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Journal of Organometallic Chemistry 690 (2005) 3970–3975
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Synthesis of chiral chelating *N*-heterocyclic carbene complexes of ruthenium

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Received 13 April 2005; received in revised form 25 May 2005; accepted 26 May 2005
Available online 11 July 2005

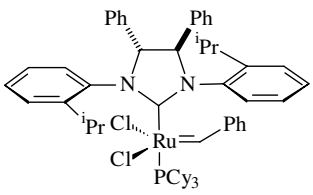
Abstract

The first 9-membered chiral chelating bidentate imidazol-2-ylidene ruthenium (II) benzylidene complexes based on a cyclopentane backbone were synthesised and characterised via NMR and HRMS.

Keywords: Chiral; Carbene complexes; Ruthenium

1. Introduction

In recent years, synthetic efforts towards transition metal complexes containing *N*-heterocyclic carbene ligands (NHC) have been the subject of intense interest [1–3]. Major stimuli for the renewed appeal of these complexes lie in their use as catalysts, where they often display significant advantages over the analogous phosphane-containing compounds [4–6]. As NHC ligands appear not to dissociate easily from the metal centre of the catalyst this makes them particularly suitable candidates for asymmetric induction reactions [7]. Development of air and moisture stable ruthenium based olefin metathesis catalysts of type **1** [8] with mixed NHC phosphane ligands have received much attention due to their increased activity when compared to the parent compound Grubbs catalyst. The literature abounds with examples of chiral monodentate NHC complexes designed for asymmetric synthesis [9,10].



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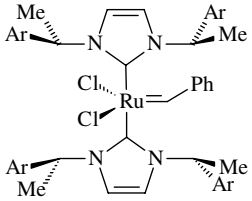

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Herrmann et al. [4] have previously demonstrated that active olefin metathesis catalysts **2** were produced by substituting monodentate NHCs for both phosphines. To date no chiral chelating bidentate NHC ruthenium alkylidene complexes have been prepared for asymmetric metathesis reactions. In contrast, highly efficient metathesis catalysts of molybdenum and tungsten have been synthesised that utilise chiral bidentate ligands. The disadvantage of these catalysts are that they require to be handled under inert atmospheres and used in anhydrous solvents [11]. With this in mind,

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doi:10.1016/j.jorganchem.2005.05.036

we began the synthesis of air stable chiral chelating NHC ruthenium alkylidene complexes with a chiral cyclopentane backbone to use in asymmetric ring closing metathesis.

2. Results and discussion

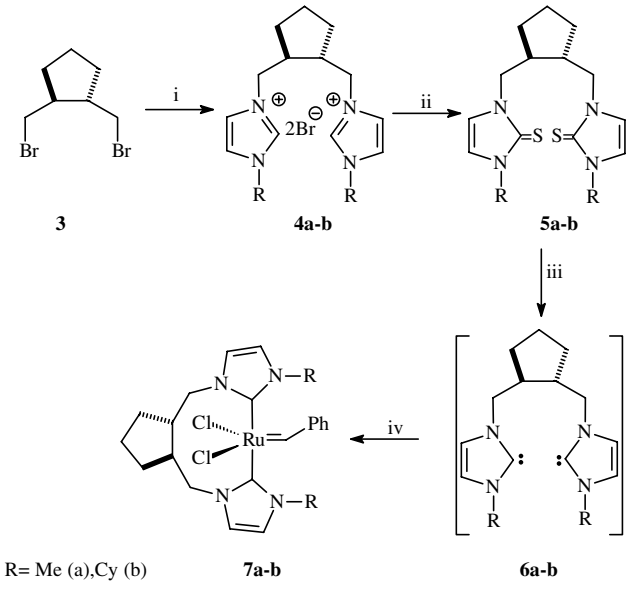
Employing methods of Yamamoto et al. [13] both enantiomers of bis(menthyl)-1,2-cyclopentanedicarboxylate were prepared [12]. Manipulation of this ester by conventional methods furnished the dibromide **3**.

