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Organometallic Rotaxanes with a Triazole Group in the Axle Component and Their Behavior as Ligands of Pt^{II} Complexes

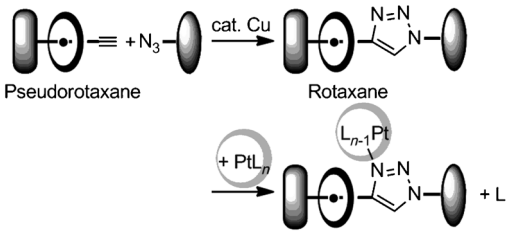
Gilbert Yu, Yuji Suzaki, Tomoko Abe, and Kohtaro Osakada*[a]

Abstract: Two ferrocenylmethyl ammonium salts were used as axle components of pseudorotaxanes with dibenzo[24]crown-8. The pseudorotaxane with an alkyne terminal group in the axle component underwent a Cu-catalyzed Huisgen coupling reaction (click reaction) with an alkyl azide to afford cationic [2]rotaxanes with a triazole group in the axle molecule. The rotaxane reacted with Ac_2O to produce neutral rotaxanes with an amide group in the axle component. Both cationic and neutral rotaxanes were treated with K-[$PtCl_3(CH_2{=}CH_2)$] to form the Pt^{II}-containing rotaxanes.

Keywords: click chemistry · copper · ferrocene · platinum · rotaxanes

Introduction

Rotaxanes are defined as supramolecules composed of interlocked macrocyclic and dumbbell-shaped axle molecules.[1–3] They have unique structures and chemical properties, which can be potentially applied to molecular machines,[4] molecular electronic devices,[5] and hydrogels with various functions.[6–9] Most of the rotaxanes reported so far are composed completely of organic molecules. Introduction of partial structures that contain transition metals to the components adds a new character to the rotaxanes. Some research groups have reported the synthesis and properties of rotaxanes that have transition metals.[10] Ferrocene is known as a stable, electrochemically active center and can be introduced into many organic molecules. Thus, various research groups have synthesized rotaxanes, the component molecule of which is equipped with ferrocenyl groups, and demonstrated their special properties.[11] Recently, we reported rotaxanes and pseudorotaxanes that contain ferrocenyl groups in the axle or as cyclic components.[12] Their electrochemical oxidation and reduction can induce the shuttling of the cyclic component depending on the valence of the Fe center. Electrochemically induced formation of pseudorotaxane was also achieved by using a ferrocene derivative as the axle component.[12a,b] Further introduction of a functional group with coordination ability to the ferrocene-containing rotaxanes would provide a new supramolecular organometallic ligand as well as a heterobimetallic transition-metal complex. We chose the click reaction of an alkyne with an organic azide because it forms a disubstituted triazole ring selectively. Scheme 1 summarizes the synthetic route of the rotaxane ligand that has a triazole group and its platinum complex in this study. The click reaction provides the triazole that can act as the coordinating site to the transition-metal complexes in the axle.[11d,13] This type of rotaxane complex is much less common than rotaxanes that contain a transition metal at the end of the axle component.[14] In this study, we report the synthesis of triazole-containing rotaxanes as well as their properties as ligand of a Pt^{II} complex.



Scheme 1. Synthesis of the rotaxane ligand and its platinum complex.

Results and Discussion

Scheme 2 summarizes the preparation procedure for the precursors of the axle component, [**1a**]PF_6 and [**1b**]PF_6, and its pseudorotaxane formation with dibenzo[24]crown-8 (DB24C8). The condensation reaction of ferrocenecarboxaldehyde with *para*-methoxybenzylamine forms [FcCH=$NCH_2C_6H_4$-4-OMe] (Fc = $Fe(C_5H_4)(C_5H_5)$). Reduction of the product with $NaBH_4$ followed by hydrolysis with HCl and exchange of the counteranion with NH_4PF_6 yielded [$FcCH_2NH_2CH_2C_6H_4$-4-OMe]PF_6 ([**1a**]PF_6). Analogous reactions with *para*-hexynoxybenzylamine yield [**1b**]PF_6, which has a terminal alkyne group. These compounds were characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and IR spectrometry as well as elemental analyses.

[a] G. Yu, Dr. Y. Suzaki, T. Abe, Prof. K. Osakada
Chemical Resources Laboratory (box R1-3)
Tokyo Institute of Technology
4259 Nagatsuta, Midori-ku
Yokohama 226-8503 (Japan)
Fax: (+81) 45-924-5224
E-mail: kosakada@res.titech.ac.jp

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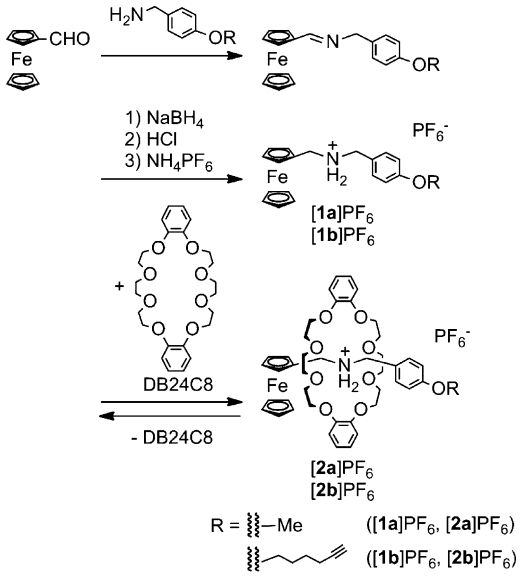


Scheme 2. Synthesis of dialkylammonium salts, [**1a**]PF_6 and [**1b**]PF_6, and their pseudorotaxanes, [**2a**]PF_6 and [**2b**]PF_6.

