Chiral Ag(i) and Pt(II) complexes of ditopic NHC ligands: synthesis, structural and spectroscopic properties†‡

Paul Marshall, a Robert L. Jenkins, a William Clegg, b Ross W. Harrington, b Samantha K. Callear, c Simon J. Coles, a Ian A. Fallis a and Athanasia Dervisi* c

Received 31st July 2012, Accepted 6th September 2012
DOI: 10.1039/c2dt31740k

The butyl and isopropyl derivatives (4I, 5Br) of chiral pool derived bis-imidazolium dehydrohexitol salts have been prepared. The ditopic N-heterocyclic carbene 4 and 5 form dinuclear Ag(i) and Pt(II) complexes. All compounds were fully characterised by multinuclear NMR spectroscopy. The bis-imidazolium salt 4I and platinum complexes cis-[Pt₂(μ-2)(dmso)₂Cl₄] and cis-[Pt₂(μ-4)(dmso)₂Cl₄] were characterised by X-ray crystallography. In the case of the Pt(II) complexes, the carbene ring is positioned in a sterically preferred orientation, approximately perpendicular to the platinum coordination plane. The 1H, 13C, 15N and 195Pt NMR spectra of the platinum complexes show the presence of rotamers due to hindered rotation about the carbene–metal bond.

Introduction

N-Heterocyclic carbene (NHC) ligands and their transition metal complexes have established themselves as a cornerstone of modern coordination chemistry and are now used in a wide range of applications. Platinum(II)–NHC complexes in particular catalyse a number of important reactions, such as hydroisylations, 1 hydroaminations, 2 tandem hydroboration-cross-coupling reactions 3 and diboration of unsaturated molecules. 4 Platinum(II)–NHC complexes have also seen recent activity in medicinal applications as possible chemotherapeutic agents. 5 Thus efficient syntheses of platinum–NHC complexes are of considerable current interest. Synthetic routes to Pt–NHC complexes include direct reaction of the carbene precursor in the presence of base, 6, 9, 10 6 of the free carbene, with suitable platinum salts. 7 Alternatively, transmetalation of Ag–NHC complexes with a platinum source is also known. 8 Silver(i) carbenes are extensively used as ligand transfer agents for the majority of imidazolium and other azolium salts, forming a part of a convenient, and sometimes the only, route for the synthesis of metal carbene complexes. 9 Ag(i)–NHC complexes have also found many medicinal applications, mainly due to their activity as antimicrobials. 10 Other potential uses include high-end materials applications, such as luminescent chemosensors. 11 Silver–carbene complexes are structurally diverse, displaying a broad range of coordination motifs, ranging from simple two-coordinate linear molecules 9c, 12 to helicates, 13 polymers, 14 rings, 15 cages 16 and clusters. 17

Based on our previously reported chiral pool derived dehydrohexitol framework precursor 1, 18 we recently described an efficient method leading to the bis-carbene precursor imidazolium salts 2X (Scheme 1) with 2,5-exo stereochemistry. 19 The endo and exo stereochemistry refers to the substitution with respect to the bent V-shaped core of the fused dehydrohexitol ring. Here we report the synthesis of the isopropyl- and butyl-imidazole derivatives (4X and 5X) following an alternative synthetic route and expand on the coordination chemistry for this family of bridging NHC ligands, to include examples of their Pt(II) complexes.

Discussion

The 2,5-exo-bisimidazole 3 was prepared from the reaction of ditosylate 1 with imidazole in dmf in the presence of Cs₂CO₃ (Scheme 1). Subsequent quaternisation with the corresponding alkyl halide afforded the bis-isopropyl- and butyl-imidazolium salts 4I and 5Br. Following counterion metathesis with potassium hexafluorophosphate in water, 4PF₆ is furnished as a crystalline white solid and 5PF₆ as a colourless viscous ionic liquid. The imidazolium salts have the expected exo stereochemistry at the 2 and 5 positions of the bicyclic ring as in the parent hexitol, L-iditol. The dicaticon salts are readily soluble in water and...
polar organic solvents such as lower alcohols, acetone, acetonitrile and dmso. Single crystals of 4I suitable for X-ray studies were grown from an acetonitrile solution of the salt, and the structure of the cation is shown in Fig. 1.