When **3** was heated with 1-alkylimidazoles the salts **4a**–**b** were produced in almost quantitative yields as glassy solids. Employing modified methods by Karkhanis et al. [14] these glassy solids were converted to their corresponding bis-imidazol-2-thiones **5a**–**b** by deprotonation in the presence of sulphur (Scheme 1). The dithiones were synthesised in yields of 76–93% and characterised by HRMS and their typical C=S resonance in the ^{13}C NMR. Crystals of a phenyl derivative were obtained from methanol. Interestingly the asymmetric unit contains two independent half molecules (Fig. 1) with the same chirality (C3 and C16 with R configuration). Each complete molecule is generated by a twofold symmetry axis passing through C1 and the C3/C3^{i} (symmetry code $i = 1 - x, -y, z$) bisector for molecule A and through C14 and the C16/C16^{ii} ($ii = -x, -y, z$) bisector for molecule B.

The structure determination of the solid dithione revealed both forms of the molecule contain planar imidazol-2-thiones and a puckered cyclopentane ring. The carbon sulphur bond lengths are consistent with literature imidazol-2-thiones [15].

Reduction of the dithiones **5a**–**b**, by an alloy of potassium and sodium in hot toluene was monitored by TLC and revealed a clean reaction. After consumption of the thione, the metal sulphide by-product was filtered to leave a colourless solution of the free dicarbenes **6a**–**b**. This solution remains colourless for several hours once separated from the reducing agent. However, a deep red colour develops slowly after this time. Removal of the solvent only accelerates this colour change and subsequent analysis of the residue reveals no typical carbene signal indicating the free dicarbene is stable in solution for a few hours only. Addition of the freshly prepared colourless diimidazol-2-ylidene solution to a toluene solution of Grubbs catalyst gave access to the chelating bidentate NHC ruthenium benzylidene complexes **7a**–**b**. The deep purple colour of Grubbs catalyst in solution quickly abates to green/brown when the NHC solution was added indicating a reaction. Upon work-up of the complexation reaction the chelates were produced in yields of 60–84%, as green air-stable solids.

The chelates were characterised by NMR spectroscopy and HRMS. Although the benzylidene carbon (Ru = *C*HPh) was not detected from the ^{13}C NMR spectra, the attached proton had a resonance between 19.91 and 19.71 ppm in the ^{1}H NMR. The ^{13}C NMR spectra of **7a**–**b** revealed the configuration of the complex to be similar to catalyst **2** with the Ru–C signals at 185 ppm indicating a *trans* spanning configuration [4]. Analysis by MS gave matching isotopic distributions with that expected of the theoretical. As NHC ruthenium alkylidene complexes are known to be active metathesis catalysts, it is anticipated the chiral chelates **7a**–**b** will allow stereodifferentiating alkene metathesis reactions.



Scheme 1. Synthesis of dicarbene ruthenium complex **7a**–**b**. (i) 1-R-imidazole, (ii) DBU, S, MeOH, C_5H_5N, (iii) Na/K, MePh, (iv) $(PCy_3)_2RuCl_2CHPh$, MePh.

3. Summary

The new chiral ligands (1*S*,2*S*) and (1*R*,2*R*)-1,2-bis-(1-alkylimidazol-2-ylidene-3-methyl)cyclopentane were prepared and used in situ to synthesise the first chiral 9-membered HNC ruthenium chelates. This was achieved by elaboration of a chiral cyclopentane dibromide backbone to the bisimidazolium salt. Conversion of the salt to the crystalline bis(imidazol-2-thione) revealed existence of two forms of the molecule in the asymmetric unit with the same chirality. Reduction of the thione functionality gave access to the bis(imidazol-2-ylidene), which when reacted with Grubbs catalyst affords the air stable chiral chelating bidentate NHC ruthenium benzylidene complexes.

