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Synthesis, Structural Characterisation and Stereochemical Investigation of Chiral Sulfur-Functionalised N-Heterocyclic Carbene Complexes of Palladium and Platinum

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Abstract: Palladium and platinum complexes containing a sulfur-functionalised N-heterocyclic carbene (S-NHC) chelate ligand have been synthesised. The absolute conformations of these novel organometallic S-NHC chelates were determined by X-ray structural analyses and solution-phase 2D ^{1}H–^{1}H ROESY NMR spectroscopy. The structural studies revealed that the phenyl substituents on the stereogenic carbon atoms invariably take up the axial positions on the Pd-C-S coordination plane to afford a skewed five-membered ring structure. All of the chiral complexes are structurally rigid and stereochemically locked in a chiral ring conformation that is either (R_s,*S*,*R*)-λ or (S_s,*R*,*R*)-δ in both the solid state and solution.

Keywords: carbenes · nitrogen heterocycles · palladium · platinum · sulfur

Introduction

Since the isolation of the first stable crystalline N-heterocyclic carbenes (NHCs) by Arduendo et al.,[1] a rapid development of NHCs as an interesting class of ligands in homogenous catalysis has occurred.[2] Transition-metal complexes incorporating NHCs in a chelating mode, such as in a metallacycle, are relatively less prone to reductive elimination than monodentate NHCs, due to the stability imposed by the chelate ring.[3] Furthermore, chelation also provides conformational rigidity in chiral variants. This is of critical importance in their application as catalysts in asymmetric synthesis. Hence, several groups have focused on the synthesis of functionalised chelating E-NHCs (E: P,[4] N,[4a,5] or O[6]) associated with hemilabile donors and their potential applications in various metal-catalysed reactions.[2h,7] In comparison with those for other donor-functionalised NHCs, the synthetic protocols for S-NHC metallacycle complexes are quite rare, although the ability of these complexes in various catalytic transformations has been demonstrated.[8] An important aspect of S-NHC metallacycles is that, upon chelation to metal, the sulfur atom exhibits stereogenicity, which can augment the stereocontrol provided by the backbone chirality in an asymmetric-synthesis scenario. However, in most cases, this stereogenicity on the sulfur atom is not configurationally stable and tends to undergo a relatively facile pyramidal inversion.[9] Apparently, by changing the electronic and steric properties of the sulfur atom, it is possible to attain an optically active and configurationally stable sulfur-functionalised metallacycle.[10] Thus, our interest lies in the development of a stereochemically rigid five-membered chiral C,S chelate NHC (Figure 1), keeping in mind the possibility that the transmission of chirality from the chiral carbon atom will occur through the sulfur moiety onto the neighbouring coordination site, which would afford a higher degree of asymmetric induction.

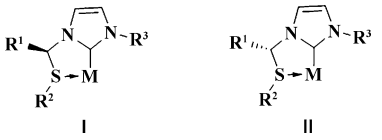

Figure 1. The skeletal structure of the five-membered C,S chelate ring.

As an extension of our on-going studies on the development and application of metallacycles in asymmetric synthesis,[11] we became interested in the structural behaviour of hetero-bidentate NHC metal complexes. Such behaviour in the Pd^{II}/Pt^{II} complexes of S-NHCs in solution has not been much explored, especially with relation to the stereochemical rigidity in chiral variants. We report herein the synthesis of chiral and configurationally stable sulfur-containing NHC complexes of Pd^{II} and Pt^{II}. The complexes reported in the current study have been prepared from the (*R*)-3-[(*tert*-butylthio)(phenyl)methyl]-1-(1-phenylethyl)-1*H*-imidazol-3-ium bromide ligand (**2**; Scheme 1), and the resultant diastereomeric metallacycles **4** and **5** have been resolved by fractional crystallisation. A detailed structural study in both the solid state and solution further revealed critical factors that impact on the stability and configurational rigidity in this class of metallacycles.

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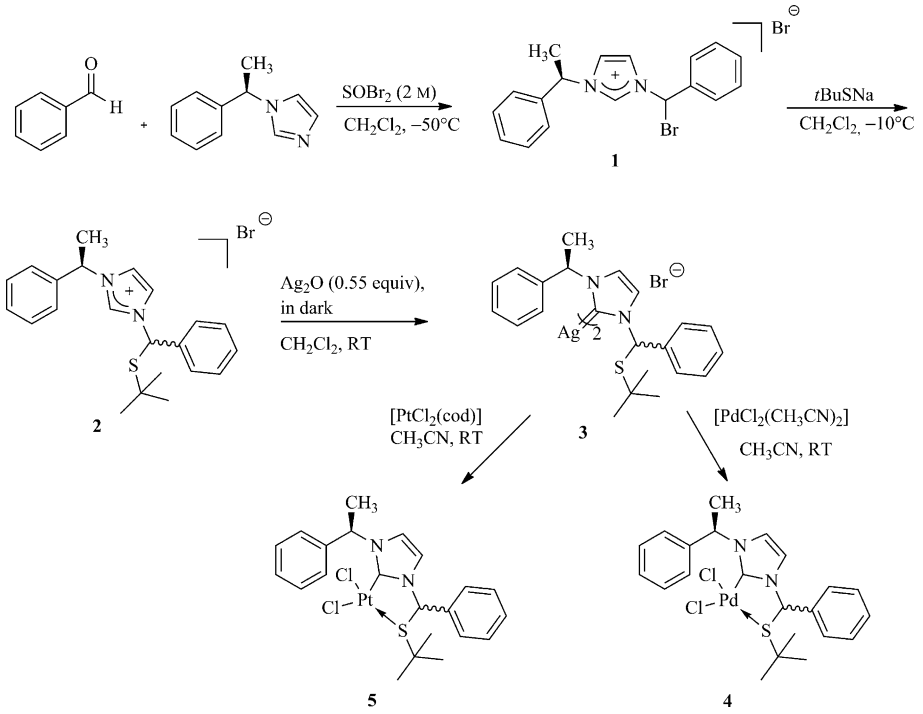

Scheme 1. Synthesis of five-membered S-NHC complexes. COD: cycloocta-1,5-diene.