Silver(I) complexes

The silver(I) complexes of carbenes 4 and 5 were prepared from the reaction of Ag₂O with the corresponding imidazolium salts, 4I, 4PF₆ and 5Br. NHC carbenes 4 and 5 form the bridged metallacyclic dinuclear silver complexes, [Ag₂(μ-NHC)₂][X]₂ shown in Scheme 1, irrespective of the metal to ligand ratio and type of counterion used. The analogous methyl-imidazolyl complex [Ag₂(μ-2)₂][PF₆]₂ and its solid-state structure has been reported previously by us.¹⁹ Unfortunately, the isopropyl and butyl derivatives, 6I and 7Br, did not afford good crystals of sufficient quality to allow for their X-ray structure determinations. As was the case for NHC ligand 2, the neutral acyclic bis-monocarbene complexes (11) were not observed. Electro-spray mass spectra show maximal mass peaks at m/z 1001 and 1009 for the silver metallacycle complexes, 6I and 7Br respectively, corresponding to loss of one of the counterions from the parent compound, [Ag(μ-NHC)₂][X]₂. In the ¹³C NMR spectra of the silver complexes the carbene resonance appears as a sharp

Scheme 1 Reagents and conditions. (a) N-Methylimidazole, 140 °C; (b) Cs₂CO₃, dmf, 100 °C; (c) 4I: excess isopropylbromide, CH₃CN, reflux, 5Br: excess butylbromide, dmf, 100 °C; (d) excess KPF₆, H₂O; (e) Ag₂O, CH₂Cl₂, room temperature, 2 days; (f/g) K₂PtCl₄ or PtCl₂, NaOAc, dmso, 70 °C, 2 days.

Fig. 1 Displacement ellipsoid plot at the 50% probability level of the bis-imidazolium cation of 4I. The iodide anions are omitted for clarity. Selected bond lengths (Å) and angles (°): N1–C2 1.333(5), C2–N3 1.341(5), N17–C18 1.331(5), C18–N19 1.329(5), N1–C2–N3 109.3(4), N17–C18–N19 109.3(5).
singlet at δ 180.6 ppm for 6I and δ 181.6 ppm for 7Br. Coupling to
$^{107}\text{Ag}$ or $^{109}\text{Ag}$ was unobserved in both cases. Silver–carbene
complexes have been used previously in transmetallation reac-
tions with platinum(II) salts to afford the corresponding Pt(NHC)
complexes. In the case of the silver complex 7Br reaction
with Pt(cod)Cl$_2$ afforded mixtures of Pt(II)-containing species
and partially protonated carbene ligand.

Platinum(II) complexes

In order to avoid time- and resource-consuming routes, the plati-
num complexes 8–10 were prepared directly from the reaction of
the corresponding ligand salts (2PF$_6$, 4PF$_6$, and 5PF$_6$) with
PtCl$_2$ or K$_2$PtCl$_4$ in quantitative yields (Scheme 1). Reactions
were carried out in the presence of NaOAc in dmso, under
aerobic conditions using unpurified technical grade solvent.
Reactions in other solvents, e.g. dma ($N,N'$-dimethylacetamide),
afforded complex mixtures of intractable products. The above
synthetic procedure afforded the bis-monocarbene complexes,
cis-[Pt$_2$(μ-NHC)(dmso)$_2$Cl$_4$], regardless of the metal to ligand
ratio used. Relatively small differences in the chemical shifts of
proton resonances, however, is seen for the platinum complexes,
supporting the existence of three isomers in solution, is
the appearance of four distinct doublets for one of the imidazo-
lyl proton resonances, with one doublet for each of the C$_2$
metric isomers and two doublets for the C$_1$ symmetric isomer.
In addition, the two methyl groups of the coordinated dmso
are diastereotopically inequivalent, as of course are the methyls
on the isopropyl group of 9. In an attempt to simplify the
1H NMR spectra, a dmso-$d_6$ solution of complex 8 was heated
to 100 °C. However, no significant changes in the chemical
shifts were observed, leading us to conclude that a high barrier
to rotation about the Pt–C$_{\text{NHC}}$ bond also exists for these
complexes.

Solution NMR measurements

Relatively small changes are observed in the 1H NMR spectra
for the hydrogen atoms of the proligands of 2, 4 and 5 upon
coordination to silver(I). More pronounced deshielding of the
proton resonances, however, is seen for the platinum complexes,
most likely due to the divalent metal. Notably, there are large
downfield shifts of the methine protons (H$_{2,5}$) adjacent to the
imidazolyl nitrogen atoms from ca. δ 5.1 ppm (CD$_3$CN) in the
imidazolyl salts to δ 5.9–6.1 ppm (CD$_3$CN) in the coordinated
ligands. A large downfield shift is also observed for the iso-
propyl methine proton of 9, from δ 4.73 ppm in 41 to 5.63 ppm
(CD$_3$CN).

