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Formation, Dynamic Behavior, and Chemical Transformation of Pt Complexes with a Rotaxane-like Structure

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Abstract: The reaction of [Pt(CH$_2$COMe)(Ph)(cod)] (cod = 1,5-cyclooctadiene) with (ArCH$_2$NH$_2$CH$_2$C$_6$H$_4$COOH)$^+$(PF$_6$)$^-$ (Ar = 4-*t*BuC$_6$H$_4$ or 9-anthryl) in the presence of cyclic oligoethers such as dibenzo[24]crown-8 (DB24C8) and dicyclohexano[24]crown-8 (DC24C8) produces {(ce)[ArCH$_2$NH$_2$CH$_2$C$_6$H$_4$COOPt(Ph)(cod)]}$^+$(PF$_6$)$^-$ (ce = DB24C8 or DC24C8, Ar = 4-*t*BuC$_6$H$_4$ or 9-anthryl) with interlocked structures. FABMS and NMR spectra of a solution of these compounds indicate that the Pt complexes with a secondary ammonium group and DB24C8 (or DC24C8) make up the axis and cyclic components, respectively. Temperature-dependent ^{1}H NMR spectra of a solution of {(DB24C8)[4-*t*BuC$_6$H$_4$CH$_2$NH$_2$CH$_2$C$_6$H$_4$COOPt(Ph)(cod)]}$^+$(PF$_6$)$^-$ ({(DB24C8)[**4**-H]}$^+$(PF$_6$)$^-$) show equilibration with free DB24C8 and the axis component. The addition of DB24C8 to a solution of {(DC24C8)[**4**-H]}$^+$(PF$_6$)$^-$ causes partial exchange of the macrocyclic component of the interlocked molecules, giving a mixture of {(DC24C8)[**4**-H]}$^+$(PF$_6$)$^-$, {(DB24C8)[**4**-H]}$^+$(PF$_6$)$^-$, and free macrocyclic compounds. The reaction of 3,5-Me$_2$C$_6$H$_3$COCl with {(DB24C8)[**4**-H]}$^+$(PF$_6$)$^-$ affords the organic rotaxane {(DB24C8)(4-*t*BuC$_6$H$_4$CH$_2$NH$_2$CH$_2$C$_6$H$_4$COOCOC$_6$H$_3$Me$_2$-3,5)}$^+$(PF$_6$)$^-$ through C–O bond formation between the aroyl group and the carboxylate ligand of the axis component. The addition of 2,2′-bipyridine (bpy) to a solution of {(DB24C8)[**4**-H]}$^+$(PF$_6$)$^-$ induces the degradation of the interlocked structure to form a complex with trigonal bipyramidal coordination, [Pt(Ph)(bpy)(cod)]$^+$(PF$_6$)$^-$, whereas the reaction of bpy with [Pt(OCOC$_6$H$_4$Me-4)(Ph)(cod)] produces the square-planar complex [Pt(OCOC$_6$H$_4$Me-4)(Ph)(bpy)].

Keywords: carboxylate ligands · crown compounds · ligand substitution · platinum · rotaxanes

Introduction

Rotaxanes[1,2] have attracted much attention because of their unique low-dimensional supramolecular structures, high macrocycle mobility along their axis component, and potential applications in molecular machines,[3] electronic devices,[4] electrically conductive polymers,[5,6] and intelligent drug-delivery systems.[7] Although rotaxanes composed of organic axes and rotor components are common, rotaxanes containing transition-metal complexes in their axis component have also had a long history[8] and exhibit unique properties as described below. A [2]rotaxane containing [Ru(4,4′-Me$_2$bpy)$_2$] (bpy = 2,2′-bipyridine) as a terminal stopper of the axis component functions as a molecular shuttle driven by the photoexcitation of the Ru complex.[9] The electrochemical oxidation of aminomethylferrocenes in the presence of dibenzo[24]crown-8 (DB24C8) and a hydrogen-radical source leads to the formation of pseudorotaxanes that contain ferrocene in their axis component.[10] A cyclic component of the rotaxane with a ferrocene-containing axis component undergoes shuttling along the axis induced by oxidation and reduction of the ferrocene group.[8e,11] Transition-metal-containing rotaxanes catalyze the epoxidation of polybutadiene.[12,13] Pt complexes serve as binders of axis molecules in forming a molecular necklace with a cyclic oligorotaxane structure.[14]

Rotaxanes with a kinetically labile bond in their axis component are expected to show dynamic behavior involving a rapid and reversible cleavage and formation of that bond. Takata and co-workers employed the activation of S–S bonds, catalyzed by PhSH, in the preparation of [2]- and [3]rotaxanes that contain an axis molecule with an S–S bond and bulky stopper groups.[15] The reversible formation and cleavage of the Pt$^{\mathrm{II}}$–N bond enable the formation of a macrocycle with Pt and of a rotaxane structure with a Pt-con-

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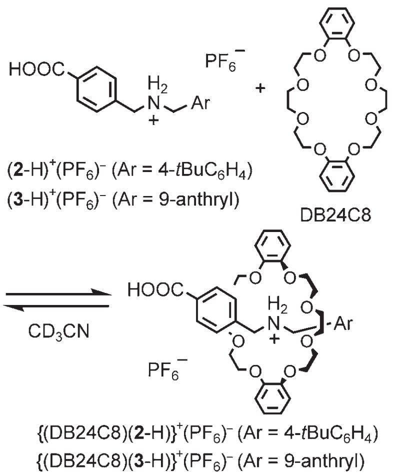
taining macrocyclic component through the clipping procedure.[16] The introduction of a kinetically labile and thermodynamically stable coordination bond to the axis component could also lead to an efficient synthesis of a rotaxane with a transition-metal center. Pd−O and Pt−O bonds of alkoxide complexes tend to undergo facile activation.[17,18] Pt−O bonds of carboxylate complexes are thermodynamically more stable than those of alkoxide complexes,[19] which are expected to show kinetic lability owing to the mismatch of soft Pt or Pd and hard oxygen atoms or pπ–dπ repulsive interactions between the atoms.[19,20]

In this paper, we report the preparation and chemical properties of semirotaxanes[21,22] that contain platinum complexes with carboxylate ligands that carry dialkylammonium moieties and crown ethers as components.



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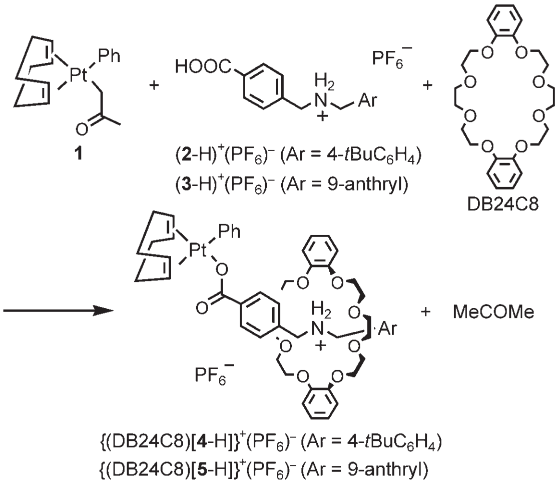
Results and Discussion

Preparation of [2]Semirotaxanes with Axis Component Containing a Carboxylate–Platinum(II) Bond

Carboxylic acids react with [Pt(CH_2COMe)(Ph)(cod)] (**1**; cod = 1,5-cyclooctadiene) to form carboxylate–platinum complexes.[23] This reaction is employed as the end-capping reaction of pseudorotaxanes whose axis molecule has a carboxy group as the terminal group. The formation of a pseudorotaxane from ($4\text{-}tBuC_6H_4CH_2NH_2CH_2C_6H_4COOH$)$^+$($PF_6$)$^-$ ((**2**-H)$^+$(PF_6)$^-$) with DB24C8 has been briefly mentioned.[24] We prepared the [2]pseudorotaxanes {(DB24C8)(**2**-H)}$^+$(PF_6)$^-$ and {(DB24C8)(**3**-H)}$^+$(PF_6)$^-$ in CD_3CN as shown in Equation (1).



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An equimolar reaction of **1** with (**2**-H)$^+$(PF_6)$^-$ in the presence of DB24C8 produces the [2]semirotaxane {(DB24C8)[**4**-H]}$^+$(PF_6)$^-$ (**4**: [$4\text{-}tBuC_6H_4CH_2NHCH_2C_6H_4COOPt$(Ph)(cod)]), as shown in Equation (2). The ^{1}H NMR spectrum of the reaction mixture exhibits signals due to {(DB24C8)[**4**-H]}$^+$(PF_6)$^-$ (70 %), free DB24C8 (22 %), and acetone generated by the reaction (75 %) (yields by NMR spectroscopy based on initial amount of **1**). The analogous [2]semirotaxane {(DB24C8)[**5**-H]}$^+$(PF_6)$^-$ (**5**: [$ArCH_2NHCH_2C_6H_4COO$-Pt(Ph)(cod)], Ar = 9-anthryl) was obtained in 48 % yield (by NMR spectroscopy) from a similar reaction with (**3**-H)$^+$(PF_6)$^-$.

Abstract in Japanese:

カルボキシラート白金錯体を軸分子、クラウンエーテルを環状分子とする含白金ロタキサンを合成した。このロタキサンの軸分子内部の白金－酸素結合は可逆な解離、再結合を繰り返しており、この過程の間に環状分子の交換反応を行なうことが可能であった。一方でこの白金－酸素結合の高い反応性を利用したロタキサンの変換反応を検討した。酸塩化物との反応では、軸分子内部のカルボキシラート白金部分が酸無水物構造へと変換され、ビピリジンとの反応ではロタキサン構造の分解が進行した。

The formation of {(DB24C8)[**4**-H]}$^+$(PF_6)$^-$ and {(DB24C8)[**5**-H]}$^+$(PF_6)$^-$ by the above reactions were confirmed with FABMS and ^{1}H NMR spectra. Figure 1 shows FABMS spectra that contain peaks due to {(DB24C8)[**4**-H]}$^+$ and {(DB24C8)[**5**-H]}$^+$ at $m/z = 1125$ and 1169, respectively. The peaks observed at $m/z = 746$ in Figure 1 a and $m/z = 790$ in Figure 1 b were assigned to {(DB24C8)(**2**-H)}$^+$ and {(DB24C8)(**3**-H)}$^+$, respectively. These species may be generated by the protonolysis of the Pt−O bond during measurement.

Figure 2 a shows a ^{1}H NMR spectrum of the reaction mixture of **1**, (**2**-H)$^+$(PF_6)$^-$, and DB24C8 in a 1:1:1 molar ratio (0.10 M for each compound) in $CDCl_3$. Signals of {(DB24C8)[**4**-H]}$^+$(PF_6)$^-$ and free DB24C8 were observed. Signals due to {(DB24C8)[**4**-H]}$^+$(PF_6)$^-$ were assigned on the basis of ^{1}H-^{1}H and ^{1}H-^{13}C{^{1}H} COSY spectra. CH_2 hydrogen signals of DB24C8, as the cyclic component in the rotaxane ($\delta = 3.44$, 3.73, 4.05 ppm), appear at lower frequen-

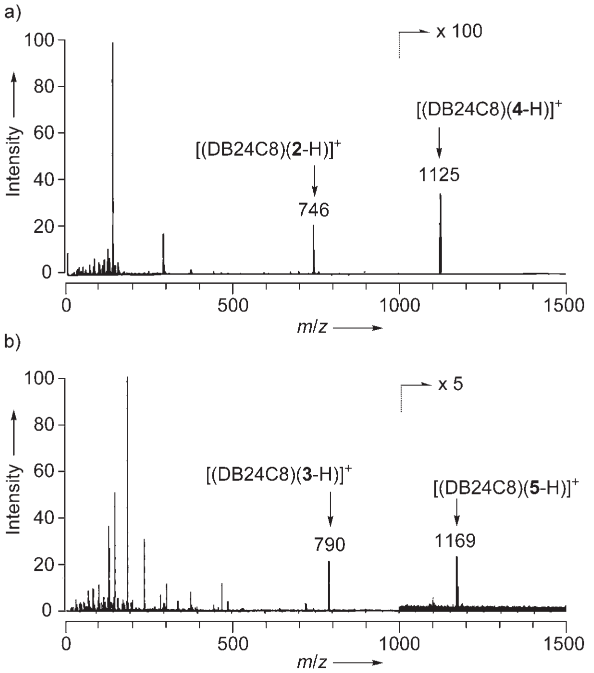


Figure 1. FABMS spectrum of a) $\{(DB24C8)[\mathbf{4}\text{-H}]\}^+(PF_6)^-$ and b) $\{(DB24C8)[\mathbf{5}\text{-H}]\}^+(PF_6)^-$.