In general, the five-membered organometallic ring undergoes rapid transformation between the two non-equivalent λ and δ conformations in solution. Hence, to gain a better understanding about the stereochemical influence of these S-NHC metallacycles in catalytic scenarios, we have studied the conformational rigidity of S-NHC-bearing Pd^{II}/Pt^{II} complexes in solution and in the solid state by means of single-crystal X-ray diffraction and ^{1}H NMR, 2D ROESY NMR and variable-temperature NMR spectroscopy techniques.

Results and Discussion

Synthesis of Pd^{II} and Pt^{II} complexes: The racemic thioether-imidazolium bromide **2** was prepared in a two-step procedure, as shown in Scheme 1. The α-bromo compound **1** was readily available from the reaction of substituted chiral imidazole and benzaldehyde with thionyl bromide in dichloromethane at −50 °C under a nitrogen atmosphere. Compound **1** was converted into **2** by subsequent nucleophilic substitution with the sodium salt of *tert*-butylsulfide at −10 °C. Complexes **4** and **5** were synthesised by the transmetallation method[12] with the addition of Ag_2O (0.55 equiv) to **2** under exclusion of light to yield **3**. The reactions of silver carbene complex **3** with [$PdCl_2(CH_3CN)_2$] and [$PtCl_2$COD] gave the neutral compounds **4** and **5**, respectively, in moderate yields.

Stereochemical investigation of palladium complex 4: The palladium compound **4** exists as a 1:1 mixture of two stable diastereomers, (R_s,*S*,*R*)-**4** and (S_s,*R*,*R*)-**4**. The eight possible ring conformations by virtue of the two newly formed stereogenic centres at C12 and S1 in the Pd-C-S coordination plane are shown in Figure 2. The separation of the two isomers, (R_s,*S*,*R*)-**4** and (S_s,*R*,*R*)-**4**, was based on their difference in solubility. A single crystallisation of the diastereomeric mixture by slow diffusion of diethyl ether into an acetonitrile solution at room temperature afforded the less soluble diastereomeric complex (R_s,*S*,*R*)-**4** as yellow crystals in 85% yield and >98% *de* (according to the ^{1}H NMR data), with $[\alpha]_D = +100$ ($c = 0.2$ in CH_3CN). The remaining mother liquor was evaporated to half the volume and seeded with the pure crystals of (R_s,*S*,*R*)-**4** to promote further resolution. After subsequent fractional crystallisation, the mother liquor was enriched in diastereomer (S_s,*R*,*R*)-**4**. Unfortunately, single crystals of (S_s,*R*,*R*)-**4** suitable for X-ray analysis were not obtained from the variety of solvent systems tested. However, according to ^{1}H NMR data, the *de* value of the (S_s,*R*,*R*)-**4** complex was >98%, with $[\alpha]_D = +214$ ($c = 0.2$ in CH_3CN). The absolute configuration of complex (R_s,*S*,*R*)-**4** was determined by single-crystal X-ray diffraction analysis. The solution structures of (R_s,*S*,*R*)-**4** and (S_s,*R*,*R*)-**4** were determined by 2D ^{1}H–^{1}H ROESY NMR spectroscopy studies.

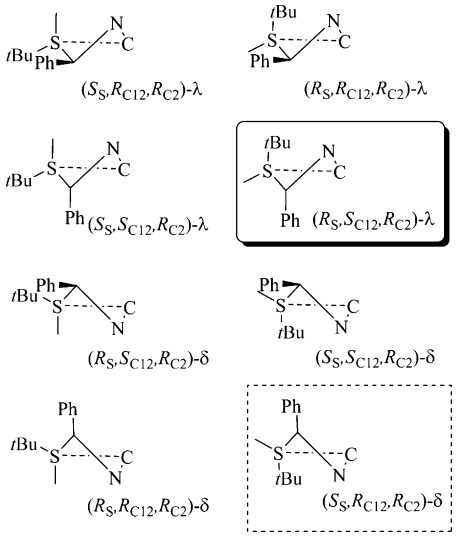

Figure 2. The possible ring conformations of complex **4**. The palladium centres, which should appear in the middle of the dashed line between the sulfur and carbon atoms, have been omitted for clarity.

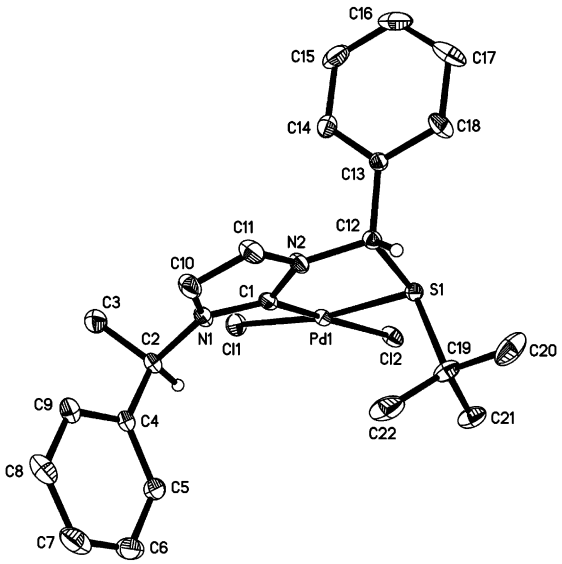

Figure 3. Molecular structure of complex (R_s,*S*,*R*)-**4**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms, except for H(C12) and H(C2) are omitted for clarity.

The molecular structure of (R_s,*S*,*R*)-**4** was studied by single-crystal structural analysis (Figure 3), and selected bond lengths and angles are listed in Table 1. The X-ray diffraction study revealed a λ conformation for complex (R_s,*S*,*R*)-**4** in the solid state, in which the phenyl substituent

Table 1. Selected bond lengths and angles in complex (R_s,*S*,*R*)-**4**.