Compound [**1b**]PF_6 forms a pseudorotaxane with DB24C8 in $CDCl_3$ at 20 °C. The ^{1}H NMR spectrum of the mixture of [**1b**]PF_6 and DB24C8 ($[[\mathbf{1b}]PF_6]_0 = 9.9$ mM, $[DB24C8]_0 = 11$ mM) shows signals assigned to the pseudorotaxane. A similar solution in CD_3CN contains an equilibrated mixture of [**1b**]PF_6, DB24C8, and their pseudorotaxane, [**2b**]PF_6. The ratio between [**2b**]PF_6 and [**1b**]PF_6 was determined to be 1:1. The association constant between DB24C8 and [**1b**]PF_6 was calculated to be 2.4×10^2 M^{-1} in CD_3CN at 20 °C.[15,16] ESI mass spectrometry of the solution of [**1b**]PF_6 and DB24C8 in CH_3CN shows signals that are assigned clearly to pseudorotaxane [**2b**]$^+$.

Recrystallization of [**1a**]PF_6 and DB24C8 in a $CHCl_3$/*n*-hexanes solution affords pseudorotaxane [**2a**]PF_6 as single crystals in 59% yield. Figure 1 depicts the molecular structure of [**2a**]PF_6 obtained by X-ray crystallography. The ammonium hydrogen atoms, H1 and H2, have short contacts with oxygen atoms of DB24C8, O1 and O7 (H1···O1 2.372 Å, H2···O7 2.092 Å), through attractive N–H···O hydrogen bonds. The IR spectroscopy of [**2a**]PF_6 shows peaks assigned to the stretching vibration of the NH_2 group at 3195 and 3065 cm^{-1}. These positions are at lower wavenumbers than those of [**1a**]PF_6 (3268 and 3235 cm^{-1}) owing to the hydrogen bonds between the ammonium and the oxygen atoms of DB24C8. A hydrogen atom of the cyclopentadienyl ligand, H4, forms an C–H···π interaction with a C_6H_4 ring

Abstract in Japanese:
ジベンゾ[24]クラウン-8-エーテル(DB24C8)とジアルキルアンモニウム塩とを構成要素とする[2]ロタキサンを合成した。合成の鍵反応には銅触媒によるアジドとアルキンの Huisgen 環化付加反応を採用した。本反応によってロタキサンの軸成分分子内部にはトリアゾール基が生成し、この部分が白金(II)へ配位して、新しい錯体を形成する。

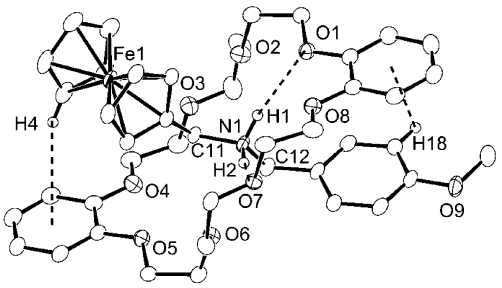
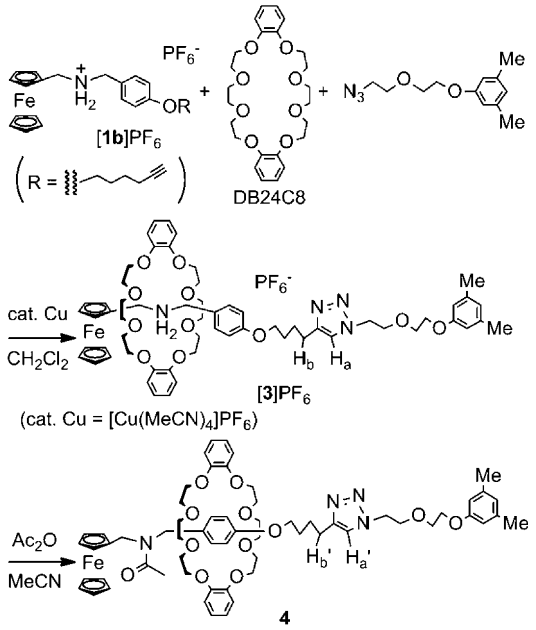


Figure 1. ORTEP drawing of [**2a**]PF_6 (50% probability). Some of the hydrogen atoms were omitted.

of DB24C8. The distance between the hydrogen and the aromatic plane is 3.15 Å. Another aromatic ring of the cyclic component also has a short contact with an aromatic hydrogen, H18, of the axle component (3.75 Å).

Scheme 3 summarizes the end-capping reaction of pseudorotaxane [**2b**]PF_6 to yield the rotaxane [**3**]PF_6 and its further conversion into neutral rotaxane **4**. Treatment of



Scheme 3. Synthesis of rotaxanes [**3**]PF_6 and **4**.

[**1b**]PF_6 with $N_3(CH_2CH_2O)_2C_6H_3$-3,5-Me_2 in the presence of DB24C8 and [Cu(MeCN)$_4$]PF_6 at room temperature for two days causes Huisgen coupling of the alkynyl group with the alkyl azide to yield [**3**]PF_6 in an isolated yield of 92%.[17–19] The ESI mass spectrum shows a peak at *m*/*z* 1085.4955 assigned to the cationic rotaxane [**3**]$^+$. The ^{1}H NMR spectrum of [**3**]PF_6 in CD_3CN shows a signal at $\delta = 7.59$ ppm, which is assigned to the triazole hydrogen, H_a (Figure 2a). The ^{1}H NMR spectroscopic signals of the NCH_2 and NH_2 hydrogen atoms of [**3**]PF_6 were observed at lower magnetic field positions ($\delta = 4.20$ (NCH_2), 4.36 (NCH_2), 7.12 ppm (NH_2)) than the corresponding signals of [**1b**]PF_6 ($\delta = 4.02$ (NCH_2),

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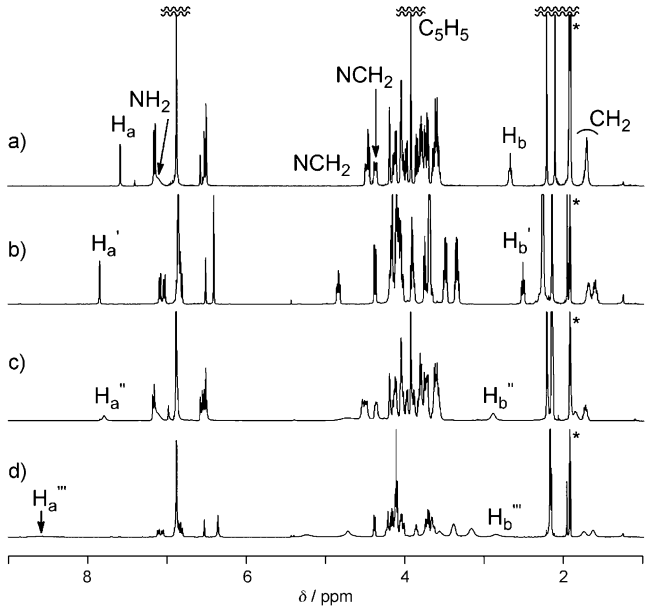


