Irreversible and reversible formation of a [2]rotaxane containing platinum(II) complex with an *N*-alkyl bipyridinium ligand as the axis component†

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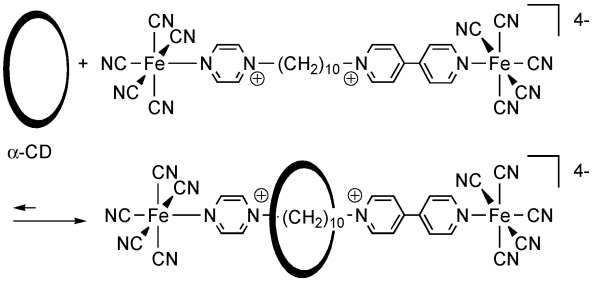
An *N*-Alkyl bipyridinium having a polymethylene chain and a bulky aryl group at the end, [4,4′-bpy-*N*-$(CH_2)_{10}OC_6H_3$-3,5-$^tBu_2$]Cl ([**1a**]Cl), reacts with K[$PtCl_3$(dmso)] to produce the Pt complex with the *N*-alkyl bipyridinium ligand [Cl_2(dmso)Pt{4,4′-bpy-*N*-$(CH_2)_{10}OC_6H_3$-3,5-$^tBu_2$}][$PtCl_3$(dmso)] as a 6 : 1 mixture of *trans* and *cis* isomers ([***trans*-2a**][$PtCl_3$(dmso)] and [***cis*-2a**][$PtCl_3$(dmso)]). Addition of α-cyclodextrin (α-CD) to a solution of [**1a**]Cl in dmso-d_6/D_2O (3 : 1) forms [2]pseudorotaxane [{4,4′-bpy-*N*-$(CH_2)_{10}OC_6H_3$-3,5-$^tBu_2$}·(α-CD)]Cl ([**3a**]Cl) which is equilibrated with [**1a**]Cl and α-CD in solution. The reaction of K[$PtCl_3$(dmso)] with [**3a**]Cl affords the [2]rotaxane [*trans*-Cl_2(dmso)Pt{4,4′-bpy-*N*-$(CH_2)_{10}OC_6H_3$-3,5-$^tBu_2$}·(α-CD)][$PtCl_3$(dmso)] ([***trans*-4a**][$PtCl_3$(dmso)]) which contains α-CD and [***trans*-2a**][$PtCl_3$(dmso)] as the cyclic and axis components, respectively. Dissolution of a mixture of [***trans*-2a**][$PtCl_3$(dmso)], [***cis*-2a**][$PtCl_3$(dmso)] and α-CD in dmso-d_6/D_2O (3 : 1) forms a mixture of the rotaxanes containing [***trans*-4a-d_6**][$PtCl_3$(dmso)] and [***cis*-4a-d_6**][$PtCl_3$(dmso)]. The reaction involves partial dissociation of the bipyridinium from Pt of [***trans*-2a**][$PtCl_3$(dmso)] or [***cis*-2a**][$PtCl_3$(dmso)] to yield [**1a**][$PtCl_3$(dmso)] and formation of pseudorotaxane with α-CD, followed by recoordination of the bipyridinium to the Pt. The reversible formation of the Pt–N coordination bond is studied in a dmso solution of the *N*-butyl compounds [*trans*-Cl_2(dmso)Pt{4,4′-bpy-*N*-^{n}Bu}][$PtCl_3$(dmso)] ([***trans*-2b**][$PtCl_3$(dmso)]).

Introduction

Rotaxanes and pseudorotaxanes have attracted growing attention because of their interlocked structure as well as their unique chemical and physical properties.[1,2] Cyclodextrins (CDs) possess a hydrophobic cavity and can form rotaxanes with various hydrophobic guest molecules in aqueous solution.[3] Rotaxanes and polyrotaxanes composed of α-CD and guest molecule with linear alkyl groups have been applied to intelligent materials such as molecular tubes,[4] conductive polymers,[5] drug delivery systems,[6] and topological gels.[7] Although sterically bulky organic groups are employed as the stoppers at the end of the axis molecules, transition metals with ligands also play roles as bulky stoppers of rotaxanes and kinetically stabilized rotaxanes.[8] Macartney *et al.* reported that diiron complexes $[(NC)_5Fe\{pyz(CH_2)_nR\}Fe(CN)_5]^{4-}$ (pyz = pyrazinium, R = pyrazinium or 4,4′-bpy) and α-CD formed rotaxanes *via* partial dissociation of the Fe–N bond (Scheme 1).[9] Recent studies on pseudorotaxanes of CD with bispyridinylalkane have revealed that α-CD prefers to reside at the alkyl chain of the axis component rather than the positively charged pyridinium group.[2,10]

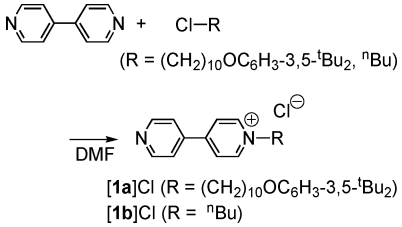
In this paper, we report the synthesis of a new [2]rotaxane that has α-CD and a Pt complex with an alkylbipyridinium ligand as the cyclic and axis components, respectively. The Pt-containing rotaxane is stable in aqueous solution but it exhibits dynamic behavior in dmso-d_6–D_2O. Chemical properties of related [2]pseudorotaxanes and Pt complexes are also described.



Scheme 1

Results and discussion

N-Alkyl bipyridinium compounds [4,4′-bpy-*N*-R]Cl ([**1a**]Cl: R = $(CH_2)_{10}OC_6H_3$-3,5-$^tBu_2$; [**1b**]Cl: R = ^{n}Bu), were prepared by reaction of 4,4′-bipyridine with the chloroalkanes in DMF, as shown in eqn (1).



(1)

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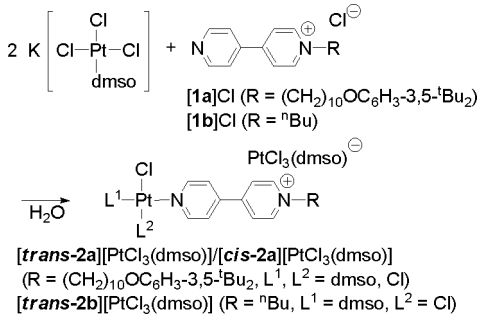
† Electronic supplementary information (ESI) available: Additional crystal structure details, ^{1}H NMR spectra of [**1a**]Cl, the mixture of [**1a**]Cl and α-CD and [***trans*-4a**][$PtCl_3$(dmso)]. See DOI: 10.1039/b610087b

Both compounds are soluble in water and were characterized by NMR spectroscopy, ESIMS (electrospray ionization mass spectrometry) and elemental analysis. Reactions of K[$PtCl_3$(dmso)] with [**1a**]Cl and with [**1b**]Cl produced the platinum complexes with [$PtCl_3$(dmso)]$^-$ as counter anion, as shown in eqn (2).