Bond	Length [Å]	Bonds	Angle [°]
Pd1–C1	1.984(13)	N1–C1–N2	104.68(12)
Pd1–S1	2.266(4)	C1–N2–C12	124.53(12)
Pd1–Cl1	2.317(4)	N2–C12–C13	112.73(12)
Pd1–Cl2	2.362(4)	N2–C1–Pd1	117.06(10)
C1–N1	1.355(19)	C1–Pd1–S1	84.40(4)
C1–N2	1.360(19)	N2–C12–S1	107.37(9)
C2–N1	1.496(2)	S1–C12–H12	180.10
C2–C4	1.520(2)	N2–C12–H12	180.10
C2–C3	1.527(2)	C12–S1–Pd1	99.21(5)
C2–H2	1.0000	C12–S1–C19	102.32(7)
C12–N2	1.444(2)	C13–C12–S1	112.24(9)
C12–C13	1.5092(18)	Cl1–Pd1–S1	170.913(14)
C12–S1	1.8368(14)	Cl1–Pd1–Cl2	172.83(4)
C19–S1	1.8633(15)	C1–Pd1–Cl1	95.71(4)
C12–H12	1.0000	Pd1–S1–C19	110.22(6)

attached at the α-carbon atom (C12) invariably adopts the axial position below the Pd-C-S coordination plane. The driving force for the phenyl substituent at the C12 position adopting the axial disposition is attributed to steric repulsion between the *t*Bu and Ph substituents in the chelate ring. Upon chelation, the S1 atom becomes a stereogenic centre with a predominantly *R* configuration. The selectivity can be explained by the lower steric interactions due to the relative *trans* disposition of the Ph(α) and *t*Bu groups. The ring conformation in (R_s,*S*,*R*)-**4** is a consequence of the *S* configuration at the C12 position and the preference for the attached phenyl substituent to adopt an axial disposition, which led to the λ-ring conformation. Furthermore, the δ conformation of (R_s,*S*,*R*)-**4** has both substituents in equatorial positions (Figure 2), and the enantiomer (S_s,*R*,*R*)-**4** has the δ conformation as a consequence of the *R* configuration at the C12 position and the Ph substituent adopting an axial *trans* disposition. The C13–C12–S1–C19 torsion angle between the Ph substituent at the α-carbon atom and the *t*Bu substituent at the S1 position is 112.24°. The longer Pd1–Cl2 bond (2.362 Å) compared to the Pd1–Cl1 bond (2.317 Å) reflects the strong *trans*-influence effect of the carbene. The complex exhibits a distorted square–planar geometry, with a $C_{carbene}$–Pd1 bond length of 1.984 Å and a decreased C1–Pd1–S1 bond angle of 84.40°. Moreover, for bidentate complex (R_s,*S*,*R*)-**4**, the M–S–C bond angles of Pd1–S1–C12 and Pd1–S1–C19 were found to be 99.21° and 110.22°, respectively, values that are smaller than the observed angle for tetrahedral geometry, and this presumably accounts for the steric factors.

In solution, the ^{1}H NMR spectroscopic characterisation of (R_s,*S*,*R*)-**4** was assisted by a combination of ^{1}H and 2D ^{1}H–^{1}H ROESY NMR spectroscopy experiments. The ring conformation of the five-membered S-NHC palladacycle was deduced from NOE data obtained from the 2D ^{1}H–^{1}H ROESY NMR spectrum. The 2D ^{1}H–^{1}H ROESY NMR spectrum of (R_s,*S*,*R*)-**4** in $(CD_3)_2SO$ is shown in Figure 4. Generally, for the *S* absolute configuration at the α-carbon (C12) chiral centre, the five-membered S-NHC palladacycle tends to adopt the λ conformation. The NOE signal A for the interaction between the *t*Bu (Me20/Me21/Me22) protons and the H12 atom is clearly recorded. On other hand, the strong interactions of the α-chiral H12 proton with the Ph(α) (D) and H11 protons (E) are also recorded. Other expected NOE interactions, namely Me3–H2 (B) and Me3–H10 (C), are also observed.

Complex (R_s,*S*,*R*)-**4** remained locked in the λ-ring conformation in solution. The possible ring inversion certainly involves a Pd–S1 bond cleavage prior to inversion. Subsequent ring closure would lead to inversion of configuration at the S1 position because the substituents on the S1 and α-C12 atoms adopt the preferred *trans* disposition. Therefore, complex (R_s,*S*,*R*)-**4** in the λ conformation is able to undergo ring inversion, which presumably proceeds through cleavage of the Pd–S1 bond, followed by ring inversion and reformation of Pd–S1 bond with concomitant inversion of configuration at the S1 position to give (S_s,*S*,*R*)-**4** with the δ-ring conformation (Figure 2). Hence, the presence of the other conformer of (S_s,*S*,*R*)-**4** with the Ph substituent in the equatorial position within the C,S chelate ring should be detected in the 2D ^{1}H–^{1}H ROESY NMR spectrum. The absence of any correlations between the Ph(α) protons and the *t*Bu (Me20/Me21/Me22) protons in the 2D ^{1}H–^{1}H ROESY NMR spectrum established the absence of the δ conformer in solution. Thus, these spectroscopic results confirm that the five-membered S-NHC palladacycle (R_s,*S*,*R*)-**4** exists predominantly in the stereochemically locked λ-ring conformation in both the solid state and in solution.