Figure 2. ^{1}H NMR spectra of a) [**3**]PF_6; b) **4**; c) a mixture of [**3**]PF_6, [$PtCl_2(CH_2{=}CH_2)$], and [(**3**)$PtCl_2(CH_2{=}CH_2)$]PF_6; and d) a mixture of **4**, [$PtCl_2(CH_2{=}CH_2)$], and [(**4**)$PtCl_2(CH_2{=}CH_2)$] (400 MHz, CD_3CN, 20 °C). Peaks with asterisk correspond to CD_2HCN.

4.04 (NCH_2), 6.75 ppm (NH_2)). These ^{1}H NMR spectroscopic results indicate that intermolecular hydrogen bonds are present between the ammonium of the axle component and the oxygen atoms of DB24C8.

Acetylation of the ammonium group of [**3**]PF_6 with Ac_2O in MeCN forms neutral rotaxane **4**, which was isolated in 75% yield.[20] The ESI mass spectrum of **4** shows a peak at *m*/*z* 1127.5040 assigned to the protonated rotaxane, [**4**+H]$^+$. The presence of the amide group was confirmed by an IR peak at 1651 cm^{-1} assigned to the C=O vibration. The ^{1}H NMR spectroscopic signal of the triazole proton of **4**, H_a', ($\delta = 7.83$ ppm; Figure 2b) is shifted downfield compared to that of [**3**]PF_6 ($\delta = 7.59$ ppm; Figure 2a). This observation seemed to be supported in the literature: Takata et al. have reported the acetylation of the rotaxane composed of bis(arylmethyl)ammonium hexafluorophosphate and DB24C8.[20] In their work, the macrocyclic component of the synthesized neutral rotaxane in the solid state includes an aromatic ring on the axle component. The ^{1}H NMR spectroscopic peaks of the NCH_2 groups are also observed at slightly higher magnetic field positions. Neutral rotaxane **4**, formed by acetylation of [**3**]PF_6 in this study, shows one of the NCH_2 signals to be more upfield ($\delta = 4.83$ ppm) than that of [**3**]PF_6 ($\delta = 4.38$ and 4.49 ppm).

Treatment of phenyl benzyl-1,2,3-triazole with K[$PtCl_3(CH_2{=}CH_2)$] was used as a model reaction for the coordination of the supramolecular ligands to transition metals. Complex [$PtCl_2(CH_2{=}CH_2)(Ph{-}C_2HN_3{-}CH_2Ph)$] (**5**), was prepared (see the Experimental Section) and characterized by ^{1}H NMR spectroscopy and X-ray crystallography. The crystal structure indicates that the dichloro(ethylene)platinum(II) moiety is coordinated to the nitrogen

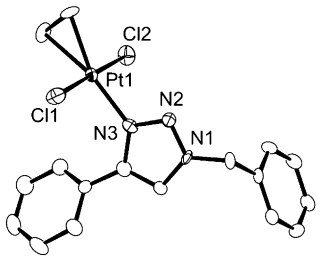
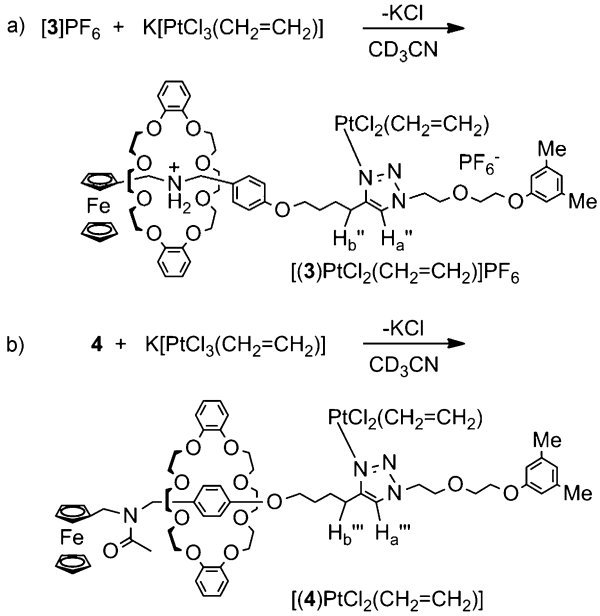


Figure 3. ORTEP drawing of **5** (50% probability). The hydrogen atoms were omitted.

at position 3 of the triazole ring (Figure 3). Ethylene and the triazole ligand occupy *trans* positions to the square-planar Pt^{II} center.

Addition of K[$PtCl_3(CH_2{=}CH_2)$] to a solution of [**3**]PF_6 ([[**3**]PF_6], [K[$PtCl_3(CH_2{=}CH_2)$]] = 25 mM) in CD_3CN smoothly produced the Pt^{II} complex with the rotaxane ligand (Scheme 4a). The ESI mass spectrum of the solution



Scheme 4. Synthesis of a) [(**3**)$PtCl_2(CH_2{=}CH_2)$]PF_6 and b) [(**4**)$PtCl_2(CH_2{=}CH_2)$].

shows the highest peak at *m*/*z* 1379.4377 owing to [(**3**)$PtCl_2(CH_2{=}CH_2)$]$^+$ (calcd 1379.4274). Distribution of the isotopomer is in agreement with the calculation for the formula of the Pt-containing rotaxane. The ^{1}H NMR spectroscopic signals of the hydrogen of the triazole as well as those α to the triazole of [(**3**)$PtCl_2(CH_2{=}CH_2)$]PF_6, H_a'' and H_b'', were observed at $\delta = 7.79$ and 2.90 ppm (Figure 2c), respectively. These signals are further downfield than those of [**3**]PF_6 ($\delta = 7.59$ (H_a), 2.68 ppm (H_b); Figure 2a).[21] A broadened ^{1}H NMR spectroscopic signal at $\delta = 4.73$ ppm is assigned to the hydrogen atoms of the ethylene ligand. The integrated peak area ratio between the signals of ethylene and triazole at −35 °C is consistent with the formulation in Scheme 4a.