(2)

The product obtained from [**1a**]Cl and K[$PtCl_3$(dmso)] contains two isomers of [Cl_2(dmso)Pt(4,4′-bpy-*N*-$(CH_2)_{10}OC_6H_3$-3,5-$^tBu_2$)][$PtCl_3$(dmso)] with *trans* and *cis* Pt centers ([***trans*-2a**][$PtCl_3$(dmso)] and [***cis*-2a**][$PtCl_3$(dmso)]), in a ratio of 6 : 1, while the reaction with [**1b**]Cl produces [***trans*-2b**][$PtCl_3$(dmso)] as a single product. Fig. 1 depicts the molecular structure of [***trans*-2b**][$PtCl_3$(dmso)] determined by X-ray crystallography. Four coordination sites of the square-planar Pt(II) center of the cationic complex are occupied by the pyridyl group, dmso and two *trans* Cl ligands. The dmso ligands coordinate to the Pt centers through their sulfur atoms.

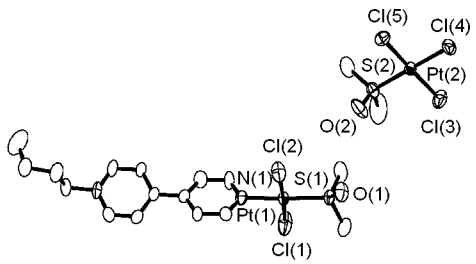
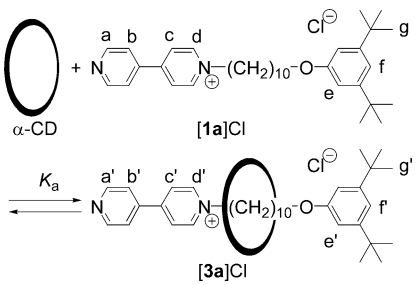


Fig. 1 ORTEP drawing of [***trans*-2b**][$PtCl_3$(dmso)] with 50% probability. Hydrogen atoms are omitted for clarity.

Dissolution of α-CD and [**1a**]Cl in dmso-d_6–D_2O (3 : 1) forms [2]pseudorotaxane [{4,4′-bpy-*N*-$(CH_2)_{10}OC_6H_3$-3,5-$^tBu_2$}·(α-CD)]Cl ([**3a**]Cl) as shown in eqn (3).



(3)

Fig. 2(a) and (b) show the ^{1}H NMR spectra of [**1a**]Cl before and after addition of α-CD, respectively. The latter spectrum contains signals of the pseudorotaxane [**3a**]Cl (e′, f′ and d′) whose positions (δ 6.58, 6.92 and 9.03) differ from the corresponding signals of [**1a**]Cl (δ 6.61, 6.90 and 8.98). Signals of the CH_2 hydrogens at β-positions of N and O atoms of the axis molecule are observed

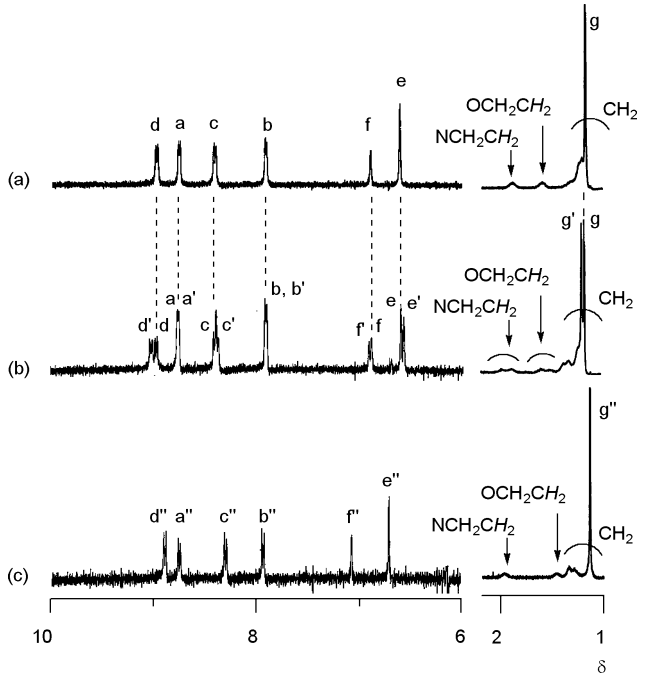


Fig. 2 ^{1}H NMR spectra of (a) [**1a**]Cl in dmso-d_6–D_2O, (b) the mixture of [**1a**]Cl and α-CD in dmso-d_6–D_2O, and (c) isolated [***trans*-4a**][$PtCl_3$(dmso)] dissolved in D_2O.

at lower magnetic field positions than those of [**1a**]Cl. The signals of both [**1a**]Cl and [**3a**]Cl are broadened. Only a set of the signals is observed for the pseudorotaxane [**3a**]Cl, although two isomers due to different orientations of the α-CD could be expected.[10,11] These results may be rationalized by assuming the same aromatic peak positions between the isomers due to complexation of α-CD with the alkyl chain by hydrophobic interactions.[2,10] ^{1}H NMR signals of CH_2 hydrogens of **1a** are shifted upon complexation with α-CD similarly to other axis molecules composed of alkyl chain and pyridinium end groups.[10] Alternatively, a small signal observed at δ 6.71 in Fig. 2(b) may be assigned to a minor isomer of the pseudorotaxane with different orientations of the α-CD ring. ROESY measurement of the solution did not provide any further information on details of the structures of the pseudorotaxane.

[**1a**]Cl and [**3a**]Cl in the solution attain equilibrium within 5 min at 25 °C. Fig. 3 shows the Job plots obtained from ^{1}H NMR peak area ratio of e and e′ of the mixtures of [**1a**]Cl and α-CD with different molar ratios. The concentration of the pseudorotaxane formed reaches a maximum at an equal amount of the initially added [**1a**]Cl and α-CD, indicating formation of [**3a**]Cl by 1 : 1 complexation of α-CD and [**1a**]Cl. The plots fit well with the curve based on 1 : 1 complexation with association constant $K_a = 44$ M^{-1}. The association constant is smaller than those for formation of the pseudorotaxane with a similar axis component [{bpy$(CH_2)_n$bpy}·(α-CD)]I_2 (n = 8–12) (72–3700 M^{-1} in D_2O).[9] Formation of the [2]pseudorotaxane [**3a**]Cl was confirmed also by ESIMS which showed the parent peak of [**3a**]$^+$ at m/z = 1473.8 (calc. 1473.7). Addition of α-CD to a D_2O solution of [**1b**]Cl shows little change in the ^{1}H NMR spectrum, indicating that [**1b**]Cl and α-CD does not form a stable [2]pseudorotaxane. Low stability of the pseudorotaxane of α-CD with [**1b**]Cl can be attributed to too short a butyl chain to form a stable inclusion complex with α-CD.