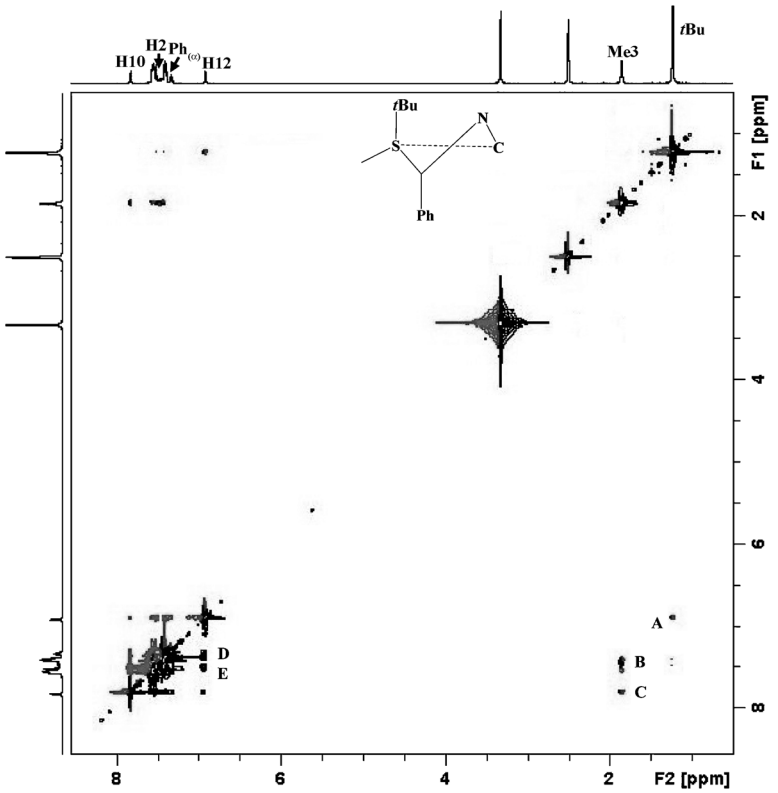

Figure 4. The 2D ^{1}H–^{1}H ROESY NMR spectrum of (R_s,*S*,*R*)-**4** in $(CD_3)_2SO$.

As mentioned earlier, suitable single crystals could not be obtained for the diastereomeric complex (S_s,*R*,*R*)-**4** in the array of solvents tested. Generally, the chiral orthopalladated complex tends to adopt the δ conformation if the chiral carbon atom has an *R* absolute configuration. As a consequence, the Ph group on the stereogenic carbon atom (C12) invariably takes the axial position above the Pd-C-S coordination plane, as illustrated in Figure 2. In solution, the ^{1}H NMR spectroscopic characterisation of (S_s,*R*,*R*)-**4** was assisted by a combination of ^{1}H and 2D ^{1}H–^{1}H ROESY NMR spectroscopy experiments. The ring conformational behaviour of the five-membered *t*BuS-NHC palladacycle was deduced from NOE data obtained from the 2D ^{1}H–^{1}H ROESY NMR spectrum. The 2D ^{1}H–^{1}H ROESY NMR spectrum of (S_s,*R*,*R*)-**4** in $(CD_3)_2SO$ is shown in Figure 5.

In this spectrum NOE signal A accounts for the interaction between the *t*Bu (Me20/Me21/Me22) protons and H12 atom. The strong NOE signals (D and E) are due to the interaction between the H12 atom and the Ph(α) and H11 protons. Other expected NOE interactions for Me3–H2 (B) and Me3–H10 (C) are also observed in the spectrum. However, the absence of key correlations between the *t*Bu (Me20/Me21/Me22) protons and the Ph(α) protons in the 2D ^{1}H–^{1}H ROESY NMR spectrum clearly and completely rules out the existence of (S_s,*R*,*R*)-**4** in the λ conformation, which has both the *t*Bu and Ph(α) groups in equatorial positions, as shown in Figure 2. Hence, the above NMR spectroscopic investigations confirmed that the complex

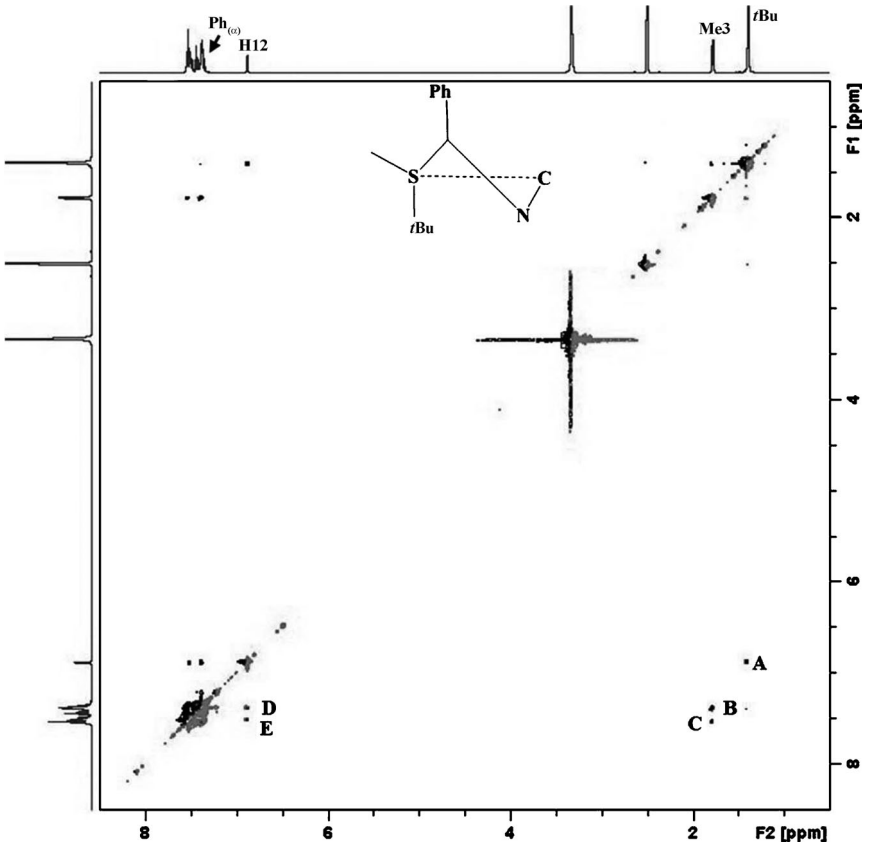

Figure 5. The 2D ^{1}H–^{1}H ROESY NMR spectrum of (S_s,*R*,*R*)-**4** in $(CD_3)_2SO$.