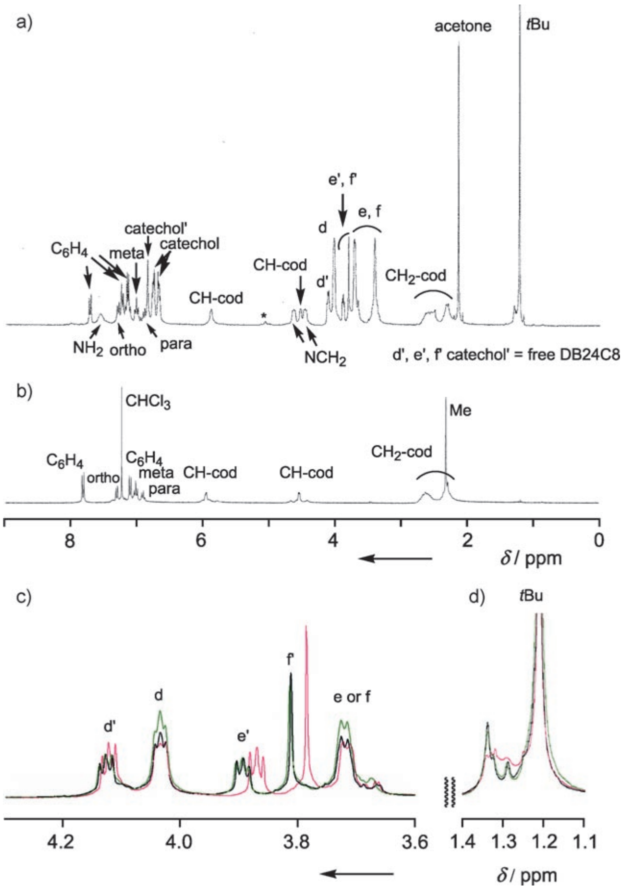
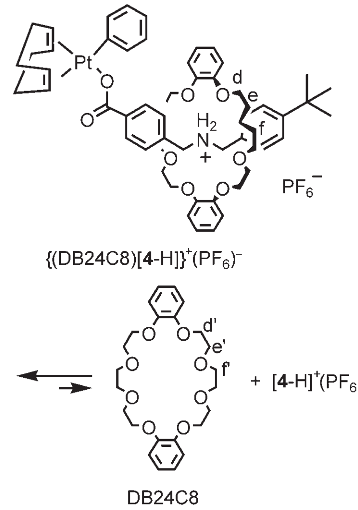


Figure 2. a) ^{1}H NMR spectrum of a solution of **1**, $(\mathbf{2}\text{-H})^+(PF_6)^-$, and DB24C8 (0.10 M each) in $CDCl_3$. The peak with the asterisk is due to $[Pt(Ph)_2(cod)]$ formed during the reaction. b) ^{1}H NMR spectrum of **6** in $CDCl_3$. c) CH_2 (DB24C8) and d) CH_3 region of ^{1}H NMR spectra of a solution of **1**, $(\mathbf{2}\text{-H})^+(PF_6)^-$, and DB24C8 (0.050 M each). The spectra were obtained at 20 °C (green), after heating to 50 °C (pink), and after cooling to 20 °C (black). For assignment of signals d, d′, e, e′, f, and f′, see Experimental Section.

cies than those of free DB24C8 ($\delta = 3.76, 3.86, 4.12$ ppm). Figure 2b shows a ^{1}H NMR spectrum of $[Pt(OCOC_6H_4Me\text{-}4)(Ph)(cod)]$ (**6**), prepared from the reaction of 4-methylbenzoic acid with **1**, for comparison of the cod and phenyl hydrogen signals. NCH_2 hydrogen signals at 4.49 and 4.67 ppm show splitting due to coupling with two NH_2 hydrogen nuclei,[25] and a broad NH_2 hydrogen signal is observed at 7.59 ppm. These signals are close to the corresponding signals of the organic [2]pseudorotaxane $\{(DB24C8)(\mathbf{2}\text{-H})\}^+(PF_6)^-$ in CD_3CN ($\delta = 4.58$ (NCH_2), 4.81 (NCH_2), 7.64 ppm (NH_2)) and are at higher frequencies than those of $(\mathbf{2}\text{-H})^+(PF_6)^-$ ($\delta = 4.22$ (NCH_2), 4.30 (NCH_2), 7.14 ppm (NH_2)). The downfield shifts of the NH_2 and NCH_2 hydrogen signals of these rotaxanes are ascribed to N–H···O and C–H···O interactions between the ammonium group of the axis component and the oxygen atoms of DB24C8.[25]

Figure 2c and d show the signals of the CH_2 hydrogen nuclei of both DB24C8 in the [2]semirotaxane and free DB24C8 and of CH_3 hydrogen nuclei of the axis component, respectively. Signals d, d′, e, e′, f, and f′ in Figure 2c were assigned to the CH_2 hydrogen nuclei shown in Equation (3). The ratio of $\{(DB24C8)[\mathbf{4}\text{-H}]\}^+(PF_6)^-$ to DB24C8 was determined to be 75:25 at 20 °C from a comparison of the relative peak areas of d and e′. Heating this solution to 50 °C changed the ratio to 63:37, which became 72:28 upon cooling the solution to 20 °C. These results indicate that an equilibrium exists between $\{(DB24C8)[\mathbf{4}\text{-H}]\}^+(PF_6)^-$ and a mixture of DB24C8 and $[\mathbf{4}\text{-H}]^+(PF_6)^-$, as shown in Equation (3), and that the formation of the [2]semirotaxane is more favorable at lower temperatures. This reversible formation and degradation of the [2]semirotaxane does not involve threading the 4-tBuC_6H_4 or $[Pt(Ph)(cod)]$ groups at the terminals of the axis component through the pore of DB24C8, which is too small for that to happen.[26,27] The reversible dissociation and formation of the labile platinum–carboxylate bond is responsible for the dynamic behavior of the semirotaxane shown above. The solution should contain $[\mathbf{4}\text{-H}]^+(PF_6)^-$, formed by the elimination of DB24C8 from the semirotaxane, together with $\{(DB24C8)[\mathbf{4}\text{-H}]\}^+(PF_6)^-$ and DB24C8. Figure 2d shows ^{1}H NMR signals at 1.24 ppm due to the 4-tBu group of $\{(DB24C8)[\mathbf{4}\text{-H}]\}^+(PF_6)^-$ as well as smaller signals at 1.25–1.33 ppm. Signals due to CH_3 hydrogen nuclei also change in shape and intensity reversibly depending on the temperature of the solution, thus indicating that the minor signals are due to $[\mathbf{4}\text{-H}]^+(PF_6)^-$ and the species equilibrating with $\{(DB24C8)[\mathbf{4}\text{-H}]\}^+(PF_6)^-$.

Semirotaxanes containing the Pt–carboxylate complex in the axis component exchange their macrocyclic component upon the addition of crown ether to the solution. Mixing **1**, $(\mathbf{2}\text{-H})^+(PF_6)^-$, and dicyclohexano[24]crown-8 (DC24C8) in a 1:1:1 molar ratio (0.10 M for each compound) in $CDCl_3$



(3)

forms {(DC24C8)[**4**-H]}$^{+}$(PF$_{6}$)$^{-}$ in 47 % yield (by NMR spectroscopy). Figure 3 a shows the CH$_{3}$ and CH$_{2}$ hydrogen regions of the ^{1}H NMR spectrum of {(DC24C8)[**4**-H]}$^{+}$(PF$_{6}$)$^{-}$. The broad signal at 1.30 ppm was assigned to the C(CH$_{3}$)$_{3}$ hydrogen nuclei; it overlaps with the signal from [**4**-H]$^{+}$(PF$_{6}$)$^{-}$. Its higher frequency relative to that of {(DB24C8)[**4**-H]}$^{+}$(PF$_{6}$)$^{-}$ ($\delta = 1.24$ ppm) is ascribed to a magnetic anisotropic effect caused by the aromatic rings of DB24C8 of the rotaxane. The addition of DB24C8 to the solution ([DB24C8]/[Pt] = 1:1) decreases the intensity of the signal at 1.30 ppm and produces a peak at 1.24 ppm (Figure 3 b). The latter signal is assigned to {(DB24C8)[**4**-H]}$^{+}$(PF$_{6}$)$^{-}$ formed by the exchange of the macrocyclic component of {(DC24C8)[**4**-H]}$^{+}$(PF$_{6}$)$^{-}$ with DB24C8.

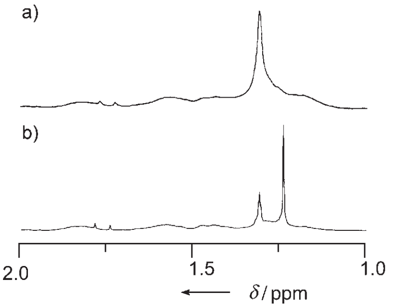


Figure 3. ^{1}H NMR spectra (in CDCl$_{3}$) of a) {(DC24C8)[**4**-H]}$^{+}$(PF$_{6}$)$^{-}$ and b) after addition of DB24C8 (1 equiv, 0.06 mmol).

Figure 4 a and b show ^{1}H NMR spectra of a solution of {(DB24C8)[**4**-H]}$^{+}$(PF$_{6}$)$^{-}$ and of the solution formed by the addition of DC24C8 ([Pt]/[DC24C8]/[DB24C8] = 1:1:1, 0.10 M for each component) to the former, respectively. The ratio of the peak areas of the signals of {(DC24C8)[**4**-H]}$^{+}$(PF$_{6}$)$^{-}$ and {(DB24C8)[**4**-H]}$^{+}$(PF$_{6}$)$^{-}$ in Figure 4 b is similar to that in Figure 3 b, thus indicating that these semirotaxanes attain the equilibrium shown in Equation (4) in the solution.

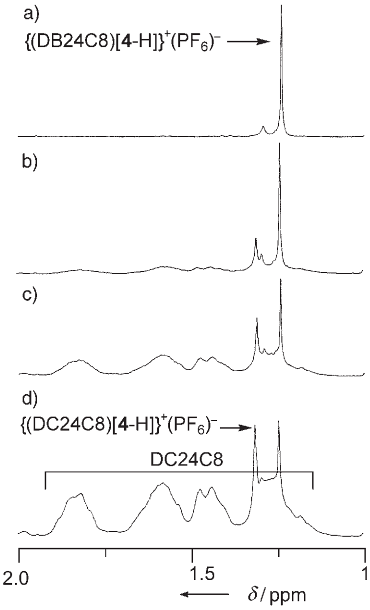
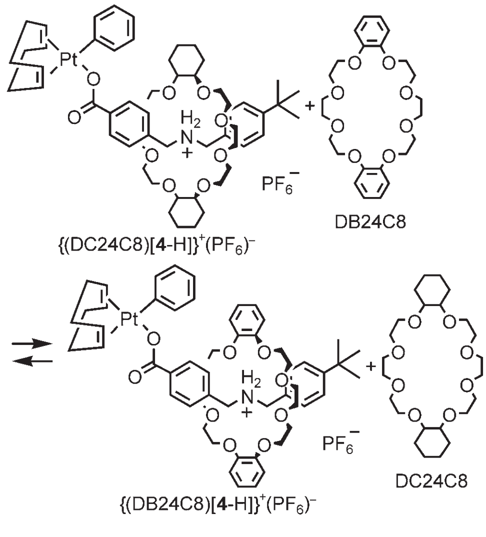


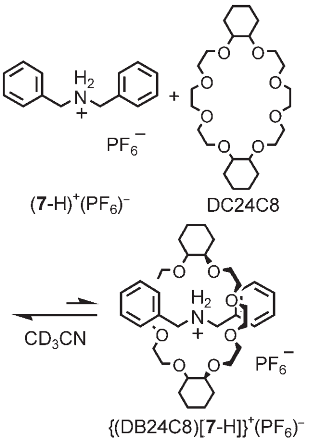
Figure 4. ^{1}H NMR spectra (CDCl$_{3}$) of a) {(DB24C8)[**4**-H]}$^{+}$(PF$_{6}$)$^{-}$ and after the addition of b) 1 equiv (0.06 mmol), c) 3 equiv (0.18 mmol), and d) 5 equiv (0.30 mmol) of DC24C8.

Further addition of DC24C8 to the solution increases the amount of {(DC24C8)[**4**-H]}$^{+}$(PF$_{6}$)$^{-}$ relative to that of {(DB24C8)[**4**-H]}$^{+}$(PF$_{6}$)$^{-}$ (Figure 4 c and d).



(4)

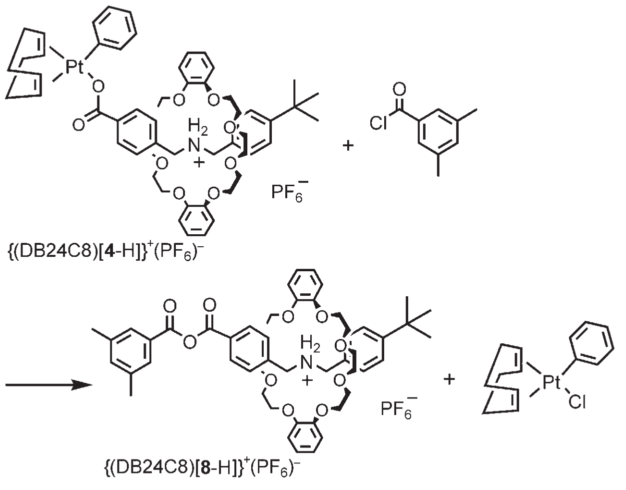
A competitive reaction of a mixture of DB24C8 and DC24C8 with dibenzylammonium cations was conducted to compare the relative stabilities of the two rotaxanes. A [2]pseudorotaxane formed from the reaction of (PhCH$_{2}$NH$_{2}$CH$_{2}$Ph)$^{+}$(PF$_{6}$)$^{-}$ ((**7**-H)$^{+}$(PF$_{6}$)$^{-}$) and DB24C8 has been reported.[25] DC24C8 also forms a [2]pseudorotaxane with (**7**-H)$^{+}$(PF$_{6}$)$^{-}$ in CD$_{3}$CN (40 mM for each compound), yielding a mixture of {(DC24C8)(**7**-H)}$^{+}$(PF$_{6}$)$^{-}$ and (**7**-H)$^{+}$(PF$_{6}$)$^{-}$ in a 1:2 ratio [Eq. (5)]. Addition of DB24C8 (1 equiv to DC24C8) to the solution yields a mixture containing $(\mathbf{7}\text{-H})^+(PF_6)^-$, $\{(DC24C8)(\mathbf{7}\text{-H})\}^+(PF_6)^-$, and $\{(DB24C8)(\mathbf{7}\text{-H})\}^+(PF_6)^-$ in a 2:2:6 ratio. Further addition of DB24C8 (3 equiv to DC24C8) changes the molar ratio to 0:3:97. A pseudorotaxane composed of a dialkylammonium derivative with 4,4′-dibenzylbipyridinium and DB24C8 has been reported to undergo exchange of the macrocyclic component with the addition of DC24C8.[28]