These mass and NMR spectroscopic results indicate 1:1 complexation of [**3**]PF_6 with [$PtCl_2(CH_2{=}CH_2)$]. Small differences in the positions of ^{1}H NMR spectroscopic signals of NCH_2 and methyl hydrogen atoms between [(**3**)$PtCl_2(CH_2{=}CH_2)$]PF_6 ($\delta = 4.49$ (NCH_2), 4.35 (NCH_2), 2.22 ppm (Me)) and [**3**]PF_6 ($\delta = 4.36$, 4.20, 2.22 ppm) suggest that the structure that has the NCH_2 group interacts with DB24C8 through multiple hydrogen bonds. Job plots obtained from the position of the ^{1}H NMR spectroscopic signal of H_a and H_a'' showed a maximum at a mole fraction of 0.5, which confirmed formation of the 1:1 complex [(**3**)$PtCl_2(CH_2{=}CH_2)$]PF_6 (Figure 4).

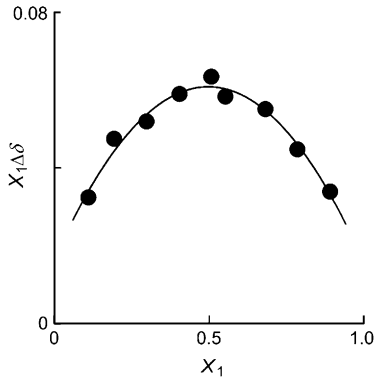


Figure 4. Job plots for treatment of [**3**]PF_6 with K[$PtCl_3(CH_2{=}CH_2)$] to afford [(**3**)$PtCl_2(CH_2{=}CH_2)$]PF_6 obtained from ^{1}H NMR spectroscopic peak position of H_a'', $\delta(H_a'')$, ([[**3**]$PF_6]_0$+[K[$PtCl_3(CH_2{=}CH_2)$]]$_0$ = 10 mM, in CD_3CN, 20 °C). (X_1 = molar fraction of [**3**]PF_6; $\Delta\delta$ [ppm] = $|\delta(H_a) - \delta(H_a''$, observed in the mixture of [**3**]PF_6 and K[$PtCl_3(CH_2{=}CH_2)$])|.

The formation constant of the Pt-containing rotaxane was estimated to be $K_a = 1.0 \times 10^2\,M^{-1}$ in CD_3CN at −20 °C by Scatchard analysis of the mixture of [**3**]PF_6 and K[$PtCl_3(CH_2{=}CH_2)$].[22] The formation constant for **5** from K[$PtCl_3(CH_2{=}CH_2)$] and phenyl benzyl-1,2,3-triazole was similarly determined to be $8.6\,M^{-1}$ (CD_3CN, −20 °C).[23] Temperature dependence of the association constants (Figure 5) gave thermodynamic parameters for formation of the platinum(II) complexes to be $\Delta G° = -7.4$ kJ mol^{-1}, $\Delta H° = -52$ kJ mol^{-1}, and $\Delta S° = -23$ J mol^{-1} K^{-1} for [(**3**)$PtCl_2(CH_2{=}CH_2)$]PF_6, and $\Delta G° = -4.0$ kJ mol^{-1}, $\Delta H° = -11$ kJ mol^{-1}, and $\Delta S° = -7.1$ J mol^{-1} K^{-1} for **5**, respectively. These results indicate that the triazole group of rotaxane [**3**]$^+$ coordinates to [$PtCl_2(CH_2{=}CH_2)$] more strongly than phenyl benzyl-1,2,3-triazole, which forms **5** upon coordination to [$PtCl_2(CH_2{=}CH_2)$].

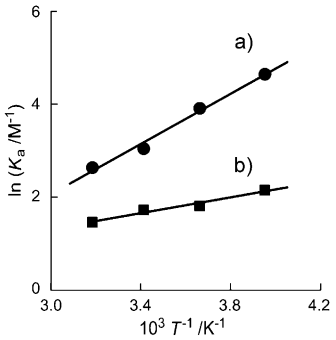


Figure 5. Van't Hoff plots of the reactions for a) formation of [(**3**)$PtCl_2(CH_2{=}CH_2)$]PF_6 and for b) formation of **5** in CD_3CN.

Neutral rotaxane **4** also reacted with K[$PtCl_3(CH_2{=}CH_2)$] to produce [(**4**)$PtCl_2(CH_2{=}CH_2)$]. The ^{1}H NMR spectrum of the mixture (Figure 2d) shows peaks due to triazole hydrogen ($\delta = 8.61$ ppm) and α-hydrogen ($\delta = 2.86$ ppm) atoms with significant broadening. They can be assigned to the signals of [(**4**)$PtCl_2(CH_2{=}CH_2)$], H_a'' and H_b'', respectively. The corresponding signals of **4** ($\delta = 7.83$, 2.51 ppm) were not observed possibly owing to severe broadening. The ESI mass spectrum of the mixture exhibits the highest peak at m/z 1459.3908 (calcd as [(**4**)$PtCl_2(CH_2{=}CH_2)$]+K: 1459.3938). Keeping the solution for two weeks caused a decrease in broadening of the signals originally at $\delta = 8.61$ ppm to $\delta =$ 7.83/7.84 ppm (free) and $\delta = 8.45/8.50$ ppm (complexed). Comparison of the peak intensity showed a relative ratio of **4** to [(**4**)$PtCl_2(CH_2{=}CH_2)$] to be 0.69:0.31 at 27 °C in CD_3CN. This corresponds to a formation constant of approximately $9.0 \times 10^2\,M^{-1}$.