(S_s,*R*,*R*)-**4** exists as a single isomer in solution and remains stereochemically locked in the δ (*R*) configuration at the C12 position, with the Ph(α) substituent adopting an axial *trans* disposition.

Variable-temperature ^{1}H NMR data for complex (S_s,*R*,*R*)-**4**, in the temperature ranges from 23 to −30 °C (Figure 6; extensive precipitation of the complex occurred below −30 °C) and from 23 to 75 °C were collected by using a

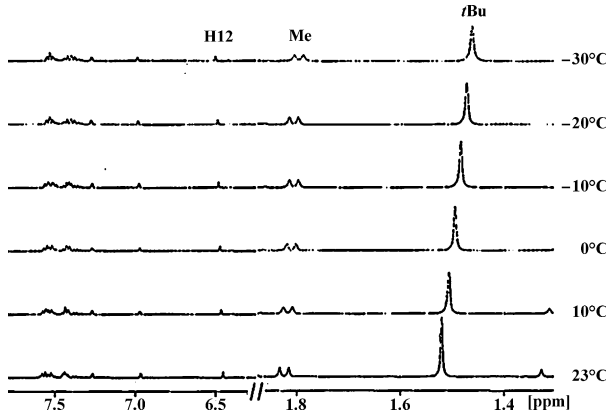

Figure 6. The variable-temperature NMR spectrum of (S_s,*R*,*R*)-**4** in CD_3CN.

[D_3]acetonitrile solution of (S_s,*R*,*R*)-**4**. In both experiments, at the aforementioned temperatures, only one sharp resonance was observed for the *t*BuS protons, which shows that complex (S_s,*R*,*R*)-**4** is not fluxional in solution. Hence, it is clear that the occurrence of a process involving ring inversion along with pyramidal sulfur inversion through Pd–S1 bond dissociation–association is certainly absent for complex (S_s,*R*,*R*)-**4**. As a result, the sulfur atom, upon coordination to the palladium(II) centre, is stereochemically locked with the *t*Bu group at the preferred axial position and the lone pair at the equatorial position.

Stereochemical investigations of platinum complex 5: The platinum(II) complex **5** also contains a 1:1 mixture of the two diastereomers, (R_s,*S*,*R*)-**5** and (S_s,*R*,*R*)-**5**. A single crystallisation of the diastereomeric mixture from acetonitrile/diethyl ether afforded the less soluble diastereomeric complex (R_s,*S*,*R*)-**5** as colourless crystals in 70% yield and >98% *de* (according to the ^{1}H NMR data) with $[\alpha]_D = +100$ ($c = 0.2$ in CH_3CN). The remaining mother liquor was evaporated to half the volume and seeded with the pure crystals of (R_s,*S*,*R*)-**5** to promote further resolution of remaining compound. Successive fractional crystallisations were carried out until the mother liquor was enriched in the diastereomer (S_s,*R*,*R*)-**5**.

Colourless single crystals of (R_s,*S*,*R*)-**5** were recrystallised from an acetone/diethyl ether mixture at room temperature. The molecular structure is presented in Figure 7. As expected, the platinum atom adopts a distorted square–planar coordination geometry. Similar to that in the (R_s,*S*,*R*)-**4** palla-

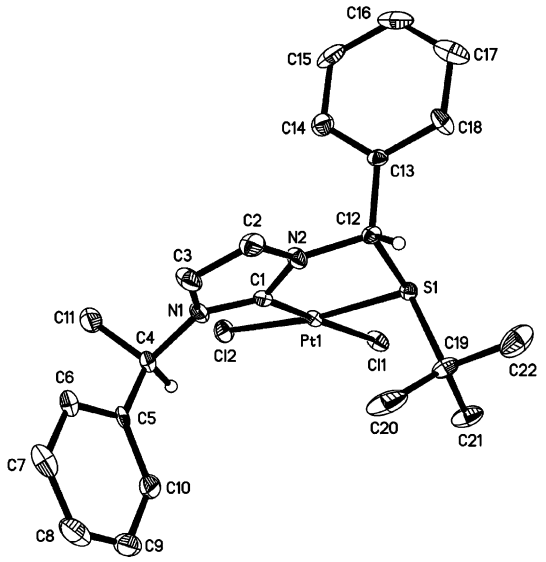

Figure 7. Molecular structure of complex (R_s,*S*,*R*)-**5**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms, except for H-(C12) and H(C4), are omitted for clarity.

dium complex, the organoplatinum five-membered ring adopts the λ conformation with the S1 atom pointing above the Pt-C-S coordination plane, with comparable bond lengths and angles (Table 2). Similarly, the Ph(α) substituent on the C,S chelate ring is also axially disposed below the co-

Table 2. Selected bond lengths and angles in complex (R_s,*S*,*R*)-**5**.