(5)

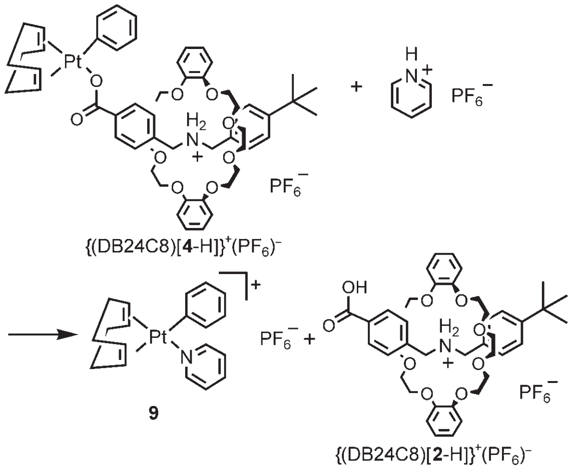
Reactions of the Organoplatinum Rotaxane

The addition of $3,5\text{-}Me_2C_6H_3COCl$ to a solution of $\{(DB24C8)[\mathbf{4}\text{-H}]\}^+(PF_6)^-$ causes the acylation of the carboxylate ligand of the axis component to afford an organic [2]rotaxane that contains an unsymmetrical acid anhydride in the axis component, $\{(DB24C8)(\mathbf{8}\text{-H})\}^+(PF_6)^-$ (**8**: $4\text{-}t\mathrm{Bu}C_6H_4CH_2NHCH_2C_6H_4COOCOC_6H_3Me_2\text{-}3,5$) [Eq. (6)]. The [2]rotaxane and [PtCl(Ph)(cod)] produced were isolated in yields of 60 and 52%, respectively. $\{(DB24C8)(\mathbf{8}\text{-H})\}^+(PF_6)^-$ was characterized by ^{1}H NMR, ^{13}C{^{1}H} NMR, NOESY, and IR spectroscopy and ESI MS. The peak in the ESI MS spectrum at $m/z = 878.8$ was assigned to the cationic rotaxane $\{(DB24C8)(\mathbf{8}\text{-H})\}^+$. ^{1}H NMR signals of NCH_2 hydrogen nuclei in the axis of $\{(DB24C8)(\mathbf{8}\text{-H})\}^+(PF_6)^-$ were observed at 4.53 and 4.82 ppm, which are at similar positions to the corresponding signals of $\{(DB24C8)(\mathbf{2}\text{-H})\}^+(PF_6)^-$ ($\delta = 4.58$, 4.81 ppm). The IR C=O stretching bands of $\{(DB24C8)(\mathbf{8}\text{-H})\}^+(PF_6)^-$ (1786 and 1723 cm^{-1}, KBr disc) are at similar positions to those of $4\text{-}MeC_6H_4COOCOC_6H_3Me_2\text{-}3,5$ (1782 and 1713 cm^{-1}, neat); however, the peaks due to vibrations of the NH_2 group in $\{(DB24C8)(\mathbf{8}\text{-H})\}^+(PF_6)^-$ are shifted to lower wavenumbers (3154 and 3067 cm^{-1}) than those of $(\mathbf{2}\text{-H})^+(PF_6)^-$ (3249 and 3225 cm^{-1}), thus indicating the N−H···O hydrogen bonds in the [2]rotaxane.



(6)

The addition of $(py\text{-H})^+(PF_6)^-$ (py = pyridine) to a solution of $\{(DB24C8)[\mathbf{4}\text{-H}]\}^+(PF_6)^-$ forms $[Pt(Ph)(py)(cod)]^+(PF_6)^-$ (**9**) and $\{(DB24C8)(\mathbf{2}\text{-H})\}^+(PF_6)^-$ [Eq. (7)]. Complex **9** was prepared independently by treating a solution of [PtI(Ph)(cod)] in THF with $AgPF_6$ in the presence of pyridine. The addition of bpy to a solution of $\{(DB24C8)[\mathbf{4}\text{-H}]\}^+(PF_6)^-$ yields the pentacoordinated platinum(II) complex $[Pt(Ph)(bpy)(cod)]^+(PF_6)^-$ (**10**), DB24C8, and **2** immediately [Eq. (8)].[29,30] The mechanism of this reaction will be discussed later.



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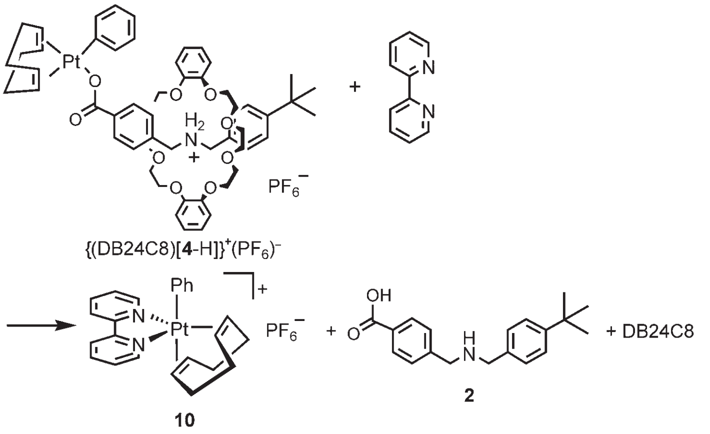
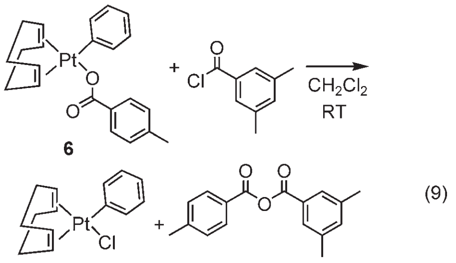


(8)

Reactions of Pt Complexes without the Semirotaxane Structure

Complex **6** has a square-planar structure with phenyl, carboxylate, and cod ligands similar to the Pt-containing rotaxanes prepared in this study. The chemical properties of **6** were compared with those of the Pt-containing rotaxanes. Complex **6** reacts with equimolar quantities of 3,5-$Me_2C_6H_3COCl$ to afford [PtCl(Ph)(cod)] (72%) and 4-$MeC_6H_4COOCOC_6H_3Me_2$-3,5 (87%) [Eq. (9)].[31] The coupling of the carboxylate ligand with the acyl group yields a carboxylic anhydride in a similar manner to the reaction of the rotaxane [Eq. (6)]. The reaction of $(py\text{-}H)^+(PF_6)^-$ with **6** affords **9** and 4-methylbenzoic acid [Eq. (10)]. A similar protonolysis of the Pt–O bond was observed in the reaction of the rotaxane [Eq. (7)]. Although the Pt-containing rotaxane reacts with bpy to afford a cationic pentacoordinated Pt complex [Eq. (8)], the reaction of bpy with **6** causes the displacement of the cod ligand to yield $[Pt(OCOC_6H_4Me\text{-}4)(Ph)(bpy)]$ (**11**) [Eq. (11)]. Figure 5 depicts the molecular structure of **11**; the coordination around the Pt center, which is bonded to both phenyl and carboxylate ligands with *cis* geometry, is square planar.



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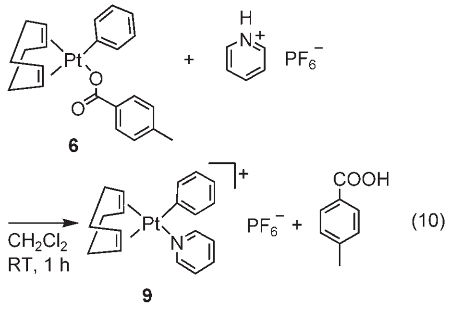

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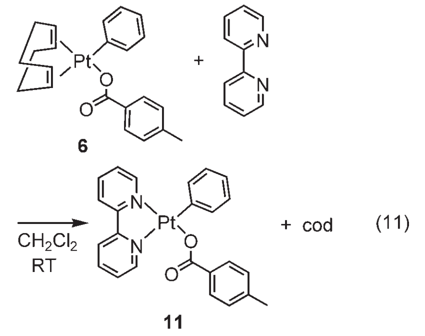

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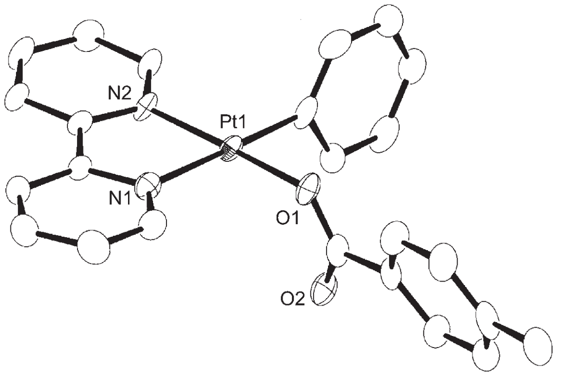


Figure 5. ORTEP drawing of **11** with 50% ellipsoidal plotting. H_2O molecules included in the crystal during crystallization and hydrogen atoms are omitted for clarity.

To compare the reactivity of the carboxylate–platinum complex and the Pt-containing rotaxane, the preparation of the Pt complex with the secondary ammonium fragment in the carboxylate ligand, that is, $[\mathbf{4}\text{-H}]^+(PF_6)^-$, was examined. The reaction of **1** with $(\mathbf{2}\text{-H})^+(PF_6)^-$, however, did not produce the carboxylate–Pt complex, but yielded a complicated mixture of acetone (31%), **2** (24%), $[Pt(Ph)_2(cod)]$ (6%), and benzene (<2%). The reaction of $(\mathbf{7}\text{-H})^+(PF_6)^-$ with **6** causes the part protonation of the phenyl ligand, which is accompanied by the formation of benzene (<27%). These results indicate that $[\mathbf{4}\text{-H}]^+(PF_6)^-$ is unstable in solution without DB24C8. The dissociation of the carboxylate ligand with the dialkylammonium group from Pt induces the transfer of a proton from the ammonium to the carboxylate group to yield **2**. DB24C8 in $\{(DB24C8)[\mathbf{4}\text{-H}]\}^+(PF_6)^-$ protects the dialkylammonium group and prevents the transfer of its proton to the carboxylate or phenyl ligand.[15d,32] As the solution contains free DB24C8 and free axis molecules, the ammonium groups are considered to be stabilized by an intermolecular interaction rather than the formation of an interlocked structure.

The ^1H NMR spectrum of a mixture of DB24C8 and $(\mathbf{12}\text{-H})^+(PF_6)^-$ (**12**: 4-tBu$C_6H_4CH_2NHCH_2C_6H_4$$t$Bu-4) in CD_2Cl_2 is shown in Figure 6a. Peaks due to *t*Bu, NCH_2, and C_6H_4

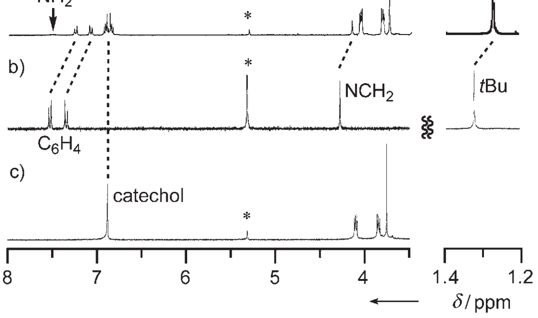
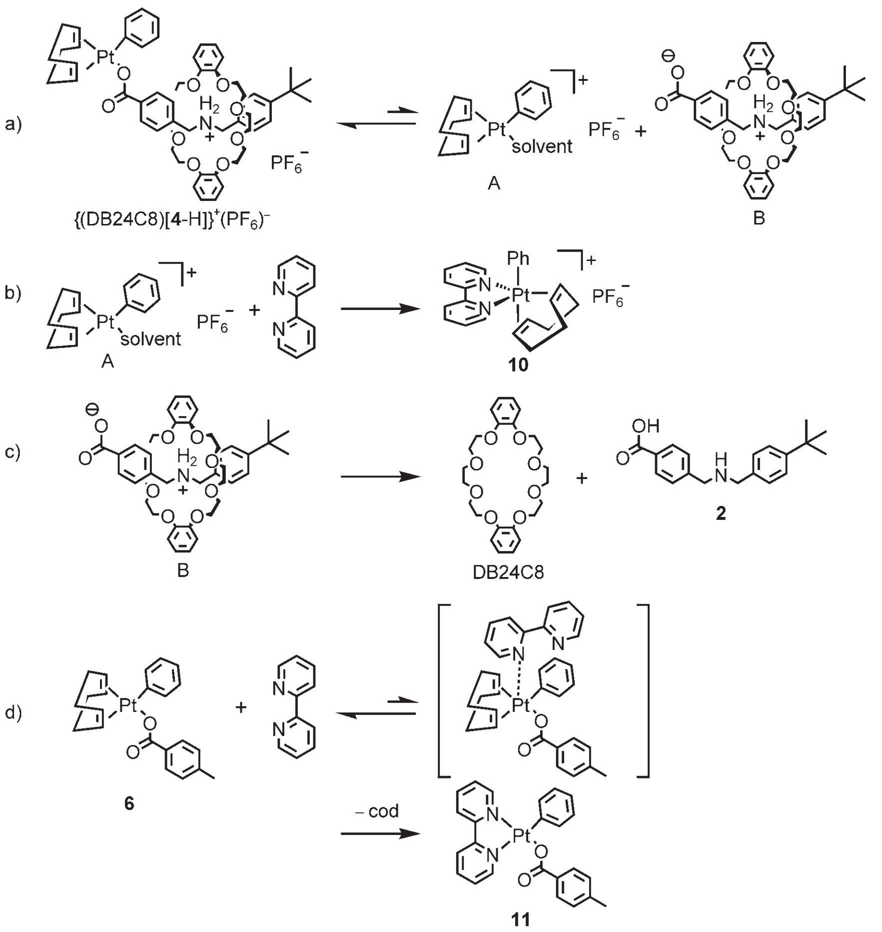
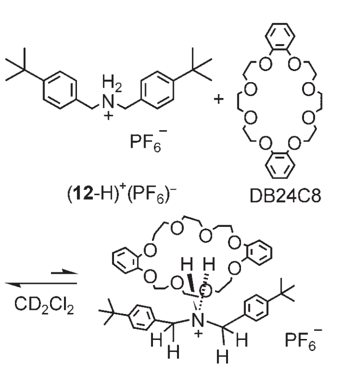