Restricted rotation about the C–Pt bond

The 1H and 13C NMR spectra of the platinum complexes, 8–10,
reveal more than one isomers present in solution which have
been attributed to rotamers arising from restricted rotation about
the Pt–C$_{\text{NHC}}$ bond. High metal–carbene rotation barriers (>92 kJ
mol$^{-1}$) have been observed for Rh(II)- and Ir(III)-NHC systems
and attributed mainly to steric effects. Similarily, for Pt(NHC)
(dmso)Cl$_2$-type complexes Rourke et al. have reported barriers
to rotation in excess of 85 kJ mol$^{-1}$.a

In the case of the dinuclear complexes, 8–10, there are three
possible rotamers arising from slow rotation about the Pt–C$_{\text{NHC}}$
bond; two of C$_2$ symmetry with the dmso ligands either
in (isomer A, Scheme 1) or out (isomer B) with respect to the
dehydrohexitol core, and one of C$_1$ symmetry with in and out
dmso ligands (isomer C). All three rotamers of 8–10 were
observed in different ratios, although due to the complexity of
the overlapping signals, these rotamers could not be individually
assigned. One common feature in the spectra of the complexes
in the corresponding 195Pt NMR spectra. For com-
parision, the δ$_{195\text{Pt}}$ reported for the related carbene complexes,
[Pt(NHC)(dmso)Me$_2$], are in the region of −3900 to
−4000 ppm. The effect of the different N-imidazolyl substitu-
tests (Me, iPr, Bu) of complexes 8–10 on the 195Pt NMR chemi-
shifts (δ$_{195\text{Pt}}$) is negligible. This is in agreement with reports for other PtCl$_2$ systems, such as those of chelating dipyr-
dyl ligands. Due to solubility limitations, different solvents
were used for each complex during these measurements
(dmso-$d_6$ for 8, CD$_3$CN for 9 and CD$_3$Cl$_2$ for 10). Contrary to
previous observations, where large Δδ$_{195\text{Pt}}$ of ca. 400 ppm were
observed with changes in the solvent from CD$_3$Cl$_2$ to dmso-$d_6$, there
were no significant solvent effects observed for complexes
8–10.a

1H–15N HMBC spectra were also collected for the platinum
complexes. In most cases analyses of the cross-peaks in the two-
dimensional spectra provided a means of differentiating and
assigning the two non-symmetrically substituted imidazolyl
15N resonances. Relatively small differences in the chemical
shifts of the imidazolyl derived nitrogens were observed (Δδ
15N), with the largest Δδ
15N, observed for complex 9 at 16 ppm and the
smallest for complex 10. In this case, the two 15N resonances centred
at 204.5 ppm remained unresolved. Although the signals for N$^0$
and N$^R$ in the 15N dimension of the spectra for 8–10 were not
resolved further, the presence of rotamers is implied after inspec-
tion of the cross-section of the peaks in the 2D-spectra (where
N$^0$ represents the nitrogen atom next to the oxolane ring and
N$^R$ the one next to the corresponding alkyl substituent).

Solid state structures of the Pt(II) complexes. The solid-state
structures of platinum complexes 8 and 9 were determined by
synchrotron X-ray crystallography. Complexes 8 and 9 adopt
the same C$_2$ symmetric spatial arrangement shown in Fig. 2, with
complex 9 containing a true C$_2$ crystallographic axis. The two
platinum centres are trans to each other, facing away from the
Experimental

General remarks

All manipulations were performed using standard glassware under aerobic conditions, except where otherwise noted. Solvents of analytical grade and deuterated solvents for NMR measurements were used as received. Literature methods were employed for the synthesis of $^{19}$F and Ag$_2$O. All other reagents were used as received. Ether means diethyl ether and dmf dimethylformamide unless specified otherwise. NMR spectra were obtained on Bruker Avance AMX 250, 400, 500, 600 (QCI Quadruple Resonance CryoProbe) or Jeol Eclipse 300 spectrometers. The chemical shifts are given as dimensionless $\delta$ values and are frequency referenced relative to TMS for $^1$H and $^{13}$C and Na$_2$PtCl$_6$ for $^{195}$Pt. For $^1$H–$^{15}$N heteronuclear multiple-bond correlation (HMBC) experiments, CH$_3$NO$_2$ was used as the standard for the $^{15}$N chemical shifts ($\delta = 381.7$ vs. liquid NH$_3$). In the HMBC experimental, N$^\delta$ stands for the alkyl substituted nitrogen of the imidazole ring and N$^\gamma$ for the one next to the dioxolane ring.