Conclusion

In summary, we succeeded in the syntheses of rotaxanes with a 1,4-disubstituted 1,2,3-triazole unit and their platinum(II) complexes. Copper-catalyzed Huisgen coupling introduced not only the bulky end group but also the triazole group to the axle component of the rotaxane. The rotaxane ligands in this study are revealed to coordinate more strongly to platinum(II) than the organic triazole. The formation constants of the platinum complexes of the triazole compounds at 27 °C decrease in the order: [(**4**)$PtCl_2(CH_2{=}CH_2)$] (ca. $9 \times 10^2\,M^{-1}$) > [(**3**)$PtCl_2(CH_2{=}CH_2)$]PF_6 ($19\,M^{-1}$) > [$PtCl_2(CH_2{=}CH_2)(Ph{-}C_2HN_3{-}CH_2Ph)$]$PF_6$ ($4.9\,M^{-1}$), with the latter two obtained by interpolation of the van't Hoff plots.

Thus, the neutral and cationic rotaxanes with a triazole group bind to the Pt^{II} center more strongly than the Ph−C_2HN_3−CH_2Ph in spite of severe steric hindrance of the cyclic component in the rotaxane ligand. The triazole−platinum bond of the rotaxanes may prevent shuttling of the cyclic component, but its dissociation might enable the motion across the entire molecule. Leigh et al. have reported that bulky trialkylsilyl groups of the axle component work as a ratchet to block molecular shuttling.[24] Further studies on controlling the dissociation of the rotaxane ligand from Pt^{II} or other transition-metal centers are now in progress.

Experimental Section

General

Dried solvents were purchased from Kanto Chemical Co., Inc. K[$PtCl_3$(CH_2=CH_2)] was prepared according to the literature.[25] Other chemicals were commercially available. NMR spectra (^{1}H, ^{13}C{^{1}H}, ^{1}H–^{1}H COSY, ^{13}C{^{1}H}-^{1}H COSY) were recorded with Varian MERCURY300 and Bruker Biospin Avance instruments. The chemical shifts were referenced with respect to $CHCl_3$ (δ = 7.26 ppm) and CD_2HCN (δ = 1.93 ppm) for ^{1}H, and $CDCl_3$ (δ = 77.0 ppm) and CD_3CN (δ = 1.30 ppm) for ^{13}C as internal standards. IR absorption spectra were recorded with Shimadzu FTIR-8100 spectrometers. Fast-atom bombardment mass spectra (FAB-MS) were obtained with a JEOL JMS-700 (matrix, *m*-nitrobenzylalcohol). Electrospray ionization mass spectrometry (ESI-MS) was recorded with a Bruker micrOTOF II. Elemental analyses were carried out with a Yanaco MT-5 CHN autorecorder.

[FcCH=NCH$_2$C$_6$H$_4$-4-OCH$_2$CH$_2$CH$_2$CH$_2$C≡CH]

A solution of ferrocenecarboxaldehyde (2.14 g, 10.0 mmol) and $H_2NCH_2C_6H_4$-4-$OCH_2CH_2CH_2CHCCH$ (2.54 g, 12.5 mmol) in *n*BuOH/EtOH (40 mL:10 mL) was heated to reflux for 1 day. The reaction mixture was then evaporated to yield the crude product, which was purified by recrystallization from Et_2O/*n*-hexane to yield [FcCH=$NCH_2C_6H_4$-4-$OCH_2CH_2CH_2CHCCH$] as a reddish-brown solid (3.99 g, 10 mmol, quantitative). ^{1}H NMR (400 MHz, [D_6]DMSO, RT): δ = 1.57 (m, 2H; CH_2), 1.77 (m, 2H; CH_2), 2.21 (td, ^3J(H,H) = 7 Hz, ^4J(H,H) = 2 Hz, 2H; CH_2CCH), 2.76 (m, 1H; CCH), 3.94 (t, ^3J(H,H) = 6 Hz, 2H; OCH_2), 4.16 (s, 5H; C_5H_5), 4.38 (m, 2H; C_5H_4), 4.49 (s, 2H; NCH_2), 4.63 (m, 2H; C_5H_4), 6.88 (d, ^3J(H,H) = 8 Hz, 2H; C_6H_4), 7.19 (d, ^{3}(H,H) = 8 Hz, 2H; C_6H_4), 8.24 ppm (s, 1H; NCH); ^{13}C{^{1}H} NMR (100 MHz, [D_6]DMSO, RT): δ = 17.4 (CH_2), 24.6 (CH_2), 27.8 (CH_2), 63.6, 66.8, 68.2, 68.8 (C_5H_5), 70.0, 71.4, 80.8, 84.3, 114.3 (C_6H_4), 129.0 (C_6H_4), 131.8 (C_6H_4), 157.4 (C_6H_4), 160.8 ppm (N=C); elemental analysis calcd (%) for $C_{24}H_{25}FeNO$: C 72.19, H 6.31, N 3.51; found: C 72.52, H 6.27, N 3.51.