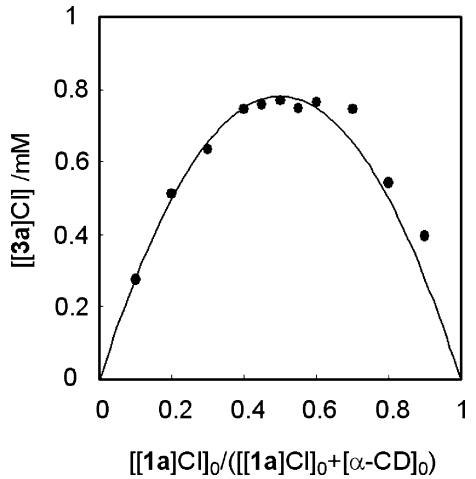
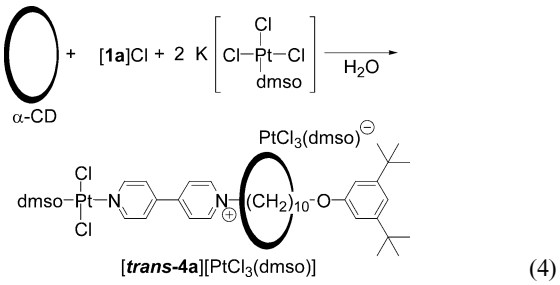


Fig. 3 Job plots of the concentration of [**3a**]Cl formed from mixtures of [**1a**]Cl and α-CD as a function of the molar fraction of [**1a**]Cl to α-CD employed in dmso-d_6–D_2O (3 : 1). Sum of the concentrations of the two components ([[**1a**]Cl]$_0$ + [α-CD]$_0$) was fixed to 10 mM in all cases. The curve calculated by assuming formation of a 1 : 1 pseudorotaxane with an association constant of 44 M^{-1} is shown.

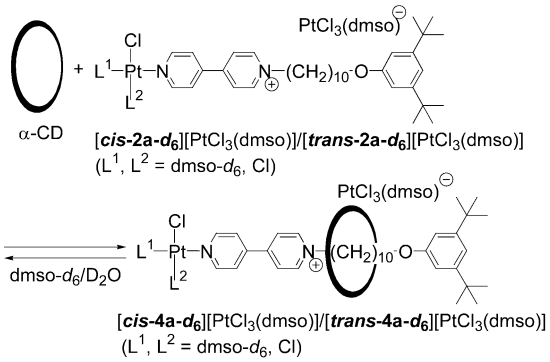
An aqueous reaction of K[$PtCl_3$(dmso)] with [**1a**]Cl in the presence of α-CD forms [2]rotaxane [***trans*-4a**][$PtCl_3$(dmso)] which is isolated in 53% yield (eqn (4)).



(4)

Fig. 2(c) shows the ^{1}H NMR spectrum of isolated [***trans*-4a**][$PtCl_3$(dmso)] in D_2O at room temperature. A set of the signals due to the rotaxane is observed in the regions of aromatic and aliphatic hydrogens, and they do not change over 24 h at room temperature. Consequently, the cationic rotaxane [***trans*-4a**], having Pt complex as the bulky end group of the axis component, keeps the interlocked structure in D_2O at room temperature. Since the distance between the two *trans* Cl ligands Cl(1) and Cl(2) of [***trans*-2b**][$PtCl_3$(dmso)] (4.58 Å) is similar to size of the cavity of α-CD (4.7 Å),[3] the $PtCl_2$(dmso) group is too bulky to pass through the cavity of α-CD (the van der Waals radius of Cl = 1.75 Å). High stability of the [2]rotaxane in D_2O solution suggests that it does not undergo dissociation of the pyridyl ligand. Dissolution of [***trans*-4a**][$PtCl_3$(dmso)] in dmso-d_6, however, results in formation of a mixture of [***cis*-2a-d_6**][$PtCl_3$(dmso)], [***trans*-2a-d_6**][$PtCl_3$(dmso)], [**1a**][$PtCl_3$(dmso)] and α-CD; 80% of [***trans*-4a**][$PtCl_3$(dmso)] is consumed within 5 min at room temperature. The dethreading of the axis molecule from [***trans*-4a**], giving [***trans*-2a-d_6**], is induced by partial decoordination of the pyridyl group from Pt.

Reaction of α-CD with the Pt complex having the *N*-alkyl-4,4′-bipyridine ligand in dmso-d_6–D_2O ([[***cis*-2a**][$PtCl_3$(dmso)]]$_0$ + [[***trans*-2a**][$PtCl_3$(dmso)]]$_0$ = 2.8 mM ([***cis*-2a**][$PtCl_3$(dmso)]/[***trans*-2a**][$PtCl_3$(dmso)] = 6 : 1), [α-CD]$_0$ = 28 mM) also yields a mixture of the Pt-containing rotaxanes. [***trans*-4a-d_6**][$PtCl_3$(dmso)] and [***cis*-4a-d_6**][$PtCl_3$(dmso)], as shown in eqn (5).



+ [**3a**][$PtCl_3$(dmso)] + [**1a**][$PtCl_3$(dmso)] + $PtCl_2$(dmso-d_6)$_2$ (5)

Dmso ligands bonded to the cationic Pt center are replaced completely with dmso-d_6, while the dmso ligands of [$PtCl_3$(dmso)]$^-$ do not exchange with the solvent. Fig. 4 plots time-dependent change of concentration of rotaxanes and pseudorotaxanes monitored by ^{1}H NMR spectroscopy. The compounds attain equilibrium in 20 h at 25 °C.

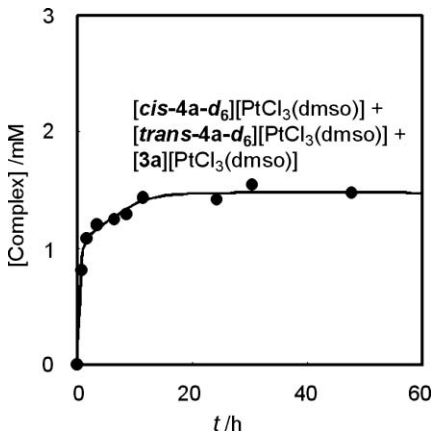
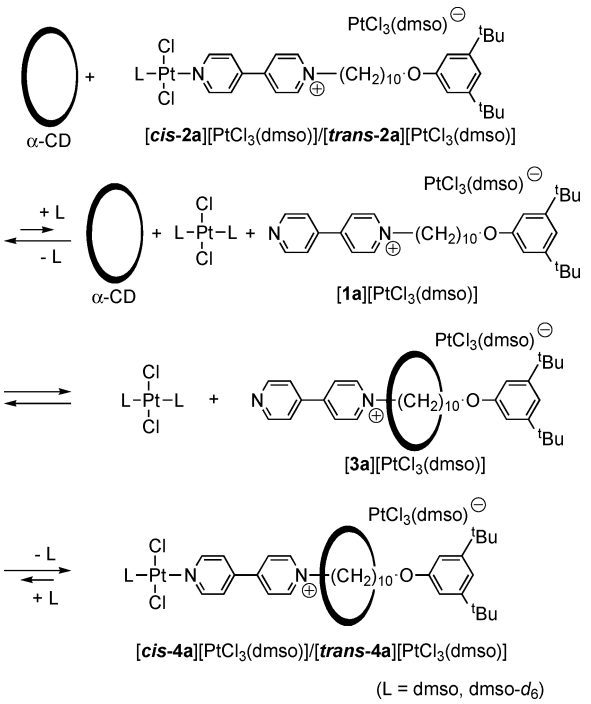