Bond	Length [Å]	Bonds	Angle [°]
Pt1–C1	1.975(5)	N1–C1–N2	104.5(5)
Pt1–S1	2.245(13)	C1–N2–C12	124.7(5)
Pt1–Cl1	2.362(14)	N2–C12–C13	113.0(4)
Pt1–Cl2	2.314(13)	N2–C1–Pt1	116.4(4)
C1–N1	1.348(6)	C1–Pt1–S1	85.60(14)
C1–N2	1.368(7)	N2–C12–S1	106.4(4)
C4–N1	1.472(7)	S1–C12–H12	180.30
C4–C11	1.492(8)	N2–C12–H12	180.30
C4–C5	1.523(8)	C12–S1–Pt1	99.57(18)
C12–N2	1.473(7)	C12–S1–C19	102.3 (3)
C12–C13	1.507(7)	C13–C12–S1	112.5(4)
C19–S1	1.873(6)	Cl1–Pt1–S1	89.54(5)
C12–S1	1.846(5)	Cl1–Pt1–Cl2	89.38(5)
C12–H12	1.0000	C1–Pt1–Cl1	174.90(15)

ordination plane because of the strong repulsive interaction between the *t*Bu group and the C12 substituents, which prevents the free interchange of the former between the axial and equatorial positions. Therefore, in the solid state, the alternative δ-ring conformation, with the Ph(α) group at the equatorial position in the Pt-C-S coordinating plane would be highly disfavoured. The chiral S1 atom has the *R* configuration upon coordination to platinum and the higher *trans* effect of the carbene towards the sulfur atom is reflected in the longer bond length of Pt–Cl1 (2.362 Å) than that of Pt–Cl2 (2.314 Å). Crystal data for compounds (R_s,*S*,*R*)-**4** and (R_s,*S*,*R*)-**5** are listed in Table 3.

Table 3. Crystal data for compounds (R_s,*S*,*R*)-**4** and (R_s,*S*,*R*)-**5**.

	4	**5**
empirical formula	$C_{22}H_{26}Cl_2N_2PdS$	$C_{22}H_{26}Cl_2N_2PtS$
formula weight	527.81	616.50
T [K]	103(2)	103(2)
λ [Å]	0.71073	0.71073
crystal system	orthorhombic	orthorhombic
space group	$P2(1)2(1)2(1)$	$P2(1)2(1)2(1)$
a [Å]	10.4613(3)	10.4741(2)
b [Å]	11.5237(3)	11.5386(2)
c [Å]	18.8138(5)	18.7933(3)
V [Å^3]	2268.06(11)	2271.29(7)
Z	4	4
D_{calcd} [mg m^{-3}]	1.546	1.803
μ [mm^{-1}]	1.156	6.515
$F(000)$	1072	1200
crystal size [mm^3]	$0.38\times0.26\times0.24$	$0.12\times0.08\times0.06$
θ range [°]	2.07 to 40.47	2.07 to 30.66
hkl range	−19 to 17, −17 to 20, −31 to 34	−8 to 14, −16 to 9, −26 to 23
N	57020	15190
N_{ind} (R_{int})	14052 (0.0333)	6936 (0.0256)
completeness to $\theta=40.47°$ [%]	99.6	99.5
max. and min. transmission	0.7688 and 0.6677	0.6959 and 0.5086
data, restraints, parameters	14052, 0, 257	6936, 0, 258
GOF on F^2	1.061	1.142
$R1(F, I>2\sigma(I))$	0.0286	0.0267
$wR2(F^2)$	0.0614	0.0633
absolute structure parameters	0.001(13)	−0.001(8)

The 2D ^{1}H–^{1}H ROESY NMR spectrum of complex (R_s,*S*,*R*)-**5** is similar to that of the (R_s,*S*,*R*)-**4** palladium complex. The presence of only one resonance for each chemically non-equivalent proton clearly indicates the existence of a single geometrical isomer in solution. Once again, the absence of NOE correlations between the Ph(α) protons and the *t*Bu protons in the 2D ^{1}H–^{1}H ROESY NMR spectrum rules out the existence of (S_s,*S*,*R*)-**5** with the δ-ring conformation in solution. Hence, for the *S* absolute configuration at the α-carbon chiral centre, the five-membered platinacycle remained in the λ conformation in both the solid state and in solution.

Unfortunately, single crystals suitable for X-ray crystallography could not be obtained for the diastereomeric complex (S_s,*R*,*R*)-**5** from the array of solvents tested. However, according to ^{1}H NMR data, the diastereomeric excess of complex (S_s,*R*,*R*)-**5** was >98%, with $[\alpha]_D=+190$ ($c=0.2$ in CH_3CN). The 2D ^{1}H–^{1}H ROESY NMR was recorded in $(CD_3)_2SO$ to allow the assignment of the absolute stereochemistry and conformation of the complex and was shown to be exactly the same as the (S_s,*R*,*R*)-**4** spectrum. The five-membered platinacycle adopts the δ conformation if the chiral centre has an *R* absolute configuration. The phenyl group on the stereogenic carbon atom invariably takes up the axial position above the C,S chelate ring. The absence of an NOE signal due to interactions between the *t*Bu (Me20/Me21/Me22) and Ph(α) protons indicates that the complex (S_s,*R*,*R*)-**5** is present as a single isomer and remains stereochemically locked in the δ (*R*) conformation in both the solid state and in solution.

Conclusion

In conclusion, five-membered chiral *t*BuS-NHC metallacycles were synthesised and their ring conformations were determined with X-ray crystallographic and solution-phase 2D ^{1}H–^{1}H ROESY NMR studies. From the results obtained, it was confirmed that both the Pd^{II} and Pt^{II} complexes are structurally rigid and stereochemically locked in chiral ring conformations, namely either (R_s,*S*,*R*)-λ or (S_s,*R*,*R*)-δ in both the solid state and in solution. The catalytic applications of these complexes are currently being evaluated.

Experimental Section

General methods: Reactions involving moisture-sensitive compounds were carried under an inert atmosphere of purified nitrogen by using Schlenk line techniques in oven-dried glassware. All solvents were distilled prior to use and reagents were used as received. ^{1}H NMR and ^{13}C NMR (400/100 MHz and 500/125 MHz) spectra were recorded in $CDCl_3$, CD_3CN, and $(CH_3)_2SO$ solutions by using Bruker Avance DPX400 and DPX500 spectrometers, respectively. Unless stated otherwise, all NMR spectroscopic experiments were performed at room temperature (300 K). High-resolution mass spectra were obtained by using a Water Q-Tof Premier, with ESI mode. Melting points were determined on a SRS-Optimelt MPA-100 apparatus and are uncorrected. Optical rotations were measured for the specified solution in a 0.1 dm cell at 20°C with a Perkin–Elmer model 341 polarimeter. Crystal data for complexes (R_s,*S*,*R*)-**4** and (R_s,*S*,*R*)-**5** were collected on a Bruker X8 CCD diffractometer.