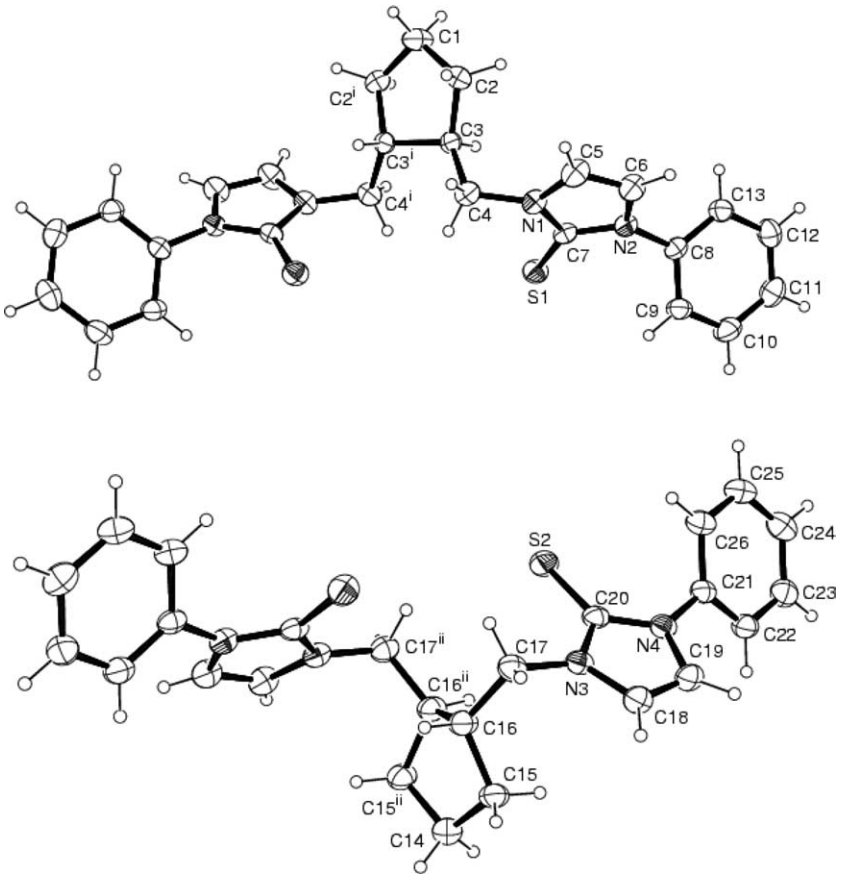


Fig. 1. ORTEP views of the two independent molecules of **5**(30% displacement ellipsoids, arbitrary spheres for H atoms). Symmetry codes: (i) $1-x$, $-y$, z, (ii) $-x$, $-y$, z. Selected bond lengths (Å) and angles (°); molecule A: N1–C7 1.356 (3), C7–S1 1.683 (3), C7–N2 1.370 (3), N1–C7–N2 105.0 (2), C4–C3–C2 114.3 (2), C4–C3–C3^{i} 113.17 (17), C4–C3–C3^{i}–C4^{i} −70.9 (3); molecule B: N4–C20 1.372 (3), C20–S2 1.686 (3), C20–N3 1.363 (3), N3–C20–N4 105.4 (2), C15–C16–C17 115.1 (2), C17–C16–C16^{ii} 117.2 (2), C17–C16–C16^{ii}–C17^{ii} −65.0 (3).