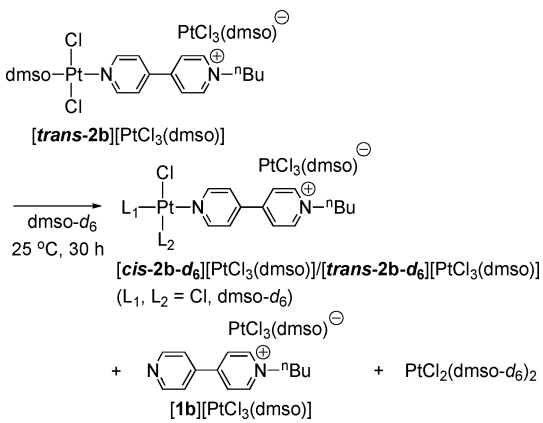
Fig. 4 Profile of formation of rotaxanes and pseudorotaxanes from α-CD (28 mM) and [***cis*-2a**][$PtCl_3$(dmso)]/[***trans*-2a**][$PtCl_3$(dmso)] ([[***cis*-2a**][$PtCl_3$(dmso)]] + [[***trans*-2a**][$PtCl_3$(dmso)]] = 2.8 mM) in dmso-d_6–D_2O (3 : 1) at 25 °C.

Scheme 2 depicts the plausible mechanism for formation of the Pt-containing rotaxane from [***cis*-2a**][$PtCl_3$(dmso)], [***trans*-2a**][$PtCl_3$(dmso)] and α-CD. A 6 : 1 mixture of [***trans*-2a**][$PtCl_3$(dmso)] and [***cis*-2a**][$PtCl_3$(dmso)], prepared in H_2O, is converted to a mixture of [**1a**][$PtCl_3$(dmso)], $PtCl_2$(dmso-d_6)$_2$, [***cis*-2a**][$PtCl_3$(dmso)] and [***trans*-2a**][$PtCl_3$(dmso)] in dmso-d_6–D_2O (3 : 1) by reversible dissociation and recoordination of the bipyridinium ligand. [**1a**][$PtCl_3$(dmso)] and α-CD produces pseudorotaxane [**3a**][$PtCl_3$(dmso)] which undergoes end-capping by $PtCl_2$(dmso)$_2$ to form the rotaxane [***cis*-4a**][$PtCl_3$(dmso)]/[***trans*-4a**][$PtCl_3$(dmso)], as shown in eqns (3) and (4). The total reaction requires almost 20 h for completion and is much slower than the pseudorotaxane formation (eqn (3)) and the end-capping of it (eqn (4)). Consequently a series of the reactions shown in Scheme 2 contains the initial dissociation of $PtCl_2L$ unit from the bipyridinium ligand as the rate-determining step.



Scheme 2

Reversible formation of the Pt–N coordination bond, accompanied by *cis–trans* isomerization, is observed in dmso solutions of the *N*-butyl compounds also. Dissolution of [***trans*-2b**][$PtCl_3$(dmso)] in dmso-d_6 gives a mixture containing [***trans*-2b-d_6**][$PtCl_3$(dmso)], [***cis*-2b-d_6**][$PtCl_3$(dmso)] and [**1b**][$PtCl_3$(dmso)] ([[***trans*-2b-d_6**][$PtCl_3$(dmso)]] : [[***cis*-2b-d_6**][$PtCl_3$(dmso)]] : [[**1b**][$PtCl_3$(dmso)]] = 28 : 52 : 20) after 30 h as shown in eqn (6).



(6)

Fig. 5(a) plots the profile of the reaction monitored by ^{1}H NMR spectroscopy. Exchange of the dmso ligand of the cationic parts, [***trans*-2b**] and [***cis*-2b**], with dmso-d_6 was completed within 20 min, whereas the counter anion [$PtCl_3$(dmso)]$^-$ did not undergo exchange of the dmso ligand throughout the reaction. Presence of [**1b**][$PtCl_3$(dmso)] in the reaction mixture suggested accompanying formation of $PtCl_2$(dmso-d_6)$_2$, although it was not detected by the ^{1}H NMR spectra. A similar equilibrated mixture of the compounds with chloro counter anion is obtained by the reaction of [**1b**]Cl and $PtCl_2$(dmso)$_2$ in dmso-d_6 (eqn (7)).

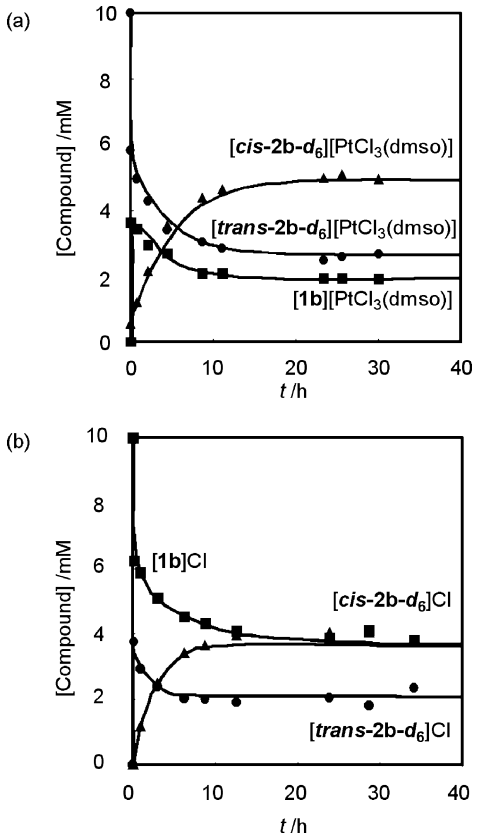
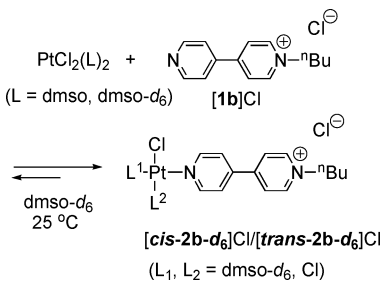


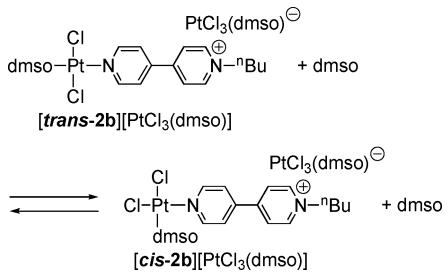
Fig. 5 Profile of the reaction of (a) [***trans*-2b**][$PtCl_3$(dmso)] and (b) $PtCl_2$(dmso)$_2$ with [**1b**]Cl in dmso-d_6 at 25 °C.