Coupling constants $J$ are given in hertz (Hz) as positive values regardless of their real individual signs. The multiplicity of the signals is indicated as s, d, or m for singlets, doublets, or multiplets, respectively. The abbreviation br is given for broadened signals. Mass spectra and high-resolution mass spectra were obtained in electrospray (ES) mode unless otherwise reported, on a Waters Q-Tof micromass spectrometer. IR spectra were measured on a JASCO 660plus FT-IR spectrometer from 4000 to 600 cm$^{-1}$.

1,4:3,6-Dianhydro-2,5-dideoxy-2,5-bisimidazole-$\alpha$-iditol, 3. I (9.1 g, 20.0 mmol) was dissolved in dmf (20 mL). Imidazole (2.9 g, 42.9 mmol) and caesium carbonate (16.3 g, 50.0 mmol) were added to the solution and the reaction temperature maintained at 100 °C for 1 day. A saturated brine solution (150 mL) was added to the reaction vessel and stirred until the yellow solid that formed had dissolved. The product was extracted with dichloromethane (3 × 50 mL) and dried over MgSO$_4$. The solution was filtered and solvent removed by reduced pressure to leave a white solid. The solid was washed with ether and dried. Yield: 3.9 g, 79%. $^1$H NMR (250 MHz, dmso-d$_6$): 4.17 (dd, $J = 10.5, 2.4$, 1H, endo-$H^{1,6}$), 4.25 (dd, $J = 10.5, 4.9$, 1H, exo-$H^{1,6}$), 4.75 (s, 1 H, $H^{3,4}$) 4.87 (dd, $J = 4.7, 2.4$, 1H, $H^{2,1}$), 7.01 (d, $J = 1.0$, 1H, imid-H) 7.02 (d, $J = 1.0$, 1H, imid-H), 7.45 (s, 1H, C$_{NHIC}$H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ ppm 63.00 (C$_2$/5), 72.75 (C$_{CIC}$). $^{15}$N NMR (from $^1$H–$^{15}$N HMBC, 600 MHz, CDCl$_3$) $\delta$ ppm $-122.5$ (N$^\delta$), 191.2 (N$^\gamma$). MS (AP$^+$) m/z (%): [M$^+$, [C$_{12}$H$_2$N$_2$O$_2$]$^+$] $^\dagger$ 247.1195; measured: 247.1183 (100); [MH + $C\text{H}_3\text{CN}^+$]$^\dagger$, 288.1459.

1,4:3,6-Dianhydro-2,5-dideoxy-2,5-bis(isopropyl imidazolium)-$\alpha$-iditol iodide, 4I. The bis-imidazole 3 (1.4 g, 5.7 mmol) was dissolved in acetonitrile (15 mL), followed by the addition of isopropyliodide (1.5 mL, 15.0 mmol). The mixture was refluxed for 1 day and subsequently left to cool to room temperature. The product crystallized out of the reaction solution and was subsequently filtered under suction and dried in air. Yield: 2.6 g, 69%. $^1$H NMR (400 MHz, D$_2$O): $\delta$ ppm 1.44

...
(d, 6H, J = 6.7, CHMe₂), 4.30 (m, 2H, H⁻¹⁶), 4.56 (m, 1H, CHMe₂), 5.10 (s, 1H, H⁻²⁵), 5.15 (m, 1H, H⁻²⁵), 7.45 (br s, 1H, imid-H), 7.55 (br s, 1H, imid-H), 8.86 (s, 1H, C=NHC). ¹³C NMR (125 MHz, D₂O) δ ppm 22.1 (CHMe₂), 53.9 (CHMe₂), 65.0 (C⁻²⁵), 72.1 (C⁻¹⁷), 87.3 (C⁻³⁴), 121.3 (imid-C), 121.7 (imid-C), 134.0 (C=NHC). MS (ES⁺) m/z: [M − H⁻]⁻, [C₆H₃N₂O₄]⁻ 119.95 (imid-C), 120.76 (imid-C), 180.62 (s, C=NHC). MS (ES⁺, CNH₃): m/z (%), calcd mass for [M − CNH₃]⁻ = C₆H₃N₂O₄−177: 177.0134; measured: 177.0133 (100).