4. Experimental

4.1. General procedures

Starting materials were used as supplied by Lancaster synthesis and Aldrich without further purification. Reactions involving air sensitive reagents were carried out in an atmosphere of nitrogen or argon using standard Schlenk techniques. Toluene was dried and distilled before use from sodium and benzophenone. NMR spectra were recorded using a Bruker AC 250 spectrometer. All ^{1}H and ^{13}C NMR spectra were obtained at 250 and 62.9 MHz, respectively. Chemical shifts are reported in ppm relative to Me_4Si and were determined by reference to the residual ^{1}H or ^{13}C solvent peaks. Coupling constants, *J*, given in Hz. Infrared spectra were recorded as KBr pellets using an ATI Mattson Genesis series FTIR instrument and reported in cm^{-1}. Mass spectrometry was recorded by the EPSRC National Mass Spectrometry Service Centre, University of Wales, Swansea. Melting point determinations were carried out using a Kufler hot-stage microscope and are uncorrected. Polarimetry was carried out on a Bellingham and Stanley P20 polarimeter and the values are given in 10^{-1} deg cm^{2} g^{-1}.

4.2. Synthesis of Dichloro-(1S,2S) and (1R,2R)-1,2-bis(1-methylimidazol-2-ylidene-3-methyl)cyclopentane benzylidene ruthenium (II) **7a** and **b**

4.2.1. (1S,2S)-1,2-Bis(1-methylimidazolium-3-methyl)cyclopentane dibromide [(1S, 2S)**5a**]

A mixture of 1-methylimidazole (0.32 g, 3.9 mmol) and (1*S*, 2*S*)-1,2-Bis(bromomethyl)cyclopentane (0.5 g, 1.96 mmol) was heated at 100 °C for 6 h to give the *dibromide* salt (0.82 g, 100%) as a light yellow glass; $[\alpha]_{D}^{23}$ −17.5 (c 0.02 in H_2O); ν_{max} (KBr)/cm^{-1} 3140 (*CH*), 3101 (*CH*), 3065 (*CH*), 2955 (*CH*), 2866 (*CH*), 1449 (*CH*), 1338 (*CH*); δ_H(250 MHz; DMSO) 1.32–1.34 (2H, m, $CH_2CH_2CH_2$), 1.54–1.70 (4H, m, CH_2CH_2), 2.16 (2H, m, C*H*), 3.87 (6H, s, NCH_3), 4.05–4.32 (4H, m, NCH_2), 7.74–7.85 (4H, 2 × s, NC*H*), 9.35 (2H, s, N_2CH); δ_C(62.9 MHz; DMSO) 23.4 (CH_2), 29.2 (CH_2), 35.9 (NCH_3), 42.4 (*C*H), 51.9 (NCH_2), 122.3

(NCH), 123.6 (NCH), 136.8 (N_2CH); (ESI), 341.0 (12%, $[M - Br^{79}]^+$), 339.0 (11%, $[M - Br^{81}]^+$), 129.9 (100%, $[M - 2Br]^{2+}$).

*(1R,2R)-1,2-Bis(1-methylimidazolium-3-methyl)-cyclopentane dibromide [(1R, 2R)**5a**]*

The procedure for the synthesis of (**1*S*,2*S*)-5a** was followed using 1-methylimidazole (0.59 g, 3.9 mmol) and (1*R*,2*R*)-1,2-Bis(bromomethyl)cyclopentane (0.5 g, 1.96 mmol) to give the *dibromide* salt (1.09 g, 100%) as a light yellow glass; $[\alpha]_D^{23}$ 17.0 (c 0.02 in H_2O).

*4.2.2. (1S,2S)-1,2-Bis(1-cyclohexylimidazolium-3- methyl)-cyclopentane dibromide [(1S, 2S)**5b**]*