(7)

Fig. 5(b) shows the profile of the reaction. [***trans*-2b-d_6**]Cl is formed as the initial product, but it is further isomerized into the thermodynamically more stable *cis*-complex to give a mixture containing [***trans*-2b-d_6**]Cl, [***cis*-2b-d_6**]Cl and [**1b**]Cl in 24 : 38 : 38 ratio after 34 h.

[***trans*-2b**][$PtCl_3$(dmso)] is stable in nitromethane-d_3 for 12 h at 25 °C, while addition of dmso (4 equiv.) to the solution of [***trans*-2b**][$PtCl_3$(dmso)] at 50 °C causes isomerization to afford [***cis*-2b**][$PtCl_3$(dmso)] as shown in eqn (8).



(8)

Fig. 6 shows the ^{1}H NMR spectra of the reaction mixture 2 min and 150 h after addition of dmso. A small signal of methyl hydrogens of $PtCl_2(dmso)_2$ is observed at δ 3.52 after 150 h. Fig. 7 plots the profile of the isomerization reaction monitored by ^{1}H NMR spectroscopy. The mixture attains equilibrium after 100 h to form a mixture containing [***trans*-2b**][$PtCl_3$(dmso)], [***cis*-2b**][$PtCl_3$(dmso)] and [**1b**][$PtCl_3$(dmso)] in 53 : 45 : 2 ratio. These results indicate that the isomerization between [***trans*-2b**][$PtCl_3$(dmso)] and [***cis*-2b**][$PtCl_3$(dmso)] is induced by addition of dmso to the complex. The reaction induced by a small amount of dmso (4 equiv. to Pt) (Fig. 7) is slower than the reaction in dmso (Fig. 5(a)).

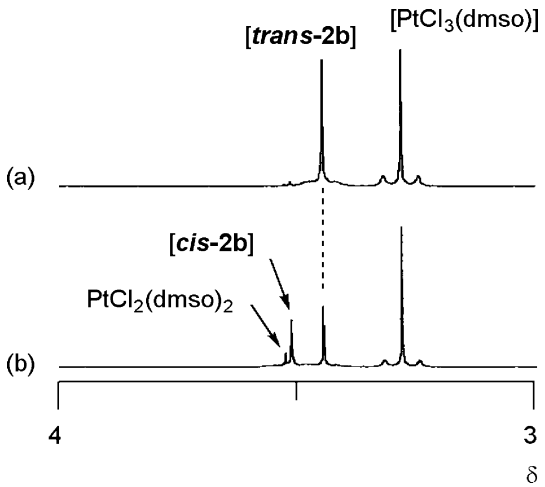


Fig. 6 ^{1}H NMR spectra of [***trans*-2b**][$PtCl_3$(dmso)] in nitromethane-d_3 (a) 2 min after addition of dmso (4 equiv.) and (b) after 150 h.

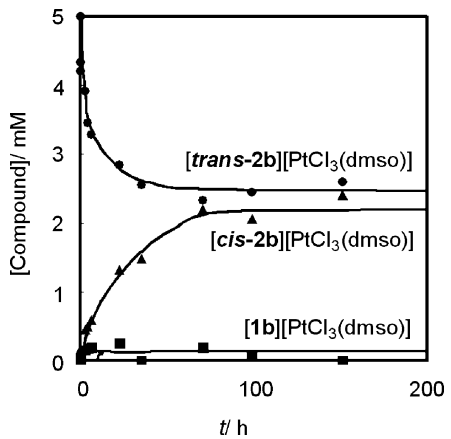
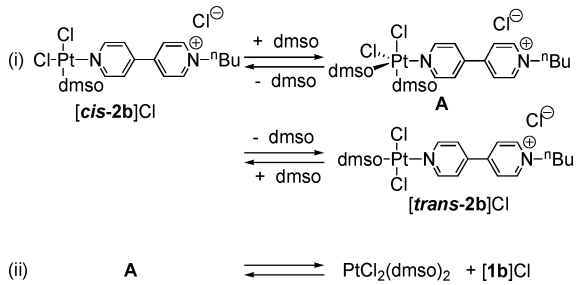


Fig. 7 Profile of the reaction of dmso with [***trans*-2b**][$PtCl_3$(dmso)] in nitromethane-d_3 at 50 °C (eqn (8)).

Scheme 3 depicts a plausible mechanism that accounts for the reactions in eqns (6)–(8). *cis–trans* Isomerization of the complex with bipyridinium ligand is initiated by coordination of dmso to Pt of [***cis*-2b**]. Formation of an associative intermediate **A** and its structure change *via* Berry pseudorotation lead to the complex with *trans* geometry of the Pt center as shown in (i). Pathway (ii) involves elimination of the *N*-butyl bipyridinium to generate $PtCl_2(dmso)_2$ and [**1b**]Cl. An alternative dissociative pathway may also be possible for the *cis–trans* isomerization, although positive



Scheme 3

effect of concentration of dmso on the reaction rate supports the pathway in Scheme 3.[12,13]

In summary, we have demonstrated the synthesis of new [2]rotaxanes composed of α-CD and bipyridinium ligand of a platinum complex as well as the platinum complexes without rotaxane structure. The Pt–N coordination bond of the bipyridinium platinum complex undergoes reversible dissociation and association upon addition of dmso to the complexes in D_2O and CD_3NO_2. Partial dissociation of the bipyridinium from the Pt center enables formal slippage of α-CD from the rotaxane. Different reactivity of the Pt–N bond toward dissociation depending on the solvent enabled switching in formation and degradation of the Pt-containing rotaxane.

Experimental

General

Dried solvents were purchased from Kanto Chemical Co., Inc. K[$PtCl_3$(dmso)] and $PtCl_2(dmso)_2$ were prepared by the literature method.[13,14] Other chemicals were commercially available. NMR spectra (^{1}H, $^{13}C\{^1H\}$) were recorded on Varian MERCURY300 and JEOL EX-400 spectrometers. The chemical shifts in the mixed solvent (dmso-d_6–D_2O = 3 : 1) were referenced with respect to dmso-d_5 (δ 2.49) as internal standard. IR absorption spectra were recorded on Shimadzu FT/IR-8100 spectrometers. JASCO V-530 UV/VIS spectrometer was used for UV absorption measurements. Electrospray ionization mass spectrometry (ESIMS) was recorded on a ThermoQuest Finnigan LCQ Duo. Elemental analyses were carried out with a Yanaco MT-5 CHN autorecorder.