Synthesis of (*R*)-3-[bromo(phenyl)methyl]-1-(1-phenylethyl)-1*H*-imidazol-3-ium bromide (1): A 2 M solution of (*R*)-1-(1-phenylethyl)-1*H*-imidazole (1 g, 5.814 mmol) and a 2 M solution of benzaldehyde (1.23 g, 11.628 mmol) were added simultaneously to a stirred 1 M solution of $SOBr_2$ (0.957 g, 4.651 mmol) in dichloromethane at −50°C under an argon atmosphere. The reaction mixture was slowly warmed to room temperature and allowed to stir for 8 h. Evaporation of the reaction mixture followed by tituration with diethyl ether gave the desired crude product. The crude product was purified by column chromatography on silica (eluent: chloroform/methanol, 40:1). Yield: 1.58 g (67%); ^{1}H NMR (500 MHz, $(CH_3)_2SO$): $\delta=11.25$ (s, 1H; NC*H*N), 8.56 (s, 1H; NC*H*Br), 7.81–7.83 (m, 2H, NC*H*=C*H*N); 7.47–7.48 (m, 1H; Ar *H*), 7.28–7.44 (m, 9H; BrCHAr *H*, Ar *H*), 5.87–5.90 (q, $J_{H-H}=7.0$ Hz, 1H; NC*H*CH_3), 2.04–2.06 ppm (d, 3H; NCHC*H*$_3$);^{13}C NMR (100 MHz, $CDCl_3$): $\delta=137.0$, 136.9, 136.8, 134.8, 134.8, 130.8, 130.8, 129.8, 129.8, 129.7, 129.4, 129.4, 128.1, 128.1, 127.0, 126.9, 121.0, 120.8, 120.7, 61.0, 60.9, 58.5, 21.4, 21.2 ppm; HRMS: calcd for $C_{18}H_{18}BrN_2Br$ $[M-Br]^+$: 341.06; found: 341.07.

Synthesis of (*R*)-3-[(*tert*-butylthio)(phenyl)methyl]-1-(1-phenylethyl)-1*H*-imidazol-3-ium bromide (2; diastereomers (*R*,*R*)- and (*R*,*S*)-2 in a 1:1 ratio): Sodium-2-methylpropane-2-thiolate (0.267 g, 2.381 mmol) was added to a stirred solution of **1** (1 g, 2.381 mmol) in dry dichloromethane (10 mL) at −10°C. The reaction mixture was warmed to room temperature and stirred for another 4 h. On completion of the reaction, as monitored by TLC, the reaction mixture was filtered and the filtrate was evaporated. This was followed by tituration with diethyl ether to yield the desired crude product. The crude product was purified by column chromatography by using silica gel (eluent: chloroform/methanol, 100:3) to obtain diastereomers (*R*,*R*) and (*R*,*S*)-**2** in a 1:1 ratio. Yield: 0.82 g

(80%); ^{1}H NMR (500 MHz, $(CD_3)_2SO$): δ=11.55 (s, 1H; NC*H*N), 11.48 (s, 1H; NC*H*N) 7.82 (s, 2H), 7.78 (s, 1H; NC*H*S), 7.73 (s, 1H; NC*H*S), 7.57–7.59 (m, 3H), 7.31–7.40 (m, 15H), 7.14–7.15 (m, 2H), 5.78–5.83 (q, J_{H-H}=7.0 Hz, 1H; NC*H*CH$_3$), 5.69–5.73 (q, J_{H-H}=6.5 Hz, 1H; NC*H*CH$_3$), 2.05–2.06(d, J_{H-H}=7.0 Hz, 3H; NCHC*H*$_3$), 2.02–2.03(d, J_{H-H}=7.0 Hz, 3H; NCHC*H*$_3$), 1.41 (s, 9H; SCC*H*$_3$), 1.40 ppm (s, 9H; SCC*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ=137.8, 137.5, 137.5, 135.8, 135.8, 129.5, 129.4, 129.3, 129.3, 129.3, 129.2, 126.8, 126.7, 126.6, 121.4, 121.1, 120.8, 120.7, 64.7, 64.7, 60.4, 60.2, 47.4, 30.9, 30.8, 21.4, 21.3 ppm; HRMS: calcd for $C_{22}H_{27}N_2SBr$ $[M-Br]^+$: 351.19; found: 351.19.

Synthesis of bis{1-[(*tert*-butylthio)(phenyl)methyl]-3-[(*R*)-1-phenylethyl]-2,3-dihydro-1*H*-imidazol-2-yl}silver(III) bromide (3): Silver(I) oxide (0.308 g, 1.327 mmol) was added to a solution of **2** (0.82 g, 1.894 mmol) in CH_2Cl_2 (10 mL) and the suspension was stirred for 4 h at room temperature in the dark. The mixture was filtered through a small celite plug and concentrated to afford the crude product. Yield: 0.865 g (85%); ^{1}H NMR (500 MHz, $CDCl_3$): δ=7.59–7.60 (m, 2H; NC*H*S), 7.27–7.34 (m, 13H), 7.20–7.24 (m, 5H), 7.01–7.02 (m, 2H), 6.79–6.80 (m, 2H), 5.72–5.75 (t, J_{H-H}=7.0 Hz, 2H; NC*H*CH$_3$), 1.83–1.87 (m, 6H; NCHC*H*$_3$), 1.32 (s, 9H; SCC*H*$_3$), 1.29 ppm (s, 9H; SCC*H*$_3$); HRMS: calcd for $C_{44}H_{52}AgN_4S_2Br$ $[M-Br]^+$: 807.28; found: 807.30.