*Complex [**1b**]PF$_6$*

[FcCH=$NCH_2C_6H_4$-4-$OCH_2CH_2CH_2CH_2C$≡CH] (500 mg, 1.25 mmol) was dissolved in MeOH (5.0 mL) at 0 °C. $NaBH_4$ (350 mg, 9.25 mmol) was added to the solution and stirred for 1 day in an ice bath, which was allowed to rise to room temperature. The resulting solution was diluted with Et_2O and mixed with HCl (6 M). The resulting solution was fractionated by the addition of *n*-hexane/EtOAc and water. The separated organic phase was evaporated to give the crude product, which was dissolved in CH_2Cl_2. The solution was washed with water, dried over $MgSO_4$, and evaporated to yield [**1b**]Cl (220 mg, 5.03 mmol, 40%). ^{1}H NMR of [**1a**]Cl (400 MHz, $CDCl_3$, RT): δ = 1.71 (m, 2H; CH_2), 1.83 (m, 2H; CH_2), 1.97 (t, ^4J(H,H) = 4 Hz, 1H; CCH), 2.23 (td, ^3J(H,H) = 8 Hz, ^4J(H,H) = 4 Hz, 2H; CH_2), 3.73 (s, 2H; NCH_2), 3.80 (s, 2H; NCH_2), 3.87 (t, ^3J(H,H) = 4 Hz, 2H; OCH_2), 4.11 (s, 5H; C_5H_5), 4.20 (s, 2H; C_5H_4), 4.42 (s, 2H; C_5H_4), 6.85 (d, ^3J(H,H) = 8 Hz, 2H; C_6H_4), 7.42 (d, ^3J-(H,H) = 8 Hz, 2H; C_6H_4), 9.78 ppm (s, 2H; NH_2). Compound [**1b**]Cl was used without further purification. A suspension of [**1b**]Cl (312 mg, 0.713 mmol) in CH_2Cl_2 (5 mL) was stirred with saturated NH_4PF_6 (aq 10 mL) for 0.5 h at room temperature. The resulting mixture was diluted with CH_2Cl_2 and the organic layer was separated. Addition of $CHCl_3$ to the solution resulted in separation of [**1b**]PF$_6$ as a yellow solid, which was collected by filtration (130 mg, 0.238 mmol, 33%). ^{1}H NMR (400 MHz, CD_3CN, RT): δ = 1.66 (m, 2H; CH_2), 1.85 (m, 2H; CH_2), 2.17 (t, ^4J(H,H) = 3 Hz, 1H; CCH), 2.25 (dt, ^3J(H,H) = 7 Hz, ^4J(H,H) = 3 Hz, 2H; CH_2), 4.01 (t, ^3J(H,H) = 6 Hz, 2H; OCH_2), 4.02 (s, 2H; NCH_2), 4.04 (s, 2H; NCH_2), 4.20 (s, 5H; C_5H_5), 4.27 (m, 2H; C_5H_4), 4.37 (m, 2H; C_5H_4), 6.75 (br, 2H; NH_2), 6.69 (d, ^3J(H,H) = 9 Hz, 2H; C_6H_4), 7.33 ppm (d, ^3J(H,H) = 9 Hz, 2H, C_6H_4); ^{13}C{^{1}H} NMR (100 MHz, CD_3CN, RT): δ = 18.6 (CH_2), 25.9 (CH_2), 29.1 (CH_2), 48.6 (NCH_2), 51.5 (NCH_2), 68.6, 70.1 (C_5H_5), 70.6, 71.6, 76.6 (C_5H_4), 85.2 (C≡C), 115.9 (C_6H_4), 123.4 (C_6H_4), 132.8 (C_6H_4), 161.1 ppm (C_6H_4); elemental analysis calcd (%) for $C_{24}H_{28}F_6FeNOP$: C 52.67, H 5.16, N 2.56; found: C 52.73, H 5.42, N 2.61.

*Complex [**2a**]PF$_6$*

A crystal of [**2a**]PF$_6$ was obtained by recrystallization from a solution of [**1a**]PF$_6$ (48 mg, 0.10 mmol) and DB24C8 (45 mg, 0.10 mmol) in $CHCl_3$ (3.0 mL) by diffusion of the vapor of *n*-hexane at room temperature (55 mg, 5.9×10^{-2} mmol, 59%). IR (KBr disk, RT): $\tilde{\nu}$ = 3195 (N–H), 3065 (N–H), 843 (P–F), 558 cm^{-1} (P–F); elemental analysis calcd (%) for $C_{43}H_{54}F_6FeNO_9P$: C 55.55, H 5.85, N 1.51; found: C 55.33, H 5.90, N 1.40.

*Complex [**2b**]PF$_6$*

The pseudorotaxane [**2b**]PF$_6$ was formed by mixing [$FcCH_2NH_2CH_2C_6H_4$-4-$OCH_2CH_2CH_2CH_2C$≡CH]PF$_6$ (2.7 mg, 4.9×10^{-3} mmol) and DB24C8 (2.5 mg, 5.6×10^{-3} mmol) in CD_3CN (0.50 mL) at 20 °C. ^{1}H NMR (400 MHz, CD_3CN, 20 °C): δ = 1.61 (m, 2H; CH_2-axle), 1.65 (m, 2H; CH_2-axle), 2.17 (m, 2H), 2.23 (t, ^4J(H,H) = 4 Hz, 1H; C≡CH), 4.27–3.58 (37H), 4.37 (m, 2H; NCH_2), 6.53 (d, ^3J(H,H) = 8 Hz, 2H; C_6H_4-axle), 6.95–6.89 (10H), 7.16 ppm (d, ^3J(H,H) = 8 Hz, 2H; C_6H_4-axle); MS (ESI): *m*/*z* calcd for $C_{48}H_{60}FeNO_9$: 850.3613 [**2b**]$^+$; found: 850.3635.

