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PAPER

Ruthenium macrocycles bearing pyridine bis(carboxamide): Synthesis, structure, and catalytic activity for hydrosilylation

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Ruthenium complexes Ru(**MC33**)$(CO)_n(L)_{2-n}$ (L = H_2O, PPh_3, $P(OEt)_3$; n = 1, 2) with a pincer-type macrocyclic ligand **MC33** with a cavity were synthesized and characterized. Ru(**MC33**)$(CO)_2(H_2O)$ was obtained in yields of up to 97% using a pincer-type ligand containing the bis(carboxamide) moiety and ruthenium(0) carbonyl precursor. Ru(**AC**)$(CO)_2(H_2O)$ having a pincer-type acyclic ligand **AC** was also synthesized in a similar manner to Ru(**MC33**)$(CO)_2(H_2O)$. Mono(phosphine) and bis(phosphite) complexes were formed via the selective thermal