$Cl(CH_2)_{10}OC_6H_3$-3,5-$^tBu_2$. A DMF (25 mL) solution containing 3,5-di-*tert*-butylphenol (4.0 g, 19 mmol), NaOH (1.6 g, 40 mmol) and $Cl(CH_2)_{10}Cl$ (8.2 mL, 39 mmol) was stirred for 25 h at 110 °C. The reaction was quenched by addition of 1 M HCl in H_2O, and the organic product was extracted with Et_2O and dried over $MgSO_4$. Evaporation of the solvent give a crude product which was purified by SiO_2 column chromatography (hexane–CH_2Cl_2 = 30 : 1) to give $Cl(CH_2)_{10}OC_6H_3$-3,5-$^tBu_2$ as a colorless oil (1.9 g, 5.0 mmol, 27%). ^{1}H NMR (300 MHz, $CDCl_3$, r.t.): δ 1.30–1.57 (m, 30H, CH_2, CH_3), 1.78–1.90 (m, 4H, CH_2), 3.58 (t, 2H, $ClCH_2$, J(HH) = 7 Hz), 4.03 (t, 2H, OCH_2, J(HH) = 7 Hz), 6.83 (s, 2H, *ortho*-C_6H_3), 7.08 (s, 1H, *papa*-C_6H_3). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, r.t.): δ 26.1 (CH_2), 26.8 (CH_2), 28.8 (CH_2), 29.4 (4C, CH_2), 31.4 (CH_3), 32.6 (CH_2), 34.9 (CCH_3), 45.0 ($ClCH_2$), 67.6 (OCH_2), 108.8 (*ortho*-C_6H_3), 114,7 (*para*-C_6H_3), 152.0 (*meta*-C_6H_3), 158.7 (C_6H_3). HRMS: Anal. Calc. for $C_{24}H_{41}ClO$: 380.2846. Found: 380.2845.

[4,4′-bpy-*N*-(CH$_2$)$_{10}$OC$_6$H$_3$-3,5-^{t}Bu$_2$]Cl ([1a]Cl). A DMF (20 mL) solution containing 4,4′-bipyridine (1.6 g, 10 mmol) and Cl(CH$_2$)$_{10}$OC$_6$H$_3$-3,5-^{t}Bu$_2$ (1.9 g, 5.0 mmol) was stirred at 100 °C for 22 h. Evaporation of the solvent gave an orange oil which was washed with Et$_2$O and toluene. Recrystallization from CH$_2$Cl$_2$–Et$_2$O yielded [**1a**]Cl as a white solid (1.5 g, 2.8 mmol, 55%). ^{1}H NMR (300 MHz, dmso-d_6, r.t.): δ 1.24 (s, 18H, CH$_3$), 1.24–1.44 (12H, CH$_2$), 1.67 (m, 2H, OCH$_2$C*H*$_2$), 1.94 (m, 2H, NCH$_2$C*H*$_2$), 3.91 (t, 2H, OCH$_2$, J(HH) = 6 Hz), 4.64 (t, 2H, NCH$_2$, J(HH) = 7 Hz), 6.67 (s, 2H, *ortho*-C$_6$H$_3$), 6.93 (s, 1H, *para*-C$_6$H$_3$), 8.04 (d, 2H, C$_{10}$H$_8$N$_2$, J(HH) = 6 Hz), 8.63 (d, 2H, C$_{10}$H$_8$N$_2$, J(HH) = 6 Hz), 8.86 (d, 2H, C$_{10}$H$_8$N$_2$, J(HH) = 6 Hz), 9.23 (d, 2H, C$_{10}$H$_8$N$_2$, J(HH) = 6 Hz). ^{13}C{^{1}H} NMR (75.5 MHz, dmso-d_6, r.t.): δ 25.4 (CH$_2$), 25.6 (CH$_2$), 28.4 (CH$_2$), 28.8 (2C, CH$_2$), 28.9 (2C, CH$_2$), 30.8 (CH$_2$), 31.2 (CH$_3$), 34.6 (*C*CH$_3$), 60.3 (NCH$_2$), 67.0 (OCH$_2$), 108.6 (*ortho*-C$_6$H$_3$), 114.0 (*para*-C$_6$H$_3$), 122.0 (C$_{10}$H$_8$N$_2$), 125.4 (C$_{10}$H$_8$N$_2$), 140.9 (C$_{10}$H$_8$N$_2$), 145.4 (C$_{10}$H$_8$N$_2$), 151.0 (C$_{10}$H$_8$N$_2$), 151.6 (C$_{10}$H$_8$N$_2$), 152.2 (*meta*-C$_6$H$_3$), 158.3 (*ipso*-C$_6$H$_3$). Calc. for C$_{34}$H$_{49}$N$_2$ClO·3H$_2$O: C, 69.07; H, 9.38; N, 4.74; Cl, 6.00. Found: C, 68.98; H, 9.09; N, 4.70; Cl, 6.37%. ESIMS: Calc. for C$_{34}$H$_{49}$N$_2$O: 501.4. Found: m/z = 501.8 [M − Cl]$^+$. UV absorption λ_{max}(H$_2$O)/nm 261 (ε/dm^3 mol^{-1} cm^{-1} 17600).

[4,4′-bpy-*N*-^{n}Bu]Cl ([1b]Cl). A toluene (20 mL) solution containing 4,4′-bipyridine (2.5 g, 16 mmol) and ^{n}BuCl (12.5 ml, 60 mmol) was refluxed for 96 h. The solid formed by the reaction was collected by filtration and washed with toluene to give [**1b**]Cl as a white solid (468 mg, 1.9 mmol, 12%). ^{1}H NMR (300 MHz, dmso-d_6, r.t.): δ 0.92 (t, 3H, CH$_3$, J(HH) =8 Hz), 1.32 (m, 2H, CH$_2$), 1.93 (m, 2H, CH$_2$), 4.65 (t, 3H, NCH$_2$, J(HH) = 8 Hz), 8.04 (d, 2H, C$_5$H$_4$N, J(HH) = 6 Hz), 8.64 (d, 2H, C$_{10}$H$_8$N$_2$, J(HH) = 6 Hz), 8.86 (d, 2H, C$_{10}$H$_8$N$_2$, J(HH) = 6 Hz), 9.25 (d, 2H, C$_{10}$H$_8$N$_2$, J(HH) = 6 Hz). ^{13}C{^{1}H} NMR (100 MHz, dmso-d_6, r.t.): δ 13.3 (CH$_3$), 18.7 (CH$_2$), 32.7 (CH$_2$), 60.0 (NCH$_2$), 121.8 (C$_{10}$H$_8$N$_2$), 125.2 (C$_{10}$H$_8$N$_2$), 140.8 (C$_{10}$H$_8$N$_2$), 145.3 (C$_{10}$H$_8$N$_2$), 150.8 (C$_{10}$H$_8$N$_2$), 151.8 (C$_{10}$H$_8$N$_2$). Calc. for C$_{14}$H$_{17}$N$_2$Cl·0.25H$_2$O: C, 66.40; H, 6.96; N, 11.06; Cl, 14.00. Found: C, 66.60; H, 7.08; N, 11.03; Cl, 14.08%. ESIMS: Calc. for C$_{14}$H$_{17}$N$_2$: 213.1. Found: m/z = 213.5 [M − Cl]$^+$.