Preparation of [Ag₂(µ-4)][PF₆]₄. 4PF₆ (0.310 g, 0.50 mmol) was dissolved in acetonitrile (1 mL). Silver(i) oxide (0.115 g, 0.5 mmol) was added to the solution along with sodium bromide (0.27 g, 2.67 mmol) and the mixture heated to 100 °C for 1 day. The solvent was removed to leave a waxy light yellow solid. Yield: 0.443 g, 76%. ¹¹H NMR (400 MHz, dmso-d₆): δ ppm 1.44 (d, J = 6.7, 6H, CHMe₂), 1.45 (d, J = 6.4, 6H, CHMe₂), 4.32 (dd, J = 10.5, 5.3, 2H, endo-H⁻¹⁸), 4.45 (br s, J = 10.5, 2H, exo-H⁻¹⁸), 4.72 (m, 2H, CH₂Me₂), 4.95 (s, 2H, H⁻³⁴), 5.29 (br s, 2H, H⁻³⁴), 7.50 (d, J = 1.8, 2H, imid-H), 7.70 (d, J = 1.8, 2H, imid-H); MS (ES⁺, CH₃CN): m/z (%), calcd mass for [M − PF₆]⁻ = C₆H₃N₂O₄−14PF₆⁻: 1019.185,5 measured 1019.1844 (100), 1033.1464 (15).

Preparation of [Ag₂(µ-5)][Br₂]₂. 7Br. The imidazolium salt 5Br (0.390 g, 0.75 mmol) was dissolved in 30 mL of CHCl₃ and Ag₂O (0.75 mmol) was added to the solution. After two hours the complex separated from the solution as an opaque oil. Volatiles were evaporated and the oil obtained was dissolved in CHCl₃ with heating, filtered through celite and dried. Yield: 0.557 g, 68%. ¹¹H NMR (400 MHz, CDCl₃) δ ppm 0.86 (t, J = 7.4, 6H, Me), 1.27 (m, J = 7.4, 4H, CH₂), 1.73 (m, 4H, CH₂), 4.08 (t, J = 7.2, 4H, NCH₂), 4.24 (dd, J = 11.0, 2.3, 2H, endo-H⁻¹⁸), 4.34 (dd, J = 11.0, 5.0, 2H, exo-H⁻¹⁸), 4.97 (s, 2H, H⁻³⁴), 5.20 (dd, J = 5.0, 2.3, 2H, H⁻³⁴), 7.02 (d, J = 2, 2H, imid-H), 7.13 (d, J = 2, 2H, imid-H); ¹³C NMR (75 MHz, CDCl₃) δ ppm 13.57 (CH₃), 19.64 (CH₂), 32.02 (CH₂), 50.20 (NCH₂), 64.96 (C⁻²⁵), 72.34 (C⁻¹⁷), 87.17 (C⁻³⁴), 122.24 (CH), 122.93 (CH), 136.8 (C=NHC). ¹⁵N NMR (from ¹H-¹⁵N HMBC, 600 MHz, CDCl₃) δ ppm 201.0 (N⁺), 202.3 (N³⁻). MS (ES⁺) m/z: [M + Br⁻]⁻, [C₂₀N₂H₂Br₂N₄O₇]⁻: 439.17 (30). Anal. Caled for C₂₀N₂H₂Br₂N₄O₇: C, 46.17; H, 6.20; N, 10.77. Found: C, 46.07; H, 6.23; N, 10.66.

1,4:3,6-Dianhydro-2,5-dideoxy-2,5-bis(3-butyl imidazolium)-l-iditol hexafluorophosphate (4PF₆). An aqueous solution of KPF₆ (2.2 g, 12.0 mmol) was added slowly to a 20 mL aqueous solution of the bis-bromide salt 5Br (0.527 g, 1.0 mmol). The reaction mixture was stirred at that temperature for 3 days. The reaction mixture was warmed to 70 °C, and solution separated from the solution as a colourless oil. This was collected and dried to afford 0.353 g of the product. Yield: 0.353 g, 54%. ¹¹H NMR (250 MHz, acetone-d₆) δ ppm 0.96 (t, J = 7.5, 3H, CH₃), 1.39 (m, 2H, CH₂), 1.96 (m, J = 7.5, 2H, CH₂), 4.40 (t, J = 7.5, 2H, NCH₂), 4.52 (m, J = 2.2, 2H, H⁻³⁴), 5.33 (s, 1H, H⁻²⁵), 5.42 (m, 1H, H⁻²⁵) 7.83 (m, J = 1.9, 1H, imid-H), 7.90 (m, 1H, imid-H), 9.20 (s, 1H, C=NHC). MS (ES⁺) m/z: [M + Br⁻]⁻, [C₆H₁₀N₂Ag₂Br₃O₇]⁻: 1009.2023; measured: 1009.1985 (30). For the ¹H and ¹³C NMR spectra of the platinum complexes, 8–10 reported below, signals for all 3 observed isomers are reported with individual peaks not assigned to a specific isomer.