The procedure for the synthesis of (**1*S*,2*S*)-5a** was followed using 1-cyclohexylimidazole (0.7 g, 4.66 mmol) and (1*S*,2*S*)-1,2-Bis(bromomethyl)cyclopentane (0.6 g, 2.33 mmol) to give the *dibromide* salt (1.3 g, 100%) as a light yellow glass; $[\alpha]_D^{23}$ 5.4 (c 0.02 in H_2O); 3126 (*CH*), 3075 (*CH*), 3043 (*CH*), 2931 (*CH*), 2857 (*CH*), 1449 (*CH*), 1365 (*CH*); δ_H(250 MHz; DMSO) 1.08–1.90 (22H, m, CH_2), 2.06 (4H, m, CH_2CH_2), 2.20 (2H, m, CH), 4.09 (2H, m, NCH), 4.25 (4H, m, NCH_2), 7.90–7.93 (4H, d,*J* 7, NCH), 9.61 (2H, s, N_2CH); δ_C(62.9 MHz; DMSO) 23.4 (CH_2), 24.4 (CyCH_2), 24.5 (CyCH_2), 29.2 (CH_2), 32.4 (CyCH_2), 42.4 (CH), 52.0 (NCH_2), 58.6 (NCH), 121.2 (NCH), 122.3 (NCH), 135.1 (N_2CH). (ESI), 477.2 (100%, $[M - Br^{79}]^+$), 475.2 (98%, $[M - Br^{81}]^+$).

*(1R,2R)-1,2-bis(1-cyclohexylimidazolium-3-methyl)-cyclopentane dibromide [(1R, 2R)**5b**]*

The procedure for the synthesis of (**1*S*,2*S*)-5a** was followed using 1-cyclohexylimidazole (0.59 g, 3.9 mmol) and (1*R*,2*R*)-1,2-bis(bromomethyl)cyclopentane (0.5 g, 1.96 mmol) to give the *dibromide* salt (1.09 g, 100%) as a light yellow glass; $[\alpha]_D^{23}$ −5.6 (c 0.02 in H_2O).

*4.2.3. (1S,2S)-1,2-bis(1-methylimidazol-2-thio-3-methyl)-cyclopentane [(1S, 2S)**6a**]*

A mixture of (1*S*,2*S*)-1,2-bis(1-methylimidazolium-3-methyl)cyclopentane dibromide (1.44 g, 3.4 mmol), sulphur (0.33 g, 10.3 mmol), methanol (20 cm^3), pyridine (1.8 g, 22.8 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (2.27 g, 15.2 mmol) was heated at 65 °C for 6 h. Once cooled to room temperature the mixture was opened to water (100 cm^3) and extracted with dichloromethane (3×30 cm^3). The combined extracts were washed with 8% (aq) HCl (2×50 cm^3) before being dried over magnesium sulphate, filtered and concentrated under reduced pressure to leave an orange residue. The residue was purified by column chromatography (SiO_2, ethyl acetate, loaded as a dichloromethane solution) to give the *dithione* (0.87 g, 79%) as a colourless solid which was recrystallised from methanol to give colourless crystals; m.p. 152 °C (from methanol); $[\alpha]_D^{23}$ 36.4 (c 2.5 in CH_2Cl_2); ν_{max} (KBr)/cm^{-1} 2956 (*CH*), 2928 (*CH*), 2867 (*CH*); δ_H(250 MHz; $CDCl_3$) 1.34–1.38 (2H, m, $CH_2CH_2CH_2$), 1.54–1.60 (2H, m, CH_2CH_2), 1.71–1.79 (2H, m, CH_2CH_2) 2.30–2.32 (2H, m, CH), 3.54 (6H, s, NCH_3), 3.84–3.90 (2H, dd, *J* 4.8 and 5.3, NCH_2), 3.98–4.08 (2H, dd,*J* 5.3 and 4.8, NCH_2), 6.62 (2H, s, NCH), 6.82 (2H, s, NCH); δ_C (62.9 MHz; $CDCl_3$) 23.9 (CH_2), 30.4 (CH_2), 35.2 (NCH_3), 43.1 (CH), 51.7 (NCH_2), 117.5 (NCH), 117.7 (NCH), 162.3 (C=S; *m/z* (ESI) 323.1363 $[M + H]^+$), $C_{15}H_{22}N_4S_2$requires 323.1364, (ESI), 323.1 (100%, $[M + H]^+$).