[*trans*-2a][PtCl$_3$(dmso)]/[*cis*-2a][PtCl$_3$(dmso)]. To a solution of K[PtCl$_3$(dmso)] (200 mg, 0.48 mmol) in H$_2$O (2 mL) was added an aqueous solution (4.0 mL) of [**1a**]Cl (60 mg, 0.12 mmol) at 0 °C. The solution was stirred for 3 min and the solid formed was collected by filtration, washed with water and dried under reduced pressure to give a mixture of [***trans*-2a**][PtCl$_3$(dmso)]/[***cis*-2a**][PtCl$_3$(dmso)] (= 6 : 1) as a yellow solid (95 mg, 0.077 mmol, 67%). Calc. for C$_{38}$H$_{61}$N$_2$Cl$_5$O$_3$Pt$_2$S$_2$: C, 37.24; H, 5.02; N, 2.29; S, 5.23; Cl, 14.47. Found: C, 37.53; H, 5.07; N, 2.33; S, 5.00; Cl, 14.84%.

^{1}H NMR data of [***trans*-2a**][PtCl$_3$(dmso)] (300 MHz, CD$_3$NO$_2$, r.t.): δ 8.06 (d, 2H, J(HH) = 7 Hz). ^{1}H NMR data of [***cis*-2a**][PtCl$_3$(dmso)] (300 MHz, CD$_3$NO$_2$, r.t.): δ 7.99 (d, 2H, J(HH) = 7 Hz). Other signals of [***trans*-2a**][PtCl$_3$(dmso)] and [***cis*-2a**][PtCl$_3$(dmso)] were not distinguished from each other due to severe overlapping; δ 1.30 (s, 18H, C(CH$_3$)$_3$), 1.30–1.44 (12H, CH$_2$), 1.76 (m, 2H, OCH$_2$C*H*$_2$), 2.16 (m, 2H, NCH$_2$C*H*$_2$), 3.28 (s, 6H, PtCl$_3${SO(CH$_3$)$_2$}, J(PtH) = 22 Hz), 3.44 (br, 6H, PtCl$_2${SO(CH$_3$)$_2$}), 4.00 (t, 2H, OCH$_2$, J(HH) = 7 Hz), 4.77 (t, 2H, NCH$_2$, J(HH) = 7 Hz), 6.78 (s, 2H, *ortho*-C$_6$H$_3$), 7.10 (s, 1H, *para*-C$_6$H$_3$), 8.49 (2H, C$_{10}$H$_8$N$_2$), 8.95–9.08 (4H, C$_{10}$H$_8$N$_2$). The low solubility of complexes prevented ^{13}C{^{1}H} NMR measurement. IR (KBr disk, r.t.): ν_{max}/cm^{-1} 2924, 1140 (S=O), 1024, 442 (PtS). UV absorption λ_{max}(CHCl$_3$)/nm 249 (ε/dm^3 mol^{-1} cm^{-1} 18500).

[*trans*-2b][PtCl$_3$(dmso)]. To a solution of K[PtCl$_3$(dmso)] (164 mg, 0.39 mmol) in H$_2$O (4 mL) was added an aqueous solution (2 mL) of [**1b**]Cl (45 mg, 0.18 mmol) at 0 °C. The solid formed immediately was collected by filtration and washed with EtOH and Et$_2$O. The crude product was purified by recrystallization from MeNO$_2$–Et$_2$O, washed with EtOH and Et$_2$O and dried under reduced pressure to give [***trans*-2b**][PtCl$_3$(dmso)] as a white solid (116 mg, 0.12 mmol, 67%). ^{1}H NMR (300 MHz, CD$_3$NO$_2$, r.t.): δ 1.00 (t, 3H, CH$_3$, J(HH) = 8 Hz), 1.48 (m, 2H, CH$_2$), 2.13 (m, 2H, CH$_2$), 3.28 (s, 6H, CH$_3$, J(PtH) = 22 Hz), 3.44 (s, 6H, CH$_3$), 4.77 (t, 2H, CH$_2$, J(HH) = 8 Hz), 8.07 (m, 2H, C$_{10}$H$_8$N$_2$), 8.49 (d, 2H, C$_{10}$H$_8$N$_2$, J(HH) = 7 Hz), 8.97 (m, 2H, C$_{10}$H$_8$N$_2$), 8.99 (d, 2H, C$_{10}$H$_8$N$_2$, J(HH) = 7 Hz). ^{13}C{^{1}H} NMR (75.5 MHz, CD$_3$NO$_2$, r.t.): δ 13.8 (CH$_2$*C*H$_3$), 20.4 (CH$_2$), 34.3 (CH$_2$), 44.1 (SCH$_3$), 44.4 (SCH$_3$), 125.7 (C$_{10}$H$_8$N$_2$), 128.1 (C$_{10}$H$_8$N$_2$), 146.5 (C$_{10}$H$_8$N$_2$), 154.2 (C$_{10}$H$_8$N$_2$). The signal of the NCH$_2$ carbon was overlapped with the signal of CD$_2$HNO$_2$ (δ 62.8). Calc. for C$_{18}$H$_{29}$N$_2$Cl$_5$O$_2$Pt$_2$S$_2$: C, 23.07; H, 3.12; N, 2.99; S, 6.84; Cl, 18.92. Found: C, 23.02; H, 3.04; N, 3.03; S, 6.70; Cl, 19.14%. IR (KBr disk, r.t.): ν_{max}/cm^{-1} 2917, 1134 (S=O), 1022, 442 (PtS).