*Complex [**3**]PF$_6$*

A solution of [**1b**]PF$_6$ (200 mg, 0.37 mmol), DB24C8 (194 mg, 0.43 mmol), $N_3CH_2CH_2OCH_2CH_2OC_6H_3$-3,5-$Me_2$ (142 mg, 0.60 mmol), and [$Cu(MeCN)_4$]PF$_6$ (274 mg, 0.74 mmol) in CH_2Cl_2 (8.0 mL) was stirred for 2 days at room temperature. The resulting solution was evaporated to give the crude product, which was purified by silica-gel column chromatography (*n*-hexane/Et_2O/acetone 10:0:0, 7:3:0, then 0:6:4) and re-precipitated from Et_2O/*n*-hexane to yield [**3**]PF$_6$ as a yellow solid (420 mg, 0.34 mmol, 92%). ^{1}H NMR (400 MHz, CD_3CN, 20 °C): δ = 1.71–1.74 (4H; CH_2-axle), 2.22 (s, 6H; Me), 2.68 (t, ^3J(H,H) = 7 Hz, 2H; CH_2), 3.56–3.66 (m, 8H; CH_2-DB24C8), 3.70–3.88 (16H), 3.93 (s, 5H; C_5H_5), 3.98 (m, 2H; CH_2-axle), 4.02–4.07 (4H), 4.06 (m, 2H), 4.10–4.17 (4H), 4.20 (m, 2H; CH_2), 4.36 (m, 2H; NCH_2), 4.46 (t, ^3J(H,H) = 5 Hz, 2H, CH_2-DB24C8), 4.49 (m, 2H; NCH_2), 6.50 (s, 2H; C_6H_3), 6.52 (d, ^3J-(H,H) = 9 Hz, 2H; C_6H_4-axle), 6.88 (s, 8H; C_6H_4-DB24C8), 7.12 (brs, 2H; NH_2), 7.16 (d, ^3J(H,H) = 9 Hz, 2H; C_6H_4), 7.59 ppm (s, 1H; $C_{triazole}$H); ^{13}C{^{1}H} NMR (100 MHz, CD_3CN, 20 °C): δ = 21.5 (Me), 26.0 (CH_2), 26.8 (CH_2), 29.4 (CH_2), 49.4 (NCH_2), 50.8 (NCH_2), 52.7, 68.1, 68.4, 69.1, 69.8, 70.0, 70.2, 70.3, 71.3, 71.7 (C_5H_4), 77.9 (C_5H_4), 113.3, 113.7, 115.2 (C_6H_4), 122.4, 123.1 ($C_{triazole}$–H), 123.5, 125.1, 131.9 (C_6H_4), 140.3 (C_6H_3), 148.3 ($C_{triazole}CH_2$), 148.8 (C_6H_4-DB24C8), 159.9 (C_6H_3), 160.4 ppm (C_6H_4); IR (KBr disk, RT): $\tilde{\nu}$ = 3156 (NH_2), 3069 (NH_2), 841 (PF_6), 558 cm^{-1} (PF_6); MS (ESI): *m*/*z* calcd for $C_{60}H_{77}FeN_4O_{11}$: 1085.4983 [**3**]$^+$; found: 1085.4955; elemental analysis calcd (%) for $C_{60}H_{77}FeN_4O_{11}PF_6(H_2O)$: C 57.69, H 6.37, N 4.49; found: C 57.63, H 6.42, N 4.38.

*Complex **4***

Et_3N (57 μL, 0.41 mmol) and acetic anhydride (39 μL, 0.41 mmol) were added to a solution of [**3**]PF$_6$ (101 mg, 0.082 mmol) in MeCN (3.0 mL), and the reaction mixture was stirred overnight at room temperature. After the removal of the solvent by evaporation, the product was purified by silica-gel column chromatography (EtOAc/*n*-hexane 2:1) to yield **4** as yellow solid (82 mg, 0.073 mmol, 89%). ^{1}H NMR (400 MHz, CD_3CN, 20 °C): δ = 1.63–1.71 (4H; CH_2), 1.97 (s, 3H; C(=O)Me), 2.15 (s, 6H; C_6H_3-3,5-(CH_3)$_2$), 2.51 (t, ^3J(H,H) = 4 Hz, 2H; CH_2), 3.67–4.20 (43H), 4.37 (m, 2H; NCH_2), 4.83 (m, 2H; NCH_2), 6.41 (s, 2H; C_6H_3), 6.51 (s, 2H; C_6H_3), 6.81–6.81 (10H), 7.02 and 7.08 (d, ^3J(H,H) = 8 Hz, 2H; C_6H_4O), 7.83 ppm (s, 1H; $C_{triazole}$H); ^{13}C{^{1}H} NMR (100 MHz, CD_3CN, 20 °C): δ = 21.4, 22.1, 22.2, 26.0, 26.6, 29.4, 44.7, 47.4, 47.7, 49.5, 51.5, 67.6, 68.6, 68.6, 68.8, 68.9, 69.1, 69.2, 69.4, 69.6, 69.6, 70.0, 70.6, 71.4, 84.7, 84.9, 113.2, 115.4, 115.7, 121.6, 122.9, 123.7, 128.9, 130.0, 130.1, 130.8, 139.3, 147.3 (C_6H_4-DB24C8), 159.3, 139.5, 160.0, 170.8, 170.9 ppm (the ^{13}C{^{1}H} NMR spectrum shows splitting signals probably, due to the s-*cis* and s-*trans* conformational structures of the amide group); IR (KBr disk, RT): $\tilde{\nu}$ = 1651 cm^{-1} (C=O); MS (ESI): *m*/*z* calcd for $C_{62}H_{79}FeN_4O_{12}$: 1127.5044 [**2**+H]$^+$; found: 1127.5040; elemental analysis calcd (%) for $C_{62}H_{78}FeN_4O_{12}$: C 66.07, H 6.97, N 4.97; found: C 65.82, H 6.98, N 4.81.

*Complex [(**3**)PtCl$_2$(CH$_2$=CH$_2$)]PF$_6$*

An NMR spectroscopy tube was charged with [**3**]PF$_6$ (14.8 mg, 1.2×10^{-2} mmol) and K[PtCl$_3$(CH$_2$=CH$_2$)] (4.4 mg, 1.2×10^{-2} mmol), which were then dissolved in CD$_3$CN (0.50 mL). ^{1}H and ^{13}C{^{1}H} NMR spectra showed formation of [(**3**)PtCl$_2$(CH$_2$=CH$_2$)]PF$_6$. ^{1}H NMR (400 MHz, CD$_3$CN, 20 °C): $\delta=1.71$ (m, 2H), 1.93 (m, 2H), 2.22 (s, 6H; C$_6$H$_3$-3,5-(CH$_3$)$_2$), 3.01 (t, ^3J(H,H) = 4 Hz, 2H; CH$_2$), 3.57–4.20 (45H), 4.35 (m, 2H; NCH$_2$), 4.49 (m, 2H; NCH$_2$), 4.57 (m, 2H), 4.73 (br, 4H; CH$_2$=CH$_2$) 6.51–6.58 (5H; C$_6$H$_4$, C$_6$H$_3$), 6.89 (s, 8H; CH$_2$-DB24C8), 7.16 (d, ^3J-(H,H) = 8 Hz, 2H; C$_6$H$_4$), 7.91 ppm (s, 1H; C$_{triazole}$H); ^{13}C{^{1}H} NMR (100 MHz, CD$_3$CN, 20 °C): $\delta=21.5$, 25.8, 26.2, 29.2, 49.4, 52.5, 52.6, 68.0, 68.2, 69.1, 69.3, 69.4, 69.5, 69.6, 69.7 (C$_5$H$_5$), 70.0 (C$_5$H$_4$), 70.3 (C$_5$H$_4$), 71.2 (CH$_2$-DB24C8), 77.8, 113.7, 115.1, 122.3, 123.5, 125.1, 126, 131.8, 140.3, 148.7 (C$_6$H$_4$-DB24C8), 149.0, 149.5, 159.8, 160.3 ppm; MS (ESI): *m*/*z* calcd for C$_{62}$H$_{81}$Cl$_2$FeN$_4$O$_{11}$Pt: 1379.4274 [(**1**)PtCl$_2$(CH$_2$=CH$_2$)]$^+$; found: 1379.4377.