*(1R,2R)-1,2-bis(1-methylimidazol-2-thio-3-methyl)-cyclopentane [(1R, 2R)**6a**]*

The procedure for the synthesis of **[(1*S*, 2*S*) 6a]** using (1*R*,2*R*)-1,2-bis(1-methylimidazolium-3-methyl)cyclopentane dibromide (0.77 g, 1.84 mmol), sulphur (0.18 g, 5.53 mmol), methanol (10 cm^3), pyridine (0.9 g, 11.0 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (1.21 g, 8.10 mmol) gave the *dithione* (0.45 g, 76%) as colourless crystals; m.p. 154 °C (from methanol); $[\alpha]_D^{25}$ −35.8 (c 1.0 in CH_2Cl_2).

*4.2.4. (1S,2S)-1,2-bis(1-cyclohexylimidazol-2-thio-3-methyl) cyclopentane [(1S, 2S)**6b**]*

The procedure for the synthesis of **[(1*S*, 2*S*) 6a]** using (1*S*,2*S*)-1,2-bis(1-cyclohexylimidazolium-3-methyl)cyclopentane dibromide (1.18 g, 2.12 mmol), sulphur (0.20 g, 6.35 mmol), methanol (15 cm^3), pyridine (1.5 g, 19 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (1.41 g, 9.42 mmol) gave the residue, which was purified by column chromatography (SiO_2, ethyl acetate: petroleum ether-1:1, loaded as a dichloromethane solution) to give the *dithione* (0.90 g, 93%) as a colourless solid; m.p. 86 °C; $[\alpha]_D^{24}$ 31.42 (c 1.5 in CH_2Cl_2); ν_{max} (KBr)/cm^{-1} 2927 (*CH*), 2854 (*CH*); δ_H(250 MHz; $CDCl_3$) 1.06–1.94 (26H, m, CH_2), 2.22–2.30 (2H, m, CH), 3.78–4.03 (4H, dddd, *J* 6, 7.5 and 11, NCH_2), 4.54–4.63 (2H, m, NCH), 6.62 (2H, d,*J* 2.3, NCH), 6.78 (2H, d,*J* 2.3, NCH); δ_C(62.9 MHz; $CDCl_3$) 23.77 (CH_2), 25.3 (CyCH_2), 25.4 (CyCH_2), 30.3 (CH_2), 32.5 (CyCH_2), 42.3 (CH), 50.9 (NCH_2), 56.1 (NCH), 113.7 (NCH), 117.6 (NCH), 160.8 (C=S); *m/z* (ESI) 459.2616 ($[M + H]^+$, $C_{25}H_{38}N_4S_2$requires 459.2616), (FAB), 481.4 (23%, $[M + Na]^+$), 459.4 (100%, $[M + H]^+$), 458.4 (76%, $[M]^+$).

*(1R,2R)-1,2-bis(1-cyclohexylimidazol-2-thio-3-methyl)-cyclopentane [(1R, 2R)**6b**]*

The procedure for the synthesis of **[(1*S*, 2*S*) 6a]** using (1*R*,2*R*)-1,2-bis(1-cyclohexylimidazolium-3-methyl) cyclopentane dibromide (1.03 g, 1.86 mmol), sulphur (0.18 g, 5.53 mmol), methanol (10 cm^3), pyridine (0.9 g, 11.13 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (1.23 g, 8.11 mmol) gave the residue, which was purified by column chromatography (SiO_2, ethyl acetate: petroleum ether-1:1, loaded as a dichloromethane solution) to give the *dithione* (0.81 g, 95%) as a colourless solid; m.p. 86 °C; $[\alpha]_D^{25}$ −30.23 (c 1.2 in CH_2Cl_2).