Synthesis of palladium complex 4: $PdCl_2(CH_3CN)_2$ (0.138 g, 0.537 mmol) was added to a stirred solution of **3** (0.4 g, 0.537 mmol) in dry acetonitrile (15 mL) under an argon atmosphere. The mixture was stirred in the dark overnight at room temperature, filtered through celite and concentrated. The residue was triturated with methanol to afford (R_s,*S*,*R*)-**4** and (S_s,*R*,*R*)-**4** as a yellow solid (0.150 g, 51%). The diastereomers were separated with an acetonitrile/diethyl ether system.

(R_s,*S*,*R*)-4: Yellow crystals; yield: 0.065 g; m.p: 216–218°C; $[\alpha]_D$=+100 (c=0.2 in CH_3CN); ^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ=7.82 (s, 1H), 7.51–7.56 (m, 5H), 7.48–7.50 (m, 1H), 7.45–7.46 (m, 1H), 7.39–7.42 (m, 4H), 7.31–7.35 (m, 1H), 6.92 (s, 1H; NC*H*S), 1.84–1.86 (d, J_{H-H}=6.8 Hz, 3H; NCHC*H*$_3$), 1.24 ppm (s, 9H; SC(C*H*$_3$)$_3$); ^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ=155.8, 141.4, 135.4, 129.7, 129.4, 128.6, 128.1, 126.6, 126.2, 121.3, 120.3, 65.2, 56.8, 55.9, 29.1, 19.4 ppm; HRMS: calcd for $C_{22}H_{27}Cl_2N_2PdS$ $[M-2Cl]^+$: 457.09; found: 457.09.

(S_s,*R*,*R*)-4: Yellow powder; yield: 0.075 g; m.p: 234–236°C; $[\alpha]_D$=+214 (c=0.2 in CH_3CN); ^{1}H NMR (400 MHz, CD_3CN): δ=7.56–7.59 (m, 3H), 7.54 (s, 1H), 7.51–7.53 (m, 1H), 7.48–7.50 (m, 1H), 7.42–7.46 (m, 4H), 7.35–7.39 (m, 1H), 7.26–7.27 (d, 1H), 6.96–6.97 (d, 1H), 6.45 (s, 1H; NC*H*S), 1.82–1.83 (d, J_{H-H}=6.8 Hz, 3H; NCHC*H*$_3$), 1.52 ppm (s, 9H; SCC*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ=157.7, 140.5, 136.0, 130.8, 130.3, 129.3, 128.8, 128.0, 127.0, 122.3, 120.7, 66.6, 57.5, 56.9, 29.9, 21.1 ppm; HRMS: calcd for $C_{22}H_{27}Cl_2N_2PdS$ $[M-2Cl]^+$: 457.09; found: 457.09.

Synthesis of platinum complex 5: This complex was prepared in a manner analogous to that described for **4**, by **3** (0.4 g, 0.537 mmol) in dry dichloromethane (10 mL) and $PtCl_2COD$ (0.4 g, 0.537 mmol) under an argon atmosphere to yield a mixture of (R_s,*S*,*R*)-**5** and (S_s,*R*,*R*)-**5** (0.153 g, 55%) as a yellow powder. The diastereomers were separated with an acetonitrile/diethyl ether system.

(R_s,*S*,*R*)-5: Colourless crystals; yield: 0.060 g; m.p: 302–304°C; $[\alpha]_D$=+100 (c=0.2 in CH_3CN); ^{1}H NMR (400 MHz, CD_2Cl_2): δ=7.77–7.78 (d, 1H), 7.48–7.54 (m, 6H), 7.43–7.46 (m, 1H), 7.36–7.41 (m, 4H), 7.30–7.34 (m, 1H), 6.80 (s, 1H; NC*H*S), 1.85–1.87 (d, J_{H-H}=6.8 Hz, 3H; NCHC*H*$_3$), 1.19 ppm (s, 9H; SC(C*H*$_3$)$_3$); ^{13}C NMR (100 MHz, CD_2Cl_2): δ=149.2, 141.1, 134.8, 130.7, 130.2, 129.4, 128.8, 127.5, 127.0, 121.8, 118.0, 67.0, 57.7, 56.0, 29.4, 20.6 ppm; HRMS: calcd for $C_{22}H_{27}Cl_2N_2PtS$ $[M-2Cl]^+$: 546.15; found: 546.17.

(S_s,*R*,*R*)-5: Colourless crystal; yield: 0.080 g; m.p: 294–298°C; $[\alpha]_D$=+190 (c=0.2 in CH_3CN; ^{1}H NMR (500 MHz, $(CD_3)_2SO$): δ=7.53–7.54 (m, 3H), 7.48–7.51 (m, 3H), 7.42–7.52 (m, 2H), 7.37–7.40 (m, 4H), 7.34–7.36 (m, 1H), 6.88 (s, 1H; NC*H*S), 1.77–1.79 (d, J_{H-H}=7.0 Hz, 3H; NCHC*H*$_3$), 1.39 ppm (s, 9H; SC(C*H*$_3$)$_3$); ^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ=146.8, 140.3, 135.9, 130.0, 129.9, 129.0, 128.4, 127.5, 126.8, 122.2, 119.7, 65.2, 56.1, 56.0, 28.9, 21.1 ppm; HRMS: calcd for $C_{22}H_{27}Cl_2N_2PtS$ $[M-2Cl]^+$: 546.15; found: 546.17.

X-ray crystallographic studies: Crystal data for complexes (R_s,*S*,*R*)-**4** and (R_s,*S*,*R*)-**5** were collected on a Bruker X8 CCD diffractometer with $Mo_{K\alpha}$ radiation (graphite monochromator). SADABS absorption corrections were applied. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were introduced at calculated positions and refined riding on their carrier atoms. CCDC 913651 ((R_s,*S*,*R*)-**4**) and 913652 ((R_s,*S*,*R*)-**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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