[2]Pseudorotaxane ([3a]Cl). To a solution of [**1a**]Cl (2.4 mg, 4.4 × 10^{-3} mmol) in dmso-d_6–D$_2$O (1.2 mL–0.4 mL) was added α-CD (42.8 mg, 4.4 × 10^{-2} mmol). A part of the solution was transferred into an NMR tube and ^{1}H NMR spectra were recorded periodically. The solution contained [**1a**]Cl and [**3a**]Cl. ^{1}H NMR data of [**3a**]Cl (300 MHz, dmso-d_6–D$_2$O (3 : 1), r.t.): δ 1.18–1.42 (12H, CH$_2$-axis), 1.21 (s, 18H, CH$_3$), 1.46–1.66 (2H, OCH$_2$C*H*$_2$), 1.84–2.06 (2H, NCH$_2$C*H*$_2$), 3.16–3.80 (36H, CH-α-CD), 3.86* (2H, OCH$_2$), 3.92–4.36 (6H, CH-α-CD), 4.46–4.64 (2H, NCH$_2$), 6.58 (s, 2H, *ortho*-C$_6$H$_3$), 6.92 (s, 1H, *para*-C$_6$H$_3$), 7.92 (2H, C$_{10}$H$_8$N$_2$), 8.36–8.44 (2H, C$_{10}$H$_8$N$_2$), 8.74–8.80 (2H, C$_{10}$H$_8$N$_2$), 9.03 (d, 2H, C$_{10}$H$_8$N$_2$, J(HH) = 7 Hz). The peak with an asterisk was overlapped significantly with the signal of the solvent. ESIMS: Calc. for C$_{70}$H$_{109}$N$_2$O$_{31}$: 1473.7. Found: m/z = 1473.8 [M − Cl]$^+$.

Reaction of α-CD with [1b]Cl). [**1b**]Cl (10 mg, 0.04 mmol) and α-CD (39 mg, 0.04 mmol) were charged to an NMR tube. After addition of D$_2$O (0.7 mL) to the mixture, the ^{1}H NMR spectrum showed almost exactly the signals of [**1b**]Cl.

[*trans*-4a][PtCl$_3$(dmso)]. To a solution of K[PtCl$_3$(dmso)] (126 mg, 0.30 mmol) in H$_2$O (6 mL) was added a solution of [**1a**]Cl (80 mg, 0.15 mmol) and α-CD (584 mg, 0.60 mmol) in H$_2$O (12 mL) at 0 °C to cause immediate separation of a colorless solid which was collected by filtration. The crude product was washed with cold water and dried *in vacuo* to give [***trans*-4a**][PtCl$_3$(dmso)] (167 mg, 0.076 mmol, 53%). ^{1}H NMR (300 MHz, D$_2$O, r.t.): δ 1.13 (s, 18H, CCH$_3$), 1.29–1.34 (br, 12H, CH$_2$), 1.46 (br, 2H, OCH$_2$C*H*$_2$), 1.98 (br, 2H, NCH$_2$C*H*$_2$), 3.34–3.74 (m, 36H, CH, CH$_2$), 3.40 (s, 12H, SCH$_3$), 3.83 (br, 2H, OCH$_2$), 4.89 (s, 6H, CH-α-CD), 6.67 (s, 2H, *ortho*-C$_6$H$_3$), 7.04 (s, 1H, *para*-C$_6$H$_3$), 7.91 (d, 2H, C$_{10}$H$_8$N$_2$, J(HH) = 7 Hz), 8.28 (d, 2H, C$_{10}$H$_8$N$_2$, J(HH) = 6 Hz), 8.74 (d, 2H, C$_{10}$H$_8$N$_2$, J(HH) = 6 Hz), 8.88 (d, 2H, C$_{10}$H$_8$N$_2$, J(HH) = 6 Hz). The low solubility of [***trans*-4a**][PtCl$_3$(dmso)] in D$_2$O prevents ^{13}C{^{1}H} NMR measurement.

Calc. for $C_{74}H_{121}N_2Cl_5O_{33}Pt_2S_2 \cdot H_2O$: C, 40.10; H, 5.59; N, 1.26; S, 2.89. Found: C, 39.92; H, 5.84; N, 1.42; S, 2.76%. UV absorption $\lambda_{max}(H_2O)$/nm 268 (ε/dm^3 mol^{-1} cm^{-1} 19000).

Reaction of dmso-d_6 with [*trans*-2b][PtCl$_3$(dmso)]. [***trans*-2b**][PtCl$_3$(dmso)] (7.0 mg, 7.5 × 10^{-3} mmol) was charged to an NMR tube. After addition of dmso-d_6 (0.75 mL) and a drop of mesitylene as an internal standard, the tube was capped with a rubber septum. ^{1}H NMR spectra were recorded occasionally to monitor the concentration of the species based on the internal standard. The NMR tube was kept in a thermostat bath (25 °C) and stored when not being actively monitored.

Reaction of PtCl$_2$(dmso)$_2$ with [1b]Cl. PtCl$_2$(dmso)$_2$ (3.2 mg, 7.5 × 10^{-3} mmol) was charged to an NMR tube. After addition of a dmso-d_6 (0.75 mL) solution of [**1b**]Cl (1.9 mg, 7.5 × 10^{-3} mmol) and a drop of mesitylene as an internal standard, the tube was capped with a rubber septum. The NMR sample was kept in a thermostat bath (25 °C) and its ^{1}H NMR spectra were recorded periodically to monitor the concentration of the species based on the internal standard.

Isomerization of [*trans*-2b][PtCl$_3$(dmso)]. [***trans*-2b**][PtCl$_3$(dmso)] (3.6 mg, 3.8 × 10^{-3} mmol) was charged to an NMR tube. After addition of CD_3NO_2 (0.75 mL), dmso (1.1 μL, 1.5 × 10^{-2} mmol) and a drop of mesitylene as an internal standard, the tube was capped with a rubber septum. The NMR sample was kept in an oil bath (50 °C) and its ^{1}H NMR spectra were recorded periodically to monitor the concentration of the species based on the internal standard.

Crystal structure determination

Crystals of [***trans*-2b**][PtCl$_3$(dmso)] suitable for X-ray diffraction study were obtained by recrystallization from MeNO$_2$–Et$_2$O and mounted in a glass capillary tube. The data was collected to a maximum 2θ value of 55°. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.26° with a take-off angle of 6.0°. Calculations were carried out by using the program package CrystalStructure™ for Windows.[15] The structure was solved by direct methods and expanded using Fourier techniques.

Crystal data for [*trans*-2b][PtCl$_3$(dmso)]. $C_{18}H_{29}Cl_5N_2O_2Pt_2S_2$, M_r = 937.00, monoclinic, space group $P2_1/a$ (no. 14), a = 13.771(3), b = 21.19(1), c = 9.604(2) Å, β = 96.80(2)°, V = 2782(2) Å^3, Z = 4, D_c = 2.237 g cm^{-3}, no. of unique reflections = 6382, no. of variables = 309, goodness of fit = 0.934, R = 0.054 ($I \geq 2\sigma(I)$), R_w = 0.072 ($I \geq 2\sigma(I)$).

CCDC reference number 614949.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b610087b

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