL) and filtered through Celite®. The solution was evaporated and the residue washed with petrol (20 mL). Re-dissolution in THF (10 mL) and layering with petrol (10 mL) led to the formation of crystals of **8** suitable for X-ray diffraction.

4.6. 3-(2,6-Diisopropylphenyl)-1-(6-hydroxymethylpyridin-2-yl)-3H-imidazol-1-ium bromide (11)

A mixture of imidazole **10** (17.01 g, 74.5 mmol) and alcohol **9** (13.95 g, 74.2 mmol) was sealed in a glass ampoule and heated to 140 °C for six days. After cooling to room temperature, the product (25.01 g, 81%) was obtained as a cream solid by dissolution in dichloromethane and trituration with ether. ^{1}H ($CDCl_3$, 300 MHz)

δ (ppm): 1.14 (d, 6H, $J = 6.4$ Hz, Me), 1.22 (d, 6H, $J = 6.4$ Hz, Me), 2.38 [sept., 2H, $J = 7.2$ Hz, CH(CH$_3$)$_2$], 4.73 (s, 2H, CH_2OH), 7.30 (d, 2H, $J = 8.0$ Hz, aromatic), 7.38 (t, 1H, $J = 1.5$ Hz, imidazole backbone CH), 7.54 (t, 1H, $J = 8.0$ Hz, aromatic), 7.54 (d, 1H, $J = 8.0$ Hz, aromatic), 7.91 (t, 1H, $J = 8.0$ Hz, aromatic), 8.65 (d, 1H, $J = 8.0$ Hz, aromatic), 9.29 (t, 1H, $J = 1.5$ Hz, imidazole backbone CH), 10.80 (s, 1H, imidazolium C^{2}H). ^{13}C (CDCl$_3$, 74.45 MHz) δ (ppm): 24.32 (Me), 24.33 (Me), 28.77 [CH(CH$_3$)$_2$], 64.09 (CH$_2$), 113.49 (aromatic CH), 121.14 (aromatic CH), 122.62 (aromatic CH), 124.73 (aromatic CH), 125.48 (aromatic CH), 130.03 (aromatic C), 132.10 (aromatic CH), 135.67 (aromatic C), 140.93 (aromatic C), 145.10 (aromatic C), 161.95 (imidazolium C^{2}H). m/z (ES+) 336.3 (M$^+$). Anal. Calc. for C$_{21}$H$_{26}$BrN$_3$O: C 60.58, H 6.29, N 10.09%; found C 60.30, H 6.18, N 9.93%.

4.7. 3-(2,6-Diisopropylphenyl)-1-[6-(trimethylsilanyloxymethyl)pyridin-2-yl]-3H-imidazol-1-ium bromide (*12*)

The imidazolium salt **11** (3.59 g, 8.63 mmol), hexamethyldisilazane (1.40 mL, 6.71 mmol) and one drop of chlorotrimethylsilane were dissolved in 1,4-dioxane (100 mL). The reaction mixture was refluxed overnight, then cooled to room temperature and the solvent removed *in vacuo*. The resulting solid was stirred overnight with ether, which after filtration yielded a beige solid (3.55 g, 84%). ^{1}H (CDCl$_3$, 300 MHz) δ (ppm): 0.19 [s, 9H, Si(CH_3)$_3$], 1.17 [d, 6H, $J = 6.6$ Hz, CH(CH_3)$_2$], 1.28 [d, 6H, $J = 6.6$ Hz, CH(CH_3)$_2$}], 2.41 [sept., 2H, $J = 6.6$ Hz, CH(CH$_3$)$_2$], 4.78 (s, 2H, CH$_2$), 7.34 (d, 1H, $J = 7.8$ Hz, aromatic), 7.37 (t, 1H, $J = 1.8$ Hz, imidazole backbone CH), 7.57 (t, 1H, $J = 7.8$ Hz, aromatic), 7.66 (d, 1H, $J = 7.8$ Hz, aromatic), 8.11 (t, 1H, $J = 7.8$ Hz, aromatic), 9.11 (d, 1H, $J = 8.4$ Hz, aromatic), 9.31 (t, 1H, $J = 1.8$, imidazole backbone CH), 10.97 (s, 1H, imidazolium C^{2}H). ^{13}CH (CDCl$_3$, 74.45 MHz) δ (ppm): −0.55 [Si(CH$_3$)$_3$], 24.24 [CH(CH$_3$)$_2$], 24.33 [CH(CH$_3$)$_2$], 28.84 [CH(CH$_3$)$_2$], 114.61 (aromatic CH) 120.93 (aromatic CH), 122.25 (aromatic CH), 125.12 (aromatic CH), 130.00 (aromatic C), 132.19 (aromatic CH), 135.41 (aromatic CH), 141.64 (aromatic CH), 144.84 (aromatic C), 145.11 (aromatic C), 161.21 (imidazolium C^{2}H). Anal. Calc. for C$_{24}$H$_{34}$BrN$_3$O, Si C 59.00, H 7.71, N 8.60%; found C 58.72, H 7.37, N 8.43%.

4.8. X-ray diffraction studies

Both data sets were collected on an Enraf-Nonius Kappa CCD area detector diffractometer, fitted with an FR591 rotating anode (Mo K$_\alpha$ radiation) and an Oxford Cryosystems low temperature device, operating in ω scanning mode with ψ and ω scans to fill the Ewald sphere. Data collection and reduction were carried out using the software packages Collect, Scalepack, and Denzo [15]. The crystals were mounted on a glass fibre with silicon grease, from Fomblin vacuum oil. In all cases refinement was carried out by full-matrix least-squares methods using SHELXL-97 [16] within the WINGX program suite [17]. All non-hydrogen atoms were refined using anisotropic thermal parameters, and hydrogens were added using a riding model. Compound **5** contained a highly disordered molecule of toluene, which could not be successfully modelled, and was handled using the BYPASS procedure [9] in the PLATON software suite [18].

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication No. CCDC-608784 (**5**) and CCDC-608785 (**8**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223336033; e-mail: deposit@ccdc.cam.ac.uk.

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Appendix A. Supplementary data

Full details of the X-ray crystal structures, including complete tables of crystal data, atomic coordinates, bond lengths and angles, and positional and anisotropic thermal parameters. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.08.023.

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