Figure 6. ^1H NMR spectra (CD_2Cl_2, RT) of a) a mixture of DB24C8 and $(\mathbf{12}\text{-H})^+(PF_6)^-$, b) $(\mathbf{12}\text{-H})^+(PF_6)^-$, and c) DB24C8.

hydrogen nuclei ($\delta = 1.27$, 4.17, 7.09, 7.26 ppm) are at lower frequencies than those of ($\mathbf{12}$-H)$^+$(PF$_6$)$^-$ ($\delta = 1.33$, 4.28, 7.35, 7.53 ppm) (Figure 6b). The aromatic hydrogen signals of the mixture appear as multiplets, whereas the corresponding signal of DB24C8 in CD_2Cl_2 (Figure 6c) is observed as a broad signal. A broad signal due to the NH_2 hydrogen nuclei ($\delta = 7.51$ ppm) is observed for the mixture at a similar position to that of {(DB24C8)($\mathbf{2}$-H)}$^+$(PF$_6$)$^-$ ($\delta = 7.64$ ppm in CD_3CN) and is at a higher frequency than that of ($\mathbf{2}$-H)$^+$(PF$_6$)$^-$ ($\delta = 7.14$ ppm in CD_3CN). Because the formation of a rotaxane from DB24C8 and ($\mathbf{12}$-H)$^+$(PF$_6$)$^-$ is not plausible owing to the bulky *t*Bu end groups of ($\mathbf{12}$-H)$^+$(PF$_6$)$^-$, another type of complex of these molecules is suggested. The formation of a complex of ($\mathbf{12}$-H)$^+$(PF$_6$)$^-$ and DB24C8 has been observed in the gas phase.[26] A solution of the mixture of these two compounds in $CDCl_3/CD_3CN$ (3:1), however, did not show NMR signals of their complex owing to the high polarity of the solvent. A possible structure of the complex, which accounts for the results of the NMR spectroscopic experiments, contains intermolecular N−H···O hydrogen bonds and a π–π stacking of aromatic planes as shown in Equation (12).[33]



Scheme 1. Proposed mechanism of the reaction of the Pt-containing semirotaxane and complex with bpy. a) Dissociation of {(DB24C8)[$\mathbf{4}$-H]}$^+$(PF$_6$)$^-$. b) Coordination of bpy to A. c) Dissociation of B. d) Displacement of the cod ligand of $\mathbf{6}$ by bpy.

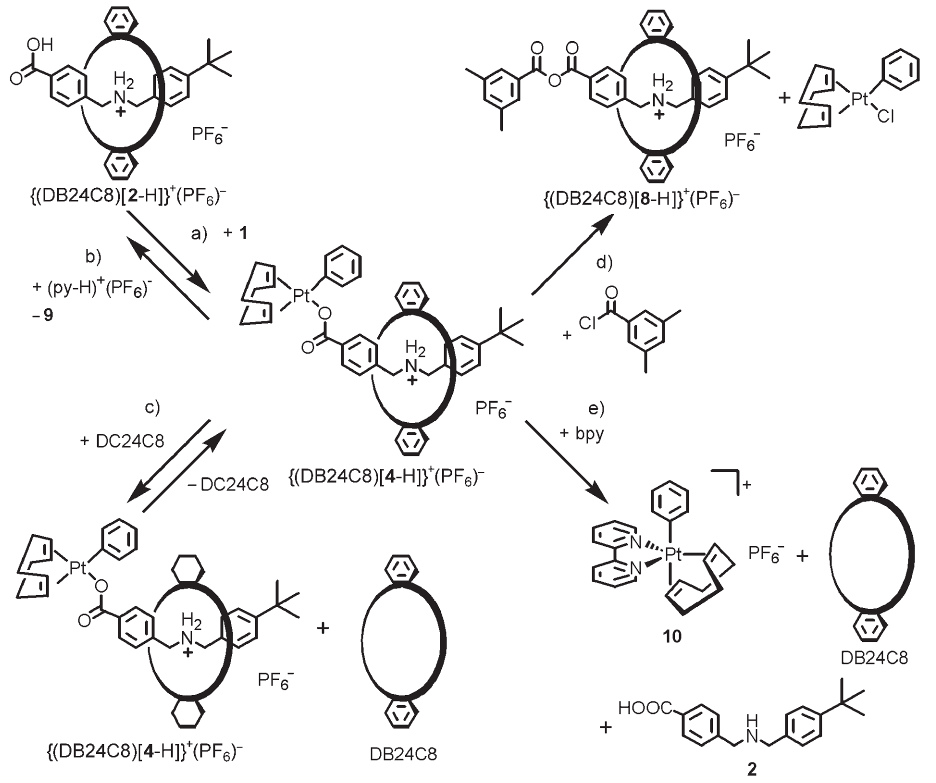


(12)

Scheme 1 summarizes the reactions of the Pt complex and the Pt-containing semirotaxane with bpy. {(DB24C8)[$\mathbf{4}$-H]}$^+$(PF$_6$)$^-$ partly dissociates in solution to yield a mixture of cationic phenylplatinum (A) and a pseudorotaxane (B) (a). The coordination of bpy to the Pt center of A leads to the pentacoordinated Pt complex $\mathbf{10}$ (b). The carboxylate ligands with and without complexation with DB24C8 (c) do not react with the 18-electron Pt complex $\mathbf{10}$. The exchange of the cod ligand of $\mathbf{6}$ with the addition of bpy (d) probably involves the precoordination of a pyridine group to form a pentacoordinated intermediate that extrudes the cod ligand. The dissociation of the carboxylate ligand of $\mathbf{6}$ is more difficult than that of {(DB24C8)[$\mathbf{4}$-H]}$^+$(PF$_6$)$^-$, which has a positive charge on the ligand.

Conclusions

The [2]semirotaxanes prepared in this study contain a labile Pt−O σ bond and exhibit the chemical properties summarized in Scheme 2. The [2]pseudorotaxane {(DB24C8)($\mathbf{2}$-H)}$^+$(PF$_6$)$^-$, with a carboxylic acid group at one end of the axis component, reacts with $\mathbf{1}$ to afford the semirotaxane {(DB24C8)[$\mathbf{4}$-H]}$^+$(PF$_6$)$^-$, which contains a Pt−OCOR bond in the axis component (a). The resulting semirotaxane is sta-



Scheme 2. The reactions of platinum complexes with a semirotaxane structure.

bilized by the N–H···O and C–H···O bonds between the axis and cyclic components. The addition of (py-H)$^+$(PF$_6$)$^-$ to a solution of {(DB24C8)[**4**-H]}$^+$(PF$_6$)$^-$ causes a facile protonolysis of the Pt–O bond to form the cationic complex **9** and {(DB24C8)(**2**-H)}$^+$(PF$_6$)$^-$ (b). The Pt–O bond in {(DB24C8)[**4**-H]}$^+$(PF$_6$)$^-$ undergoes reversible partial dissociation and re-formation in solution. The carboxylate anion formed by partial dissociation may exist as a face-to-face complex with DB24C8. This reversible dissociation and the formation of the Pt–O bond induces, with the addition of DC24C8, an exchange of the macrocyclic molecules of the rotaxane {(DB24C8)[**4**-H]}$^+$(PF$_6$)$^-$ (c). The high reactivity of the carboxylate–platinum(II) bond of {(DB24C8)[**4**-H]}$^+$(PF$_6$)$^-$ enables the transformation of the semirotaxane, whereas the phenyl ligand bonded to the Pt center behaves as the spectator. The replacement of the {PtPh(cod)} fragment of {(DB24C8)[**4**-H]}$^+$(PF$_6$)$^-$ with the aroyl group of 3,5-$Me_2C_6H_3COCl$ immobilizes the rotaxane structure, whose axis component consists of only covalent bonds (d). The coordination of bpy to the Pt center of {(DB24C8)[**4**-H]}$^+$(PF$_6$)$^-$ induces the degradation of the semirotaxane to yield the pentacoordinated platinum complex **10** (v). These results are in contrast with those of the reaction of bpy with **6**, which causes a simple displacement of cod with bpy and forms a square-planar carboxylate–platinum complex. Thus, the transition-metal-containing fragment in the semirotaxane exhibits chemical properties similar not only to those of the discrete molecular transition-metal complexes but also to those unique to the metal-containing rotaxanes. A facile transformation of thermodynamically stable rotaxanes caused by the activation of the metal–ligand bond could lead to a basic concept of smart supramolecular systems in future studies.

Experimental Section

General

NMR spectra (^{1}H, ^{13}C{^{1}H}, ^{1}H-^{1}H COSY, ^{13}C{^{1}H}-^{1}H COSY, NOESY) were recorded on Varian MERCURY300, JEOL EX-400, and JEOL GX-500 spectrometers. IR spectra were recorded on a Shimadzu FT/IR-8100 spectrometer. Elemental analyses were carried out with a Yanaco MT-5 CHN autorecorder. FABMS was performed with a JEOL JMS-700 instrument (*m*-nitrobenzyl alcohol as matrix). ESIMS was performed with a ThermoQuest Finnigan LCQ Duo instrument.

1,[23] [Pt(X)(Ph)(cod)] (X = Cl, I, Ph),[34] {(DB24C8)(**2**-H)}$^+$(PF$_6$)$^-$,[24] ($ArCH_2NH_2CH_2Ar$)$^+$(PF$_6$)$^-$ ((**7**-H)$^+$(PF$_6$)$^-$: Ar = Ph, (**12**-H)$^+$(PF$_6$)$^-$: Ar = 4-*t*BuC_6H_4),[25,26] and (py-H)$^+$(PF$_6$)$^-$[35] were prepared according to the methods in the literature. Other chemicals were commercially available. Manipulation of the complexes was carried out under nitrogen or argon with standard Schlenk techniques. Dried solvents were purchased from Kanto Chemical Co., Inc. and used without further purification.

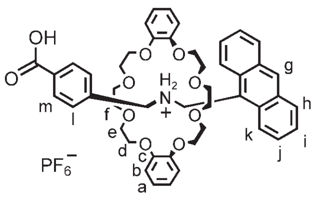
Syntheses

(**2**-H)$^+$(PF$_6$)$^-$: This was prepared by the method in the literature.[22b,24,36] IR (KBr): $\tilde{\nu}$ = 3249 (ν_{N-H}), 3225 (ν_{N-H}), 1705 ($\nu_{C=O}$), 843 (ν_{P-F}), 559 cm^{-1} (ν_{P-F}); ^{1}H NMR (300 MHz, CD_3CN, RT): $\delta = 1.31$ (s, 9H, CH_3), 4.22 (br s, 2H, CH_2), 4.30 (br s, 2H, CH_2), 7.14 (br s, 2H, NH_2), 7.39 (d, 2H, C_6H_4, $J_{H,H} = 8.7$ Hz), 7.50 (d, 2H, C_6H_4, $J_{H,H} = 8.7$ Hz), 7.57 (d, 2H, C_6H_4, $J_{H,H} = 8.4$ Hz), 8.05 ppm (d, 2H, C_6H_4, $J_{H,H} = 8.4$ Hz); MS (ESI): *m*/*z* calcd for $C_{19}H_{24}NO_2$: 298.4 [*M*−PF$_6$]$^+$; found: 298.3.

(**3**-H)$^+$(PF$_6$)$^-$: This was prepared by the method in the literature.[22b,24,36] IR (KBr): $\tilde{\nu}$ = 3654 (ν_{N-H}), 3582 (ν_{N-H}), 839 (ν_{P-F}), 559 cm^{-1} (ν_{P-F}); ^{1}H NMR (300 MHz, CD_3CN, RT): 4.56 (2H, NCH_2), 5.28 (2H, NCH_2), 7.60 (m, 2H), 7.63 (d, 2H, $J_{H,H} = 8.4$ Hz), 7.68 (m, 6H), 8.08 (d, 2H, $J_{H,H} = 8.4$ Hz), 8.16 (d, 2H, $J_{H,H} = 8.4$ Hz), 8.17 (d, 2H, $J_{H,H} = 8.7$ Hz), 8.74 ppm (s, 1H); MS (ESI): *m*/*z* calcd for $C_{23}H_{20}NO_2$: 342.1 [*M*−PF$_6$]$^+$; found: 342.0.