Preparation of cis-[Pt(µ-5)(dmso)Cl₂], 8. 2PF₆ (0.187 g, 0.33 mmol), K₂PtCl₆ (0.278 g, 0.67 mmol) and NaOAc (0.057 g, 0.70 mmol) were dissolved in 1 mL of dmso at 70 °C. The reaction mixture was stirred at that temperature for 3 days. The solution was dried under vacuum and the yellowish solid obtained was washed three times with methanol and subsequently dried. The white solid obtained was recrystallised by diffusion of hexane into a dichloromethane solution to afford block colourless plates of the product. Yield: 0.300 g (94%). ¹¹H NMR (400 MHz, CDCl₃) δ ppm 3.43/3.45/3.47/3.51/3.52/3.53 (s, 12H, Me₂SO), 3.96/3.97/3.97/3.98 (s, 6H, Me), 4.14 (dd,
Preparation of cis-[Pt2(μ-4)(dmso)Cl4], 9. In a round bottom flask, K2PtCl4 (0.278 g, 0.67 mmol) and 4PF6 (0.208 g, 0.33 mmol) were dissolved in 2 mL of dmso. NaOAc (0.057 g, 0.70 mmol) was subsequently added, and the mixture heated to 70 °C for 1 day. The solution was dired in a Kugelrohr under vacuum and the yellowish solid obtained was extracted with CHCl3. The yellowish oil obtained was extracted with CHCl3 (2 × 2.5 days). The pale yellow solution was dried under vacuum and was subsequently added, and the mixture heated to 65 °C for 70 °C for 1 day. The solution was dried in a Kügelrohr under vacuum and the yellowish solid obtained was extracted with CHCl3.

X-ray crystallography

Data for 4I were measured at 120 K on a Bruker Nonius KappaCCD diffractometer at the window of a Bruker Nonius FR591 rotating anode (λMo-Kα = 0.71073 Å) driven by COLLECT and processed by DENZO software. The structure was determined in SHELXS-97 and refined using SHELXL-97. Data for 8 and 9 were obtained from very small and weakly diffracting crystals by use of synchrotron radiation (λ = 0.6889 Å) at 120 K, with a Crystal Logics kappa diffractometer and Rigaku Saturn 724+ CCD detector at beamline I19 of Diamond Light Source; software was Rigaku CrystalClear, and Bruker APEX21 and SHELXTL.29 Key crystallographic data are shown in Table 1.

In addition to the intended compound 9 (with 8 identical molecules in the tetragonal unit cell, all of the same chirality), the structure also contains highly disordered solvent and/or other components that could not be modelled as discrete atoms and could not be identified from the observed electron density distribution. This has been treated with the SQUEEZE option of the program PLATON. The refined structural model contains only the ordered part of the crystal structure and the unidentified disordered components are not included in any of the tabulated or deposited values. The crystal structure of 8 contains disordered dichloromethane solvent molecules, which it was possible to model with discrete atom positions. For all three structures, the correct enantiomer was confirmed on the basis of significant anomalous scattering effects.

Crystallographic data for all compounds have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 893546–893548.

Conclusions

Short synthetic routes to the chiral, ether-functionalized NHC precursors, 201Ts, 4I and 5Br have been developed. The bridging ligands 2, 4 and 5 form either cationic dinuclear cyclic structures with Ag(i) or neutral linear complexes in the case of Pt(n). The robust nature of the Pt(n) complexes is indicated by their synthesis being achieved under aerobic conditions using bench grade solvents. For the cis-Pt(dmso)Cl2 complexes,
hindered rotation of the carbene ligand about the metal-NHC bond is evident in their $^1\text{H}$, $^{13}\text{C}$, $^{15}\text{N}$ and $^{195}\text{Pt}$ NMR spectra, where more than one rotamers can be observed.

Acknowledgements

We thank the EPSRC for funding for the National Crystallography Service (Southampton and Newcastle Universities), and Diamond Light Source for access to beamline I19.

Notes and references