4.2.5. Dichloro(1S,2S)-1,2-bis(1-methylimidazol-2-ylidene-3-methyl)cyclopentane benzylidene ruthenium (II) [(1S, 2S)7a]

Oil free sodium (86 mg, 3.7 mmol) and potassium (0.33 g, 8.37 mmol) was heated gently under vacuum to yield an alloy. To this alloy was added (1*S*,2*S*)-1,2-bis(1-methylimidazol-2-thio-3-methyl)cyclopentane (0.2 g, 0.62 mmol) and toluene (20 cm^3). The suspension was heated to 60 °C for 4 h before cooling to room temperature. The colourless dicarbene solution was filtered from the solid metal sulphide residue and had Dichlorotris(tricyclohexylphosphine)benzylidene ruthenium (II) (0.46 g, 0.56 mmol) in toluene (30 cm^3) added. An immediate colour change was observed. The mixture was stirred at room temperature for 3 h, filtered and concentrated to ~1 cm^3. Addition of petroleum ether (10 cm^3) resulted in a green precipitate, which was filtered, dissolved in toluene and reprecipitated by petroleum ether. This procedure was repeated three times to give the *bidentate carbene complex*(0.25 g, 84%) as a green solid; m.p. 215 °C (decomp); ν_{max} (KBr)/cm^{-1} 2935 (*CH*), 2863 (*CH*), 2852 (*CH*); δ_H(250 MHz; $CDCl_3$) 1.23–2.28 (8H, m, CH_2, C*H*), 3.47 (6H, s, NCH_3), 3.54–4.25 (4H, m, NCH_2), 6.91 (2H, s, NC*H*), 6.99 (2H, s, NC*H*), 7.25–7.48 (4H, m, Ar*H*), 8.26 (1H, d,*J* 7.5, Ar*H*), 19.91 (1H, s, Ru=C*H*); δ_C(62.9 MHz; $CDCl_3$) 26.4 (*C*H_2), 26.8 (*C*H_2), 27.0 (*C*H_2), 34.8 (*C*H), 35.8 (*C*H) 38.1 (N*C*H_3), 45.4 (N*C*H_2), 122.5 (N*C*H), 122.6 (N*C*H), 123.4 (N*C*H), 123.6 (N*C*H), 126.5 (C_p), 127.6 ($C_{o/m}$), 128.7 ($C_{o/m}$), 153.2 (C_i), 185.4 (N_2*C*Ru); *m/z* (ESI) 485.1052 ($[M-Cl]^+$, $C_{22}H_{28}N_4RuCl$ requires 485.1046), (ESI), 485.1 (100%, $[M-Cl]^+$).

Dichloro(1R,2R)-1,2-bis(1-methylimidazol-2-ylidene-3-methyl)cyclopentane benzylidene ruthenium (II) [(1R, 2R)7a]

The procedure for the synthesis of **[(1*S*, 2*S*) 7a]** was followed using sodium (43 mg, 1.9 mmol), potassium (0.16 g, 4.09 mmol), (1*R*,2*R*)-1,2-bis(1-methylimidazol-2-thio-3-methyl)cyclopentane (0.1 g, 0.31 mmol) in toluene (10 cm^3) and Dichlorotris(tricyclohexylphosphine)benzylidene ruthenium (II) (0.23 g, 0.28 mmol) in toluene (15 cm^3) to give the *bidentate carbene complex*(0.12 mg, 81%) as a green solid.

4.2.6. Dichloro(1S,2S)-1,2-bis(1-cyclohexylimidazol-2-ylidene-3-methyl)cyclopentane benzylidene ruthenium (II) [(1S, 2S)7b]