{(DB24C8)(**2**-H)}$^+$(PF$_6$)$^-$: (**2**-H)$^+$(PF$_6$)$^-$ (19 mg, 0.043 mmol) and DB24C8 (6.3 mg, 0.014 mmol) were placed in an NMR tube and CD_3CN (0.7 mL) was added to the mixture. ^{1}H NMR spectroscopy showed the formation of {(DB24C8)(**2**-H)}$^+$(PF$_6$)$^-$. ^{1}H NMR (300 MHz, CD_3CN, RT): $\delta = 1.23$ (s, 9H, CH_3), 3.55 (s, 8H, OCH_2), 3.74 (t, 8H, OCH_2, $J_{H,H} = 4.2$ Hz), 4.01 (m, 8H, OCH_2), 4.58 (m, 2H, NCH_2), 4.81 (m, 2H, NCH_2), 6.76–6.82 (8H, C_6H_4-DB24C8), 7.26 (4H, C_6H_4), 7.41 (d, 2H, C_6H_4, $J_{H,H} = 8.1$ Hz), 7.64 (br s, 2H, NH_2), 7.68 ppm (d, 2H, C_6H_4, $J_{H,H} = 8.1$ Hz); MS (ESI): *m*/*z* calcd for $C_{43}H_{56}NO_{10}$: 746.4 [*M*−PF$_6$]$^+$; found: 746.5.

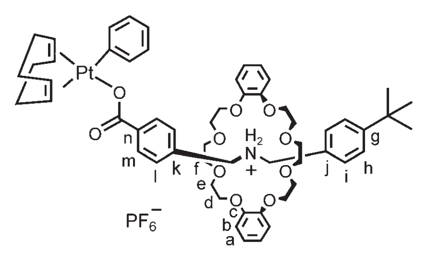
{(DB24C8)(**3**-H)}$^+$(PF$_6$)$^-$: (**3**-H)$^+$(PF$_6$)$^-$ (3.5 mg, 0.0072 mmol) and DB24C8 (3.3 mg, 0.0074 mmol) were placed in an NMR tube and



{(DB24C8)(**3**-H)}$^+$(PF$_6$)$^-$

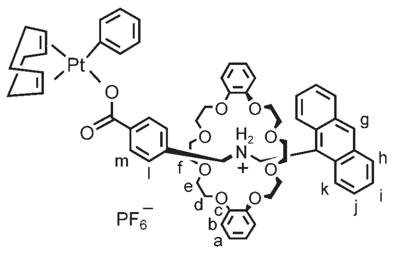
CD_3CN (0.7 mL) was added to the mixture at room temperature. Although a part of the axis molecule remained undissolved, ^{1}H NMR spectroscopy showed the formation of {(DB24C8)(**3**-H)}$^+$(PF$_6$)$^-$. ^{1}H NMR (300 MHz, CD_3CN, RT): $\delta = 3.39$ (m, 8H, OCH_2), 3.63–3.84 (m, 16H, OCH_2), 5.40 (m, 2H, NCH_2), 5.58 (m, 2H, NCH_2), 6.32 (m, 8H, a or b), 6.60 (m, 8H, a or b), 7.46 (dd, 2H, $J_{H,H} = 7.8$, 7.8 Hz, i or j), 7.58–7.64 (4H), 7.65 (br s, 2H, NH_2), 7.86 (d, 2H, $J_{H,H} = 8.4$ Hz, l, h, or k), 7.98 (d, 2H, $J_{H,H} = 8.4$ Hz, l, h, or k), 8.18 (s, 1H, g), 8.46 ppm (d, 2H, $J_{H,H} = 8.4$ Hz, m); MS (ESI): *m*/*z* calcd for $C_{47}H_{52}NO_{10}$: 790.4 [$M-PF_6$]$^+$; found: 790.5.

{(DB24C8)[**4**-H]}$^+$(PF$_6$)$^-$: A suspension of (**2**-H)$^+$(PF$_6$)$^-$ (27 mg, 0.061 mmol) and DB24C8 (27 mg, 0.060 mmol) in $CDCl_3$ (0.6 mL) was stirred for 1 h at 0 °C. **1** (26 mg, 0.060 mmol) was added to the mixture, which was stirred for a further 12 h. The temperature was gradually raised to room temperature during the reaction. Most of the starting materials were dissolved in the solvent. The ^{1}H NMR spectrum of the solution with 1,2-diphenylethane as an internal standard showed the existence of {(DB24C8)[**4**-H]}$^+$(PF$_6$)$^-$ (0.042 mmol, 70 %), free DB24C8 (0.013 mmol, 22 %), acetone (0.045 mmol, 75 %), and [Pt(Ph)$_2$(cod)] (2×10^{-3} mmol, 3 %). A similar reaction with [(**2**-H)$^+$(PF$_6$)$^-$]$_o$ = [DB24C8]$_o$ = [[Pt(CH$_2$COMe)(Ph)(cod)]]$_o$ = 0.05 M gave a homogeneous $CDCl_3$ solution of the reaction products. The molar ratio [DB24C8]/[{(DB24C8)[**4**-H]}$^+$(PF$_6$)$^-$] was determined by ^{1}H NMR spectra obtained at 20 °C, 50 °C, and after cooling to 20 °C. ^{1}H NMR (400 MHz, $CDCl_3$, RT): $\delta = 1.24$ (s, 9H, CH_3), 2.22–2.68 (8H, CH_2-cod), 3.44 (m, 8H, e or f), 3.73 (m, 8H, e or f), 4.05 (m, 8H, d), 4.49 (m, 2H, NCH_2), 4.57 (br s, 2H, CH-cod (*trans* to O)), 4.67 (m, 2H, NCH_2), 5.92 (br s, CH-cod (*trans* to C)), 6.70 (m, 4H, a or b), 6.79 (m, 4H, a or b), 6.98 (m, 1H, *p*-Ph), 7.04 (m, 2H, *m*-Ph), 7.16 (d, 2H, $J_{H,H} = 8.5$ Hz, h or i), 7.20 (d, 2H, $J_{H,H} = 8.5$ Hz, h or i), 7.27* (d, 2H, l), 7.33 (d, 2H, *o*-Ph, $J_{H,H} = 7.3$ Hz), 7.59 (br s, 2H, NH_2), 7.75 ppm (d, 2H, m, $J_{H,H} = 8.3$ Hz) (peak with asterisk overlapped with the signal of solvent ($CHCl_3$)); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, RT; selected): $\delta = 31.0$ (CH_3), 34.4 ($C(CH_3)_3$), 51.9 (NCH_2), 52.2 (NCH_2), 67.8 (d), 69.9 (e or f), 70.3 (e or f), 82.3 (br s, CH-cod (*trans* to O)), 112.3 (a or b), 114.7 (CH-cod (*trans* to C)), 121.5 (a or b), 124.5 (*p*-Ph), 125.3 (h or i), 127.3 (*m*-Ph), 128.2 (l), 128.7 (h or i), 133.5 (br s, *o*-Ph), 129.6 (n), 170.0 ppm (CO); MS (FAB): *m*/*z* calcd for $C_{57}H_{72}NO_{10}Pt$: 1125 [$M-PF_6$]$^+$; found: 1125.



{(DB24C8)[**4**-H]}$^+$(PF$_6$)$^-$

{(DB24C8)[**5**-H]}$^+$(PF$_6$)$^-$: A suspension of (**3**-H)$^+$(PF$_6$)$^-$ (20 mg, 0.041 mmol) and DB24C8 (18 mg, 0.040 mmol) in $CDCl_3$ (0.6 mL) was stirred for 1 h at 0 °C followed by the addition of **1** (17 mg, 0.040 mmol). After another 12 h of stirring, a large part of the solids was dissolved in $CDCl_3$, although a small amount remained undissolved. The mixture was warmed to room temperature during the reaction. The ^{1}H NMR spectrum of the resulting mixture with 1,2-diphenylethane as an internal standard showed the existence of {(DB24C8)[**5**-H]}$^+$(PF$_6$)$^-$ (0.019 mmol, 48 %), free DB24C8 (≈0.018 mmol, ≈45 %), acetone (0.020 mmol, 50 %), and [Pt(Ph)$_2$(cod)] (≈4×10^{-4} mmol, ≈1 %). ^{1}H NMR (300 MHz, $CDCl_3$, RT): $\delta = 2.30$–2.72 (8H, CH_2-cod), 3.35 (m, 8H, d, e, or f), 3.57–3.77 (16H, d, e, or f), 4.56 (m, 2H, CH-cod, $J_{Pt,H} = 67$ Hz), 5.33 (m, 2H, NCH_2), 5.48 (m, 2H, NCH_2), 5.93 (br s, 2H, CH-cod), 6.26 (m, 4H, a or b), 6.61 (m, 4H, a or b), 6.94–7.06 (3H, *m*-Ph, *p*-Ph), 7.26–7.36 (br s, *o*-Ph), 7.39–7.46 (4H, l, i or j), 7.58 (m, 2H, i or j), 7.77 (br s, 2H, NH_2), 7.79 (d, 2H, $J_{H,H} = 8.4$ Hz, h or k), 7.92 (d, 2H, $J_{H,H} = 8.4$ Hz, h or k), 8.06 (s, 1H, g), 8.39 ppm (d, 2H, m, $J_{H,H} = 8.7$ Hz) (peaks without multiplicities stated overlapped severely with other peaks); MS (FAB): *m*/*z* calcd for $C_{61}H_{68}NO_{10}Pt$: 1169 [$M-PF_6$]$^+$; found: 1169. The low solubility of [(DB24C8)(**5**-H)]$^+$[PF$_6$]$^-$ prevented ^{13}C{^{1}H} NMR measurements.



{(DB24C8)[**5**-H]}$^+$(PF$_6$)$^-$

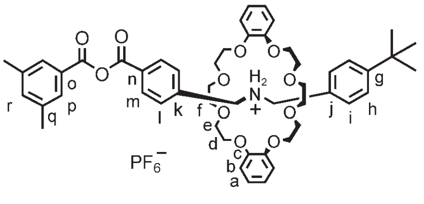
6: 4-MeC$_6$H$_4$COOH (29 mg, 0.21 mmol) was added to a solution of **1** (87 mg, 0.20 mmol) in $CHCl_3$ (4.0 mL). The reaction mixture was stirred for 15 h at room temperature. Removal of the solvent under reduced pressure gave a white solid whose ^{1}H NMR spectrum ($CDCl_3$, diphenylmethane as an internal standard) indicated the presence of **6** in quantitative yield. Recrystallization of the crude product from CH_2Cl_2 and cold Et_2O afforded **6** as a white solid, which was washed with cold Et_2O and dried in vacuo (64 mg, 0.13 mmol, 65 %). ^{1}H NMR (300 MHz, $CDCl_3$, RT): $\delta = 2.28$ (m, 4H, CH_2), 2.31 (s, 3H, CH_3), 2.62 (m, 4H, CH_2), 4.54 (m, 2H, CH, $J_{Pt,H} = 75$ Hz), 5.96 (m, 2H, CH, $J_{Pt,H} \approx 26$ Hz), 6.91 (m, 1H, *p*-Ph), 7.05 (m, 2H, *m*-Ph), 7.09 (d, 2H, *m*′-C$_6$H$_4$, $J_{H,H} = 8.1$ Hz), 7.31 (m, 2H, *o*-Ph, $J_{Pt,H} \approx 20$ Hz), 7.80 ppm (d, 2H, *o*′-C$_6$H$_4$, $J_{H,H} = 8.1$ Hz); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, RT): $\delta = 21.5$ (CH_3), 27.7 (CH_2), 31.9 (CH_2), 81.7 (CH), 114.6 (CH, $J_{Pt,C} = 30$ Hz), 124.7, 127.7 ($J_{Pt,C} = 61$ Hz), 128.3, 129.6, 132.9, 133.4, 140.9, 143.3, 171.5 ppm (C=O); elemental analysis: calcd (%) for $C_{22}H_{24}O_2Pt$: C 51.26, H 4.69; found: C 50.97, H 4.71.

{(DC24C8)[**4**-H]}$^+$(PF$_6$)$^-$ and reaction with DB24C8: A suspension of (**2**-H)$^+$(PF$_6$)$^-$ (27 mg, 0.061 mmol) and DC24C8 (28 mg, 0.061 mmol) in $CDCl_3$ (0.6 mL) was stirred for 1 h at 0 °C followed by the addition of **1** (26 mg, 0.060 mmol). After another 12 h of stirring, a large part of the solids was dissolved in $CDCl_3$, although a small amount remained undissolved. The mixture was warmed to room temperature during the reaction. The ^{1}H NMR spectrum of the resulting mixture with 1,2-diphenylethane as an internal standard showed the existence of {(DC24C8)[**4**-H]}$^+$(PF$_6$)$^-$ (0.028 mmol, 47 %), free DC24C8, acetone (<0.040 mmol, <68 %), and [Pt(Ph)$_2$(cod)] (≈6×10^{-3} mmol, ≈3 %). DB24C8 (27 mg, 0.060 mmol) was then added to the mixture. The NMR tube was stored at room temperature. After 4 h, the ^{1}H NMR spectrum showed the presence of {(DB24C8)[**4**-H]}$^+$(PF$_6$)$^-$ (0.021 mmol, 37 %) and free DB24C8 (≈0.033 mmol, ≈54 %). {(DC24C8)[**4**-H]}$^+$(PF$_6$)$^-$: ^{1}H NMR (300 MHz, $CDCl_3$, RT): 1.12–1.85 (20H, C_6H_{10}), 1.31 (s, 9H, CH_3), 2.30–2.45 (4H, CH_2-cod), 2.50–2.75 (4H, CH_2-cod), 3.13–3.40 (br s, 8H, OCH_2), 3.40–3.72 (16H, OCH_2), 4.43–4.65 (6H, CH, NCH_2), 5.91 (br s, 2H, CH), 6.80–7.55 (11H, C_6H_4, Ph), 7.76 (br s, 2H, NH_2), 7.97 ppm (d, 2H, $J_{H,H} = 8.1$ Hz, C_6H_4). Peaks without multiplicities stated overlapped severely with other peaks.