*Complex [(**4**)PtCl$_2$(CH$_2$=CH$_2$)]*

An NMR spectroscopy tube was charged with **2** (13.6 mg, 1.2×10^{-2} mmol) and K[PtCl$_3$(CH$_2$=CH$_2$)] (4.4 mg, 1.2×10^{-2} mmol), which were then dissolved in CD$_3$CN (0.50 mL). ^{1}H and ^{13}C{^{1}H} NMR spectra showed formation of [(**4**)PtCl$_2$(CH$_2$=CH$_2$)]. ^{1}H NMR (400 MHz, CD$_3$CN, 20 °C): $\delta=1.75$–1.81 (CH$_2$), 1.97 (s, 3H; COCH$_3$), 2.15 (s, 6H; C$_6$H$_3$-3,5-(CH$_3$)$_2$), 2.74 (s, 2H), 3.40–4.24 (47H), 4.38 (m, 2H; NCH$_2$), 5.25 (m, 2H; NCH$_2$), 6.36 (s, 2H; C$_6$H$_3$), 6.53 (s, 1H; C$_6$H$_3$), 6.80–6.89 (10H), 7.04 and 7.10 (d, ^3J(H,H) = 8 Hz, 2H; C$_6$H$_4$), 8.61 ppm (s, 1H; C$_{triazole}$H); selected ^{13}C{^{1}H} NMR data (100 MHz, CD$_3$CN, 20 °C): $\delta=21.4$, 22.1, 22.2, 25.8, 25.9, 29.0, 44.7, 47.4, 47.7, 51.0, 51.1, 67.5, 67.8, 68.2, 69.1, 69.2, 69.6, 69.8, 67.0, 70.7, 71.7, 113.0, 113.1, 115.4, 115.7, 121.7, 123.1, 128.2, 128.9, 130.0, 140.0 149.0, 159.8, 170.8 ppm (the ^{13}C{^{1}H} NMR spectrum shows splitting signals probably due to the s-*cis* and s-*trans* conformational structures of the amide group); MS (ESI): *m*/*z* calcd for C$_{64}$H$_{82}$Cl$_2$FeN$_4$O$_{12}$PtNa and C$_{64}$H$_{82}$Cl$_2$FeN$_4$O$_{12}$PtK: 1443.4200 [(**4**)PtCl$_2$(CH$_2$=CH$_2$)+Na]$^+$ and 1459.3938 [(**4**)PtCl$_2$(CH$_2$=CH$_2$)+K]$^+$; found: 1443.4152 and 1459.3908.

*Complex **5***

Crystals of **5** suitable for X-ray diffraction studies were obtained as follows. The mixing of Ph−C$_2$HN$_3$−CH$_2$Ph (30 mg, 0.13 mmol) with K[PtCl$_3$(CH$_2$=CH$_2$)] (70 mg, 0.19 mmol) in a solution of acetone/acetonitrile (2.0 mL:1.0 mL) induced KCl solids, which were separated by filtration. The filtrate was then concentrated and the product was recrystallized from an acetone/*n*-hexane solution to give **5** as yellow crystals (20 mg, 0.038 mmol), which were analyzed by crystallography. ^{1}H NMR (400 MHz, CD$_3$CN, RT): $\delta=5.59$ (s, 2H; CH$_2$), 7.45–7.33 (8H; Ph), 7.85 (d, ^3J(H,H) = 8 Hz, 2H; C$_6$H$_5$), 8.13 ppm (s, 1H; C$_2$HN$_3$).

*Estimation of the Association Constants for Platinum Complexes [**3**]PF$_6$ and **5***

Several NMR spectroscopic samples that contained [**3**]PF$_6$ at a fixed concentration (25 mM) and K[PtCl$_3$(CH$_2$=CH$_2$)] at various concentrations in CD$_3$CN were prepared. ^{1}H NMR spectra of the samples were measured at several fixed temperatures. Chemical shifts of the triazole hydrogen atoms (δH) were obtained at each temperature. The concentrations, [K-[PtCl$_3$(CH$_2$=CH$_2$)]] = 17–30 mM, were found to be optimal for the following Scatchard analysis with the appropriate "*P* value."[22a] Values of K_a are determined by calculation on the basis of the following equation [Eq. (1)] (Scatchard equation[22]):

$$\frac{\delta(H_a'')-\delta(H_a)}{[K[PtCl_3(CH_2=CH_2)]]_{eq}} = -K_a(\delta(H_a'')-\delta(H_a)) + Z \quad (1)$$

in which $\delta(H_a)$ is the chemical shift of the observed triazole hydrogen signal in the equilibrium mixture, $\delta(H_a'')$ is the chemical shift of triazole hydrogen of [**3**]PF$_6$, $[K[PtCl_3(CH_2=CH_2)]]_{eq}$ is the concentration of K-[PtCl$_3$(CH$_2$=CH$_2$)] in the equilibrium mixture, and *Z* is the constant. The association constants for **5** were similarly determined.

Crystal Structure Determination

Crystals of [**2a**]PF$_6$ and **5** suitable for X-ray diffraction studies were obtained by recrystallization from CHCl$_3$/*n*-hexane and acetone/acetonitrile, respectively. CCDC 818203 ([**2a**]PF$_6$) and 818204 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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