The procedure for the synthesis of **[(1*S*, 2*S*) 7a]** was followed using sodium (60 mg, 2.6 mmol), potassium (0.23 g, 5.9 mmol), (1*S*,2*S*)-1,2-bis(1-cyclohexylimidazol-2-thio-3-methyl)cyclopentane (0.2 g, 0.44 mmol) in toluene (30 cm^3) and Dichlorotris(tricyclohexylphosphine)benzylidene ruthenium (II) (0.33 g, 0.4 mmol) in toluene (30 cm^3) to give the *bidentate carbene complex*(0.17 g, 63%) as a light green solid; m.p. 180 °C (decomp); ν_{max} (KBr)/cm^{-1} 2927 (*CH*), 2854 (*CH*); δ_H(250 MHz; $CDCl_3$) 1.10–2.45 (28H, br m, CH_2, C*H*), 4.06 (4H, br m, NCH_2), 4.58 (2H, br m, NC*H*), 6.96 (2H, s, NC*H*), 6.99 (2H, s, NC*H*), 7.25–7.55 (4H, m, Ar*H*), 8.26 (1H, br m, Ar*H*), 19.71 (1H, s, Ru=C*H*); δ_C(62.9 MHz; $CDCl_3$) 25.4 (*C*H_2), 25.7 (*C*H_2), 25.9 (*C*H_2), 29.9 (*C*H_2), 30.0 (*C*H_2), 30.5 (*C*H_2), 30.6 (*C*H_2), 34.8 (*C*H_2), 34.9 (*C*H_2), 45.6 (*C*H), 46.8 (*C*H), 54.2 (N*C*H_2), 54.6 (N*C*H_2), 59.0 (N*C*H), 59.1 (N*C*H) 118.4 (N*C*H), 118.6 (N*C*H), 124.0 (N*C*H), 124.1 (N*C*H), 128.9 ($C_{o/m}$), 129.3 (C_p), 130.1 ($C_{o/m}$), 131.4 ($C_{o/m}$), 153.5 (C_i), 185.9 (N_2*C*Ru); *m/z* (ESI) 621.2310 ($[M-Cl]^+$, $C_{32}H_{44}N_4RuCl$ requires 621.2298), (ESI), 621.2 (100%, $[M-Cl]^+$).

Dichloro(1R,2R)-1,2-bis(1-cyclohexylimidazol-2-ylidene-3-methyl)cyclopentane benzylidene ruthenium (II) [(1R, 2R)7b]

The procedure for the synthesis of **[(1*S*, 2*S*) 7a]** was followed using sodium (18 mg, 0.8 mmol), potassium (64 mg, 1.64 mmol), (1*R*,2*R*)-1,2-bis(1-cyclohexylimidazol-2-thio-3-methyl)cyclopentane (56 mg, 0.12 mmol) in toluene (10 cm^3) and Dichlorotris(tricyclohexylphosphine)benzylidene ruthenium (II) (100 mg, 0.12 mmol) in toluene (10 cm^3) to give the *bidentate carbene complex* (48 mg, 60%) as a light green solid.

4.3. X-ray structure analysis

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 265305. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, fax: +44 0 1223 336033, or e-mail: deposit@ccdc.cam.ac.uk. Crystal data for **5**: empirical formula $C_{25}H_{26}N_4S_2$, formula weight 446.64, temperature 298 (2) K, wavelength 0.71073 Å, orthorhombic, space group $P2_12_12$ (No. 18), unit cell dimensions a = 12.6595 (7) Å, b = 17.5962 (9) Å, c = 10.41211 (5) Å, V = 2319.4 (2) $Å^3$, Z = 4, D_c = 1.279 Mg m^{-3}, absorption coefficient 0.249 mm^{-1}, F(000) = 944, crystal size 0.52 × 0.24 × 0.22 mm, theta range for data collection 1.98–25.01°, index ranges $-11 \Leftarrow h \Leftarrow 15$, $-20 \Leftarrow k \Leftarrow 20$, $-12 \Leftarrow l \Leftarrow 12$, reflections collected 13 123, independent reflections 4094 [R_{int} = 0.031], completeness to θ = 25.01°, 99.7%, max. and min. transmission = 0.881 and 0.947, refinement method full-matrix least-squares on F^2, data/restraints/parameters 4094/0/281, goodness-of-fit on F^2 = 0.962, final R indices [$I > 2\sigma(I)$], R_1 = 0.036, wR_2 = 0.083, R indices (all data), R_1 = 0.053, wR_2 = 0.088, absolute structure parameter −0.04 (9), largest diff. peak and hole 0.36 and −0.16 e $Å^{-3}$.

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