Reaction of {(DB24C8)[**4**-H]}$^+$(PF$_6$)$^-$ with DC24C8: A suspension of (**2**-H)$^+$(PF$_6$)$^-$ (27 mg, 0.061 mmol) and DB24C8 (27 mg, 0.060 mmol) in $CDCl_3$ (0.6 mL) was stirred for 1 h at 0 °C followed by the addition of **1** (26 mg, 0.060 mmol). After another 12 h of stirring, a large part of the solids was dissolved in $CDCl_3$, although a small amount remained undissolved. The mixture was warmed to room temperature during the reaction. The ^1H NMR spectrum of the resulting mixture with 1,2-diphenylethane as an internal standard showed the existence of {(DB24C8)[**4**-H]}$^+$(PF_6)$^-$ (0.045 mmol, 75 %) and free DB24C8 (0.016 mmol, 27 %). ^1H NMR spectra were also recorded after the addition of DB24C8 (28 mg, 0.061 mmol), DB24C8 (85 mg, 0.18 mmol), and DB24C8 (140 mg, 0.30 mmol).

{(DC24C8)(**7**-H)}$^+$(PF_6)$^-$ and {(DB24C8)(**7**-H)}$^+$(PF_6): (**7**-H)$^+$(PF_6)$^-$ (9.6 mg, 0.028 mmol) and DC24C8 (13 mg, 0.028 mmol) were placed in an NMR tube and CD_3CN (0.7 mL) was added to the mixture. ^1H NMR spectroscopy showed the formation of {(DC24C8)(**7**-H)}$^+$(PF_6)$^-$. The ratio of (**7**-H)$^+$(PF_6)$^-$ to {(DC24C8)(**7**-H)}$^+$(PF_6)$^-$ was determined as 66:34 from the ratio of the peak areas of the ^1H NMR signals of the CH_2 hydrogen nuclei of the axis molecules at room temperature. DB24C8 (13 mg, 0.028 mmol) was then added to the mixture, and the ^1H NMR spectrum of the solution showed the generation of {(DB24C8)(**7**-H)}$^+$(PF_6)$^-$. The molar ratio (**7**-H)$^+$(PF_6)$^-$/{(DC24C8)(**7**-H)}$^+$(PF_6)$^-$/{(DB24C8)(**7**-H)}$^+$(PF_6)$^-$ was 2:2:6 at room temperature, which changed to 0:3:97 by further addition of DB24C8 (38 mg, 0.085 mmol). {(DC24C8)(**7**-H)}$^+$(PF_6)$^-$: ^1H NMR (300 MHz, CD_3CN, RT): $\delta = 1.15$–1.78 (20H, C_6H_{10}), 3.25–3.33 (12H, OCH_2), 3.49–3.65* (12H, OCH_2), 4.60 (m, 4H, NCH_2), 7.38–7.49* (6H, Ph), 7.59 (m, 4H, Ph), 7.86 ppm (br s, 2H, NH_2). The peaks with asterisks overlapped significantly with signals of free axis (**7**-H)$^+$(PF_6)$^-$, those without multiplicities stated overlapped severely with other peaks.

{(DB24C8)(**8**-H)}$^+$(PF_6)$^-$: A suspension of (**2**-H)$^+$(PF_6)$^-$ (27 mg, 0.061 mmol) and DB24C8 (27 mg, 0.060 mmol) in CH_2Cl_2 (0.6 mL) was stirred for 1 h at 0°C followed by the addition of **1** (26 mg, 0.060 mmol). After further stirring for 12 h, most of the solid was dissolved in CH_2Cl_2, although a small amount remained undissolved. The mixture was warmed to room temperature during the reaction. 3,5-$Me_2C_6H_3COCl$ (12 mg, 0.070 mmol) was added to the resulting mixture, which was stirred for a further 2 h at room temperature to give a suspension. The solids were removed by filtration and the filtrate was purified by preparative gel permeation chromatography ($CHCl_3$) to give {(DB24C8)(**8**-H)}$^+$(PF_6)$^-$ (37 mg, 0.036 mmol, 60 %), [PtCl(Ph)(cod)] (13 mg, 0.031 mmol, 52 %), and DB24C8 (<7.0 mg, <0.016 mmol, <27 %). {(DB24C8)(**8**-H)}$^+$(PF_6)$^-$: IR (KBr): $\tilde{\nu} = 3154$ (ν_{N-H}), 3067 (ν_{N-H}), 1786 ($\nu_{C=O}$), 1723 ($\nu_{C=O}$), 841 (ν_{P-F}), 558 cm^{-1} (ν_{P-F}); ^1H NMR (300 MHz, $CDCl_3$, RT): $\delta = 1.25$ (s, 9H, $C(CH_3)_3$), 2.40 (s, 6H, 3,5-$(CH_3)_2C_6H_3$), 3.52 (m, 8H, e or f), 3.78 (m, 8H, e or f), 4.06 (m, 8H, d), 4.53 (m, 2H, NCH_2), 4.82 (m, 2H, NCH_2), 6.70 (m, 4H, b), 6.83 (m, 4H, a), 7.21–7.29* (5H, h, i, r; overlapped severely with other peaks), 7.44 (d, 2H, $J_{H,H} = 8$ Hz, l), 7.69 (br s, 2H, NH_2), 7.72 (s, 2H, p), 7.83 ppm (d, 2H, $J_{H,H} = 8$ Hz, m) (peak with asterisk overlapped significantly with signal from solvent); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, RT): $\delta = 21.2$ (3,5-$(CH_3)_2C_6H_3$), 31.2 ($C(CH_3)_3$), 34.7 ($C(CH_3)_3$), 51.9 (NCH_2), 51.9 (NCH_2), 67.8 (d), 69.9 (e or f), 70.3 (e or f), 112.5 (b), 121.8 (a), 125.8 (h or i), 128.3 (l), 128.4, 128.8 (h or i), 129.3, 129.7 (l), 130.4 (m), 136.5 (r), 138.2, 138.8, 147.2 (c), 152.8, 161.8 (C=O), 162.6 ppm (C=O). One signal for an *ipso* carbon nucleus was not found probably due to overlapping with the other signal. These assignments were supported by ^1H-^1H COSY, ^1H-$^{13}C\{^1H\}$ COSY, and NOESY spectroscopy in $CDCl_3$. Geometrical contacts between the C_6H_4 and CH_2 groups in DB24C8 and between the CH_3 and o-C_6H_3 groups in 3,5-$Me_2C_6H_3$ were detected in the NOESY spectrum. MS (ESI): m/z calcd for $C_{52}H_{64}NO_{11}$: 878.4 $[M-PF_6]^+$; found: 878.8.



{(DB24C8)[**8**-H]}$^+$(PF_6)$^-$

Reaction of (py-H)$^+$(PF_6)$^-$ with {(DB24C8)[**4**-H]}$^+$(PF_6)$^-$: A suspension of (**2**-H)$^+$(PF_6)$^-$ (27 mg, 0.061 mmol) and DB24C8 (27 mg, 0.060 mmol) in CH_2Cl_2 (0.6 mL) was stirred for 1 h at 0°C followed by the addition of **1** (26 mg, 0.060 mmol). After stirring for another 12 h, most of the solid was dissolved in CH_2Cl_2, although a small amount remained undissolved. The mixture was warmed to room temperature during the reaction. (py-H)$^+$(PF_6)$^-$ (14 mg, 0.062 mmol) was added to the resulting mixture, which was stirred for a further 1 h at room temperature followed by evaporation of the solvent. ^1H NMR spectroscopic analysis of the resulting solids with $CDCl_3$ solvent and trichloroethylene as an internal standard showed the existence of **9** (0.047 mmol, 78 %), {(DB24C8)(**2**-H)}$^+$(PF_6)$^-$ (0.044 mmol, 73 %), and benzene (0.009 mmol, 15 %).

9: $AgPF_6$ (230 mg, 0.91 mmol) was added to a solution (30 mL) of [PtI(Ph)(cod)] (409 mg, 0.81 mmol) and pyridine (65 μL, 0.80 mmol) in THF to induce the separation of AgI. After 1 h at room temperature, the insoluble AgI was removed by filtration, and subsequent addition of Et_2O (200 mL) to the filtrate caused separation of a white solid, which was washed with Et_2O and dried in vacuo to give **9** (400 mg, 0.66 mmol, 83 %). ^1H NMR (300 MHz, $CDCl_3$, RT): $\delta = 2.48$–2.90 (8H, CH_2), 5.15 (m, 2H, $J_{Pt,H} = 72$ Hz, CH-cod (*trans* to N)), 5.57 (m, 2H, $J_{Pt,H} \approx 30$ Hz, CH-cod (*trans* to C)), 6.89 (m, 1H, *p*-Ph), 7.02 (m, 2H, *m*-Ph), 7.16 (m, 2H, $J_{Pt,H} = 41$ Hz, *o*-Ph), 7.51 (m, 2H, 3-py), 7.81 (m, 1H, 4-py), 8.68 ppm (dd, 2H, 2-py, $J_{H,H} = 6.6$, 1.7 Hz, $J_{Pt,H} = 43$ Hz); $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN, RT): $\delta = 28.9$ ($J_{Pt,C} = 17$ Hz, CH_2), 31.9 ($J_{Pt,C} = 22$ Hz, CH_2), 97.5 ($J_{Pt,C} = 174$ Hz, CH-cod (*trans* to N)), 116.9 ($J_{Pt,C} = 29$ Hz, CH-cod (*trans* to C)), 126.0 (*p*-Ph), 128.2 (3-py), 129.7 ($J_{Pt,C} = 51$ Hz, *m*-Ph), 133.9 (*o*-Ph), 141.4 (4-py), 144.4 (*ipso*-Ph), 151.0 ppm (2-py). These assignments were supported by ^1H-$^{13}C\{^1H\}$ NMR spectroscopy. Elemental analysis: calcd (%) for $C_{19}H_{22}F_6NPPt$: C 37.76, H 3.67, N 2.32; found: C 37.52, H 3.66, N 2.22.

Reaction of bpy with {(DB24C8)[**4**-H]}$^+$(PF_6)$^-$. A suspension of (**2**-H)$^+$(PF_6)$^-$ (27 mg, 0.060 mmol) and DB24C8 (27 mg, 0.060 mmol) in $CDCl_3$ (0.6 mL) was stirred for 1 h at 0°C followed by the addition of **1** (26 mg, 0.060 mmol). After another 12 h of stirring, a large part of the solids was dissolved in $CDCl_3$, although a small amount remained undissolved. The mixture was warmed to room temperature during the reaction. Addition of bpy (9.4 mg, 0.060 mmol) to the mixture caused the smooth separation of white solids which were filtered and washed with $CHCl_3$. Evaporation of the filtrate gave DB24C8, which was analyzed by ^1H NMR spectroscopy with $CDCl_3$ solvent and 1,1,2,2-tetrachloroethane as an internal standard to show quantitative recovery. ^1H NMR spectroscopic analysis of the white solid in [D$_6$]acetone with trichloroethylene as internal standard showed formation of **10** (0.036 mmol, 60 %). The white solid, which was insoluble in [D$_6$]acetone, was collected and analyzed by ^1H NMR spectroscopy with [D$_4$]MeOH as solvent to show the formation of **2** (13 mg, 0.044 mmol, 73 %). **2**: ^1H NMR (300 MHz, [D$_4$]MeOH, RT): $\delta = 1.32$ (s, 9H, CH_3), 4.16 (s, 2H, CH_2), 4.19 (s, 2H, CH_2), 7.38–7.51 (6H, C_6H_4; overlapped severely with other peaks), 7.98 ppm (d, 2H, $J_{H,H} = 8.2$ Hz, C_6H_4).

Reaction of 3,5-$Me_2C_6H_3COCl$ with **6**: 3,5-$Me_2C_6H_3COCl$ (15 mg, 0.089 mmol) was added to a solution of **6** (45 mg, 0.087 mmol) in CH_2Cl_2 (5.0 mL), and resulting mixture was stirred for 4 h at room temperature followed by evaporation of the solvent. The resulting white solids were washed with hexane to give [PtCl(Ph)(cod)] (26 mg, 0.063 mmol, 72 %). The washings were analyzed by ^1H NMR, $^{13}C\{^1H\}$ NMR, and IR spectroscopy and GC–MS. The products contained 4-$MeC_6H_4COOCOC_6H_3Me_2$-3,5 (0.076 mmol, 87 %), 4-$MeC_6H_4COOCOC_6H_4Me$-4 (trace), and 3,5-$Me_2C_6H_3COOCOC_6H_3Me_2$-3,5 (trace). 4-$MeC_6H_4COOCOC_6H_3Me_2$-3,5: IR (neat): $\tilde{\nu} = 1782$ ($\nu_{C=O}$), 1713 cm^{-1} ($\nu_{C=O}$); ^1H NMR (300 MHz, $CDCl_3$, RT): $\delta = 2.37$ (m, 6H, $CH_3C_6H_3$), 2.44 (br s, 3H, $CH_3C_6H_4$), 7.27 (m, 1H, *p*-C_6H_3), 7.30 (dd, 2H, $J_{H,H} = 8.4$, 0.6 Hz, C_6H_4), 7.73 (m, 2H, *o*-C_6H_3), 8.02 ppm (m, 2H, C_6H_4); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, RT): $\delta = 21.1$ ($CH_3C_6H_3$), 21.8 ($CH_3C_6H_4$) 126.2, 128.2, 128.8, 129.6, 130.6, 136.2, 138.6, 145.5, 162.6 (CO), 162.9 ppm (CO); GC–MS: m/z calcd for $C_{17}H_{16}O_3$: 268; found: 268.

11: A solution of **6** (52 mg, 0.10 mmol) and bpy (16 mg, 0.10 mmol) in CH_2Cl_2 (4.0 mL) was stirred for 40 h at room temperature followed by the addition of hexane (20 mL) to precipitate yellow solids from the reaction mixture. The solids were collected by filtration and washed with hexane (2×10 mL) and Et_2O (5 mL). Further purification of the solids by recrystallization from CH_2Cl_2/Et_2O (2:15 *v*/*v*) gave **11** (29 mg, 0.051 mmol, 51 %). ^1H NMR (300 MHz, $CDCl_3$, RT): $\delta = 2.34$ (s, 3H, CH_3), 6.94 (m, 1H, *p*-Ph), 7.06 (m, 2H, *m*-Ph), 7.13 (d, 2H, $J_{H,H} = 8.0$ Hz, C_6H_4), 7.52 (ddd, 1H, $J_{H,H} = 5.2$, 5.2, 3.3 Hz, 5′-H-bpy), 7.56 (m, 2H, *o*-Ph), 7.98–8.10 (5H, 3-H-bpy, 3′-H-bpy, 4-H-bpy, 4′-H-bpy, 5-H-bpy; overlapped severely with other peaks), 8.00 (d, 2H, $J_{H,H} = 8.0$ Hz, C_6H_4), 8.81–8.83 ppm (2H, 6-H-bpy, 6′-H-bpy,); $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2, RT): $\delta = 21.6$ (CH_3), 122.8 (C3-bpy), 123.3 (C3′-bpy), 123.7 (*p*-Ph), 126.9 (*m*-Ph), 127.0 (C5-bpy), 127.5 (C5′-bpy), 128.5 (*o*-C_6H_4 or *m*-C_6H_4), 129.7 (*o*-C_6H_4 or *m*-C_6H_4), 133.3 (*p*-C_6H_4), 137.5 (*ipso*-Ph), 137.8 (C4-bpy), 138.9 (C4′-bpy), 140.9, 141.2, 147.9 (C6-bpy), 152.4 (C6′-bpy), 154.3, 157.5, 172.1 ppm (C=O); elemental analysis: calcd (%) for $C_{24}H_{22}O_3N_2Pt$ (**12**+H_2O): C 49.57, H 3.81, N 4.82; found: C 49.60, H 3.50, N 4.75.

Reaction of **1** with (**2**-H)$^+$(PF_6)$^-$: **1** (6.1 mg, 0.014 mmol), (**2**-H)$^+$(PF_6)$^-$ (6.7 mg, 0.014 mmol), and $CDCl_3$ (0.7 mL) were placed in an NMR tube, which was stored at room temperature. ^1H NMR spectra were recorded occasionally with 1,1,2,2-tetracholoroethane as an internal standard and showed that after 7 days, the solution contained acetone ($<4.3\times10^{-3}$ mmol, $<31\,\%$), $[Pt(Ph)_2(cod)]$ (7.8×10^{-4} mmol, 6 %), and benzene ($<3.3\times10^{-3}$, $<2\,\%$). A white solid insoluble in $CDCl_3$ was collected and analyzed by ^1H NMR spectroscopy with $[D_4]$MeOH as solvent to show the formation of **2** (1.0 mg, 0.0034 mmol, 24 %).

Reaction of **6** with (**7**-H)$^+$(PF_6)$^-$: **6** (7.2 mg, 0.014 mmol), (**7**-H)$^+$(PF_6)$^-$ (4.8 mg, 0.014 mmol), and $CDCl_3$ (0.7 mL) were placed in an NMR tube. Part of the solids remained undissolved. The NMR tube was stored at room temperature. ^1H NMR spectra were recorded occasionally with trichloroethylene as an internal standard and showed that after 10 days, the solution contained benzene ($<3.8\times10^{-3}$ mmol, $<27\,\%$).

Complexation of DB24C8 with (**12**-H)$^+$(PF_6)$^-$: DB24C8 (5.4 mg, 0.012 mmol), (**12**-H)$^+$(PF_6)$^-$ (5.5 mg, 0.012 mmol), and CD_2Cl_2 (0.6 mL) were placed in an NMR tube. Part of solids remained undissolved. ^1H NMR spectroscopy showed the complexation of DB24C8 with (**12**-H)$^+$(PF_6)$^-$. ^1H NMR (300 MHz, CD_2Cl_2, RT): $\delta = 1.27$ (s, 18H, CH_3), 3.75 (s, 8H, OCH_2), 3.82 (s, 8H, OCH_2), 4.07 (s, 8H, OCH_2), 4.17 (s, 4H, NCH_2), 6.84–6.94 (6H, C_6H_4-DB24C8; overlapped severely with other peaks), 7.09 (d, 4H, $J_{H,H} = 8.2$ Hz, C_6H_4), 7.26 (d, 4H, $J_{H,H} = 8.2$ Hz, C_6H_4), 7.51 ppm (br s, NH_2). (**12**-H)$^+$(PF_6)$^-$: ^1H NMR (300 MHz, CD_2Cl_2, RT): $\delta = 1.33$ (s, 18H, CH_3), 4.28 (s, 4H, NCH_2), 7.35 (d, 4H, $J_{H,H} = 8.5$ Hz, C_6H_4), 7.53 ppm (d, 4H, $J_{H,H} = 8.5$ Hz, C_6H_4).

Crystal Structure Analysis

Crystals of **11** suitable for X-ray diffraction were obtained by recrystallization from CH_2Cl_2/hexane and mounted in glass capillary tubes. The data was collected to a maximum 2θ value of 55.0°. A total of 720 oscillation images were collected. Data sweep was done using ω scans from −110.0 to 70.0° in 0.5° steps at $\chi = 45.0°$ and $\phi = 0.0°$. The detector swing angle was −20.32°. A second sweep was performed using ω scans from −110.0 to 70.0° in 0.5° step, at $\chi = 45.0°$ and $\phi = 90.0°$. The crystal-to-detector distance was 45.06 mm. Readout was performed in the 0.070-mm pixel mode. Calculations were carried out by using the program package Crystal Structure™ for Windows.[37]

Crystal data of **11**: $C_{24}H_{24}N_2O_4Pt$, $M_r = 599.55$, monoclinic, space group $P2_1/n$ (No. 14), $a = 12.593(8)$, $b = 13.967(9)$, $c = 13.246(8)$ Å, $\beta = 95.172(7)°$, $V = 2320(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.918$ g cm^{-3}, no. of unique reflections = 5180 ($I > 3\sigma(I)$), $R = 0.057$, $R_w = 0.089$. CCDC-288879 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK or at www.ccdc.cam.ac.uk/data_request/cif.

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[1] a) G. Schill, *Catenanes, Rotaxanes, and Knots*, Academic Press, New York, **1971**; b) *Molecular Catenanes, Rotaxanes, and Knots* (Eds.: J.-P. Sauvage, C. Dietrich-Buchecker), Wiley-VCH, Weinheim, **1999**.

[2] a) D. B. Amabilino, J. F. Stoddart, *Chem. Rev.* **1995**, *95*, 2725; b) A. Harada, *Coord. Chem. Rev.* **1996**, *148*, 115; c) A. Harada, *Carbohydr. Polym.* **1997**, *34*, 183; d) R. Jäger, F. Vögtle, *Angew. Chem.* **1997**, *109*, 966; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 930; e) S. A. Nepogodiev, J. F. Stoddart, *Chem. Rev.* **1998**, *98*, 1959; f) J.-C. Chambron, J.-P. Sauvage, *Chem. Eur. J.* **1998**, *4*, 1362; g) T. J. Hubin, D. H. Busch, *Coord. Chem. Rev.* **2000**, *200–202*, 5; h) T. Takata, N. Kihara, *Rev. Heteroato. Chem.* **2000**, *22*, 197; i) C. A. Schalley, K. Beizai, F. Vögtle, *Acc. Chem. Res.* **2001**, *34*, 465; j) K. Kim, *Chem. Soc. Rev.* **2002**, *31*, 96; k) J.-P. Collin, J.-P. Sauvage, *Chem. Lett.* **2005**, *34*, 742.

[3] a) V. Balzani, A. Credi, F. M. Raymo, J. F. Stoddart, *Angew. Chem.* **2000**, *112*, 3484; *Angew. Chem. Int. Ed.* **2000**, *39*, 3348; b) *Molecular Machines Special Issue* (Ed.: P. F. Barbara), *Acc. Chem. Res.* **2001**, *34*, 409; c) *Molecular Machines and Motors* in *Structure & Bonding, Vol. 99* (Ed.: J.-P. Sauvage), Springer, Berlin, **2001**; d) *Molecular Switches* (Ed.: B. L. Feringa), Wiley-VCH, Weinheim, **2001**; e) V. Balzani, M. Venturi, A. Credi, *Molecular Devices and Machines: A Journey into the Nanoworld*, Wiley-VCH, Weinheim, **2003**; f) A. H. Flood, R. J. A. Ramirez, W.-Q. Deng, R. P. Muller, W. A. Goddard III, J. F. Stoddart, *Aust. J. Chem.* **2004**, *57*, 301.

[4] a) C. P. Collier, E. W. Wong, M. Belohradský, F. M. Raymo, J. F. Stoddart, P. J. Kuekes, R. S. Williams, J. R. Heath, *Science* **1999**, *285*, 391; b) E. W. Wong, C. P. Collier, M. Bělohradský, F. M. Raymo, J. F. Stoddart, J. R. Heath, *J. Am. Chem. Soc.* **2000**, *122*, 5831; c) C. P. Collier, J. O. Jeppesen, Y. Luo, J. Perkins, E. W. Wong, J. R. Heath, J. F. Stoddart, *J. Am. Chem. Soc.* **2001**, *123*, 12632; d) Y. Luo, C. P. Collier, J. O. Jeppesen, K. A. Nielsen, E. Delonno, G. Ho, J. Perkins, H.-R. Tseng, T. Yamamoto, J. F. Stoddart, J. R. Heath, *ChemPhysChem* **2002**, *3*, 519; e) Y. Chen, D. A. A. Ohlberg, X. Li, D. R. Stewart, R. S. Williams, J. O. Jeppesen, K. A. Nielsen, J. F. Stoddart, D. L. Olynick, E. Anderson, *Appl. Phys. Lett.* **2003**, *82*, 1610; f) H. Yu, Y. Luo, K. Beverly, J. F. Stoddart, H.-R. Tseng, J. R. Heath, *Angew. Chem.* **2003**, *115*, 5884; *Angew. Chem. Int. Ed.* **2003**, *42*, 5706; g) H.-R. Tseng, D. Wu, N. X. Fang, X. Zhang, J. F. Stoddart, *ChemPhysChem* **2004**, *5*, 111; h) D. W. Steuerman, H.-R. Tseng, A. J. Peters, A. H. Flood, J. O. Jeppesen, K. A. Nielsen, J. F. Stoddart, J. R. Heath, *Angew. Chem.* **2004**, *116*, 6648; *Angew. Chem. Int. Ed.* **2004**, *43*, 6486; i) P. M. Mendes, A. H. Flood, J. F. Stoddart, *Appl. Phy. A: Mater. Sci. Process* **2005**, *80*, 1197.

[5] a) J. L. Segura, N. Martín, *Angew. Chem.* **2001**, *113*, 1416; *Angew. Chem. Int. Ed.* **2001**, *40*, 1372; b) D. J. Cardin, *Adv. Mater.* **2002**, *14*, 553; c) J.-M. Kern, J.-P. Sauvage, G. Bidan, B. Divisia-Blohorn, *J. Polym. Sci. Part A* **2003**, *41*, 3470.

[6] a) M. J. Marsella, P. J. Carroll, T. M. Swager, *J. Am. Chem. Soc.* **1994**, *116*, 9347; b) S. S. Zhu, P. J. Carroll, T. M. Swager, *J. Am. Chem. Soc.* **1996**, *118*, 8713; c) S. S. Zhu, T. M. Swager, *J. Am. Chem. Soc.* **1997**, *119*, 12568; d) K. Yoshida, T. Shimomura, K. Ito, R. Hayakawa, *Langmuir* **1999**, *15*, 910; e) C. Lagrost, J.-C. Lacroix, K. I. Chane-Ching, M. Jouini, S. Aeiyach, P.-C. Lacaze, *Adv. Mater.* **1999**, *11*, 664; f) P. L. Vidal, B. Divisia-Blohorn, M. Billon, G. Bidan, J.-M. Kern, J.-P. Sauvage, *Synth. Met.* **1999**, *102*, 1478; g) J. Buey, T. M. Swager, *Angew. Chem.* **2000**, *112*, 622; *Angew. Chem. Int. Ed.* **2000**, *39*, 608; h) T. Shimomura, K. Yoshida, K. Ito, R. Hayakawa, *Polym. Adv. Technol.* **2000**, *11*, 837; i) A. Farcas, M. Grigoras, *J. Optoelectron. Adv. Mater.* **2000**, *2*, 525; j) F. Cacialli, J. S. Wilson, J. J.

Michels, C. Daniel, C. Silva, R. H. Friend, N. Severin, P. Samorí, J. P. Rabe, M. J. O'Connell, P. N. Taylor, H. L. Anderson, *Nat. Mater.* **2002**, *1*, 160; k) K. Naka, T. Uemura, Y. Chujo, *Bull. Chem. Soc. Jpn.* **2002**, *75*, 2053; l) B. Divisia-Blohorn, F. Genoud, C. Borel, G. Bidan, J.-M. Kern, J.-P. Sauvage, *J. Phys. Chem. B* **2003**, *107*, 5126; m) R. V. Belosludov, H. Sato, A. A. Farajian, H. Mizuseki, Y. Kawazoe, *Mol. Cryst. Liq. Cryst.* **2003**, *406*, 195; n) Y. Takashima, Y. Oizumi, K. Sakamoto, M. Miyauchi, S. Kamitori, A. Harada, *Macromolecules* **2004**, *37*, 3962; o) I. Yamaguchi, K. Kashiwagi, T. Yamamoto, *Macromol. Rapid Commun.* **2004**, *25*, 1163; p) M. van den Boogaard, G. Bonnet, P. van't Hof, Y. Wang, C. Brochon, P. van Hutten, A. Lapp, G. Hadziioannou, *Chem. Mater.* **2004**, *16*, 4383.

[7] a) N. Yui, *Supramolecular Design for Biological Applications*, CRC Press, Boca Raton, **2002**; b) N. Yui, T. Ooya, *J. Artif. Organs* **2004**, *7*, 62.

[8] a) H. Ogino, *J. Am. Chem. Soc.* **1981**, *103*, 1303; b) K. Yamanari, Y. Shimura, *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2283; c) K. Yamanari, Y. Shimura, *Bull. Chem. Soc. Jpn.* **1984**, *57*, 1596; d) H. Ogino, K. Ohata, *Inorg. Chem.* **1984**, *23*, 3312; e) R. Isnin, A. E. Kaifer, *J. Am. Chem. Soc.* **1991**, *113*, 8188; f) R. S. Wylie, D. H. Macartney, *J. Am. Chem. Soc.* **1992**, *114*, 3136; g) R. S. Wylie, D. H. Macartney, *Supramol. Chem.* **1993**, *3*, 29; h) D. H. Macartney, C. A. Waddling, *Inorg. Chem.* **1994**, *33*, 5912; i) L. A. Godínez, S. Patel, C. M. Criss, A. E. Kaifer, *J. Phys. Chem.* **1995**, *99*, 17449; j) D. J. Cárdenas, P. Gaviña, J.-P. Sauvage, *Chem. Commun.* **1996**, 1915; k) S. J. Loeb, J. A. Wisner, *Chem. Commun.* **1998**, 2757; l) K. Chichak, M. C. Walsh, N. R. Branda, *Chem. Commun.* **2000**, 847; m) A. J. Baer, D. H. Macartney, *Inorg. Chem.* **2000**, *39*, 1410; n) E. Lee, J. Kim, J. Heo, D. Whang, K. Kim, *Angew. Chem.* **2001**, *113*, 413; *Angew. Chem. Int. Ed.* **2001**, *40*, 399; o) M. J. Gunter, N. Bampos, K. D. Johnstone, J. K. M. Sanders, *New J. Chem.* **2001**, *25*, 166; p) G. J. E. Davidson, S. J. Loeb, N. A. Parekh, J. A. Wisner, *J. Chem. Soc. Dalton Trans.* **2001**, *21*, 3135; q) M. Asakawa, T. Ikeda, N. Yui, T. Shimizu, *Chem. Lett.* **2002**, *31*, 174; r) K.-M. Park, D. Whang, E. Lee, J. Heo, K. Kim, *Chem. Eur. J.* **2002**, *8*, 498; s) G. J. E. Davidson, S. J. Loeb, *Angew. Chem.* **2003**, *115*, 78; *Angew. Chem. Int. Ed.* **2003**, *42*, 74; t) G. J. E. Davidson, S. J. Loeb, *Dalton Trans.* **2003**, *22*, 4319; u) M. Álvaro, B. Ferrer, H. García, E. J. Palomares, V. Balzani, A. Credi, M. Venturi, J. F. Stoddart, S. Wenger, *J. Phys. Chem. B.* **2003**, *107*, 14319; v) S. J. Loeb, *Chem. Commun.* **2005**, 1511; w) B. A. Blight, K. A. Van Noortwyk, J. A. Wisner, M. C. Jennings, *Angew. Chem.* **2005**, *117*, 1523; *Angew. Chem. Int. Ed.* **2005**, *44*, 1499; x) D. S. Marlin, D. G. Cabrera, D. A. Leigh, A. M. Z. Slawin, *Angew. Chem.* **2006**, *118*, 83; *Angew. Chem. Int. Ed.* **2006**, *45*, 77; y) D. S. Marlin, D. G. Cabrera, D. A. Leigh, A. M. Z. Slawin, *Angew. Chem.* **2006**, *118*, 1413; *Angew. Chem. Int. Ed.* **2006**, *45*, 1385; z) H. Sasabe, N. Kihara, K. Mizuno, A. Ogawa, T. Takata, *Chem. Lett.* **2006**, *35*, 212.

[9] P. R. Ashton, R. Ballardini, V. Balzani, A. Credi, K. R. Dress, E. Ishow, C. J. Kleverlaan, O. Kocian, J. A. Preece, N. Spencer, J. F. Stoddart, M. Venturi, S. Wenger, *Chem. Eur. J.* **2000**, *6*, 3558.

[10] a) M. Horie, Y. Suzaki, K. Osakada, *J. Am. Chem. Soc.* **2004**, *126*, 3684; b) M. Horie, Y. Suzaki, K. Osakada, *Inorg. Chem.* **2005**, *44*, 5844; c) Y. Suzaki, K. Osakada, *Chem. Lett.* **2006**, *35*, 374; d) K. Osakada, T. Sakano, M. Horie, Y. Suzaki, *Coord. Chem. Rev.* **2006**, *250*, 1012.

[11] a) V. Balzani, J. Becher, A. Credi, M. B. Nielsen, F. M. Raymo, J. F. Stoddart, A. M. Talarico, M. Venturi, *J. Org. Chem.* **2000**, *65*, 1947; b) N. Kihara, M. Hashimoto, T. Takata, *Org. Lett.* **2004**, *6*, 1693.

[12] P. Thordarson, E. J. A. Bijsterveld, A. E. Rowan, R. J. M. Nolte, *Nature* **2003**, *424*, 915.

[13] For other examples on rotaxane catalysts, see: Y. Tachibana, N. Kihara, T. Takata, *J. Am. Chem. Soc.* **2004**, *126*, 3438.

[14] a) D. Whang, K.-M. Park, J. Heo, P. Ashton, K. Kim, *J. Am. Chem. Soc.* **1998**, *120*, 4899; b) K.-M. Park, S.-Y. Kim, J. Heo, D. Whang, S. Sakamoto, K. Yamaguchi, K. Kim, *J. Am. Chem. Soc.* **2002**, *124*, 2140.

[15] a) Y. Furusho, T. Hasegawa, A. Tsuboi, N. Kihara, T. Takata, *Chem. Lett.* **2000**, 18; b) T. Oku, Y. Furusho, T. Takata, *J. Polym. Sci. Part A Polym. Chem.* **2003**, *41*, 119; c) Y. Furusho, T. Oku, T. Hasegawa, A. Tsuboi, N. Kihara, T. Takata, *Chem. Eur. J.* **2003**, *9*, 2895; d) T. Oku, Y. Furusho, T. Takata, *Org. Lett.* **2003**, *5*, 4923.

[16] S.-Y. Chang, H.-Y. Jang, K.-S. Jeong, *Chem. Eur. J.* **2003**, *9*, 1535.

[17] a) M. A. Bennet, G. B. Robertson, P. O. Whimp, T. Yoshida, *J. Am. Chem. Soc.* **1973**, *95*, 3028; b) M. A. Bennett, T. Yoshida, *J. Am. Chem. Soc.* **1978**, *100*, 1750; c) H. E. Bryndza, *Organometallics* **1985**, *4*, 406; d) H. E. Bryndza, *Organometallics* **1985**, *4*, 1686; e) N. W. Alcock, A. W. G. Platt, P. G. Pringle, *Inorg. Chim. Acta* **1987**, *128*, 215; f) N. W. Alcock, A. W. G. Platt, H. H. Powell, P. G. Pringle, *J. Organomet. Chem.* **1989**, *361*, 409; g) Y.-J. Kim, K. Osakada, A. Takenaka, A. Yamamoto, *J. Am. Chem. Soc.* **1990**, *112*, 1096; h) K. Osakada, Y.-J. Kim, A. Yamamoto, *J. Organomet. Chem.* **1990**, *382*, 303; i) K. Osakada, Y.-J. Kim, M. Tanaka, S. Ishiguro, A. Yamamoto, *Inorg. Chem.* **1991**, *30*, 197; j) G. M. Kapteijn, A. Dervisi, D. M. Grove, H. Kooijman, M. T. Lakin, A. L. Spek, G. van Koten, *J. Am. Chem. Soc.* **1995**, *117*, 10939; k) G. M. Kapteijn, D. M. Grove, H. Kooijman, W. J. J. Smeets, A. L. Spek, G. van Koten, *Inorg. Chem.* **1996**, *35*, 526; l) S. A. Macgregor, G. W. Neave, *Organometallics* **2003**, *22*, 4547; m) S. A. Macgregor, G. W. Neave, *Organometallics* **2004**, *23*, 891.

[18] H. E. Bryndza, W. Tam, *Chem. Rev.* **1988**, *88*, 1163.

[19] a) J. M. Mayer, *Comments Inorg. Chem.* **1988**, *8*, 125; b) T. K. G. Erikson, J. C. Bryan, J. M. Mayer, *Organometallics* **1988**, *7*, 1930.

[20] *Inorganic Chemistry 2nd ed.* (Eds.: D. F. Shriver, P. W. Atkins, C. H. Langford), Oxford University Press, Oxford, **1994**, chap. 5.

[21] The interlocked cyclic and linear molecules with a labile bond in one of the molecules are in equilibrium with the discrete molecules formed by cleavage of the bond, even when the linear molecules have bulky groups at both ends. This study as well as previous ones on the effect of interlocked molecules on kinetically stabilized rotaxanes have revealed the different chemical behavior of rotaxanes and pseudorotaxanes. Herein we classified our Pt complexes with interlocked structures as semirotaxanes, although this terminology is applied similarly to pseudorotaxanes. For examples, see references [8f,h] and [22].

[22] a) N. Armaroli, V. Balzani, J.-P. Collin, P. Gaviña, J.-P. Sauvage, B. Ventura, *J. Am. Chem. Soc.* **1999**, *121*, 4397; b) C. Reuter, R. Schmieder, F. Vögtle, *Pure Appl. Chem.* **2000**, *72*, 2233; c) T. Clifford, A. Abushamleh, D. H. Busch, *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 4830; d) S. J. Rowan, J. F. Stoddart, *Polym. Adv. Technol.* **2002**, *13*, 777.

[23] Y. Suzaki, T. Yagyu, Y. Yamamura, A. Mori, K. Osakada, *Organometallics* **2002**, *21*, 5254.

[24] Y. Tokunaga, S. Kakuchi, K. Akasaka, N. Nishikawa, Y. Shimomura, K. Isa, T. Seo, *Chem. Lett.* **2002**, 810.

[25] a) P. R. Ashton, P. J. Campbell, E. J. T. Chrystal, P. T. Glink, S. Menzer, D. Philp, N. Spencer, J. F. Stoddart, P. A. Tasker, D. J. Williams, *Angew. Chem.* **1995**, *107*, 1997; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1865; b) P. R. Ashton, E. J. T. Chrystal, P. T. Glink, S. Menzer, C. Schiavo, N. Spencer, J. F. Stoddart, P. A. Tasker, A. J. P. White, D. J. Williams, *Chem. Eur. J.* **1996**, *2*, 709.

[26] P. R. Ashton, I. Baxter, M. C. T. Fyfe, F. M. Raymo, N. Spencer, J. F. Stoddart, A. J. P. White, D. J. Williams, *J. Am. Chem. Soc.* **1998**, *120*, 2297.

[27] The rotaxane with 4-tBuC$_6$H$_4$ terminal groups on the axis and DB24C8 could undergo unthreading of the cyclic component if hydrogen bonds did not exist between the axis and cyclic component; see: Y. Tachibana, N. Kihara, Y. Furusho, T. Takata, *Org. Lett.* **2004**, *6*, 4507.

[28] P. R. Ashton, R. Ballardini, V. Balzani, M. C. T. Fyfe, M. T. Gandolfi, M.-V. Martínez-Díaz, M. Morosini, C. Schiavo, K. Shibata, J. F. Stoddart, A. J. P. White, D. J. Williams, *Chem. Eur. J.* **1998**, *4*, 2332.

[29] Y. Suzaki, K. Osakada, *Organometallics* **2006**, *25*, 3251.

[30] F. D. Bianca, G. Bandoli, A. Dolmella, S. Antonaroli, B. Crociani, *J. Chem. Soc. Dalton Trans.* **2002**, 212.

[31] Acid anhydrides are generally prepared by the reaction of a carboxylate salt with acid chloride; see: a) G. E. Philbrook, *J. Org. Chem.* **1954**, *19*, 623; b) P. A. Finan, G. A. Fothergill, *J. Chem. Soc.* **1962**, 2824.

[32] a) N. Kihara, Y. Tachibana, H. Kawasaki, T. Takata, *Chem. Lett.* **2000**, 506; b) N. Kihara, J.-I. Shin, Y. Ohga, T. Takata, *Chem. Lett.* **2001**, 592.

[33] For an example of a perched complex with a crown ether containing a pendant ammonium group, see: O. P. Kryatova, S. V. Kryatov, R. J. Staples, E. V. Rybak-Akimova, *Chem. Commun.* **2002**, 3014.

[34] H. C. Clark, L. E. Manzer, *J. Organomet. Chem.* **1973**, *59*, 411.

[35] R. Naejus, D. Lemordant, R. Coudert, P. Willmann, *J. Fluorine Chem.* **1998**, *90*, 81.

[36] P. R. Ashton, R. Ballardini, V. Balzani, M. Gómez-López, S. E. Lawrence, M. V. Martínez-Díaz, M. Montalti, A. Piersanti, L. Prodi, J. F. Stoddart, D. J. Williams, *J. Am. Chem. Soc.* **1997**, *119*, 10641.

[37] Crystal Structure (version 3.19) crystal-analysis package, Rigaku Corporation, Tokyo (Japan) and Rigaku/MSC Inc., Texas (USA), **2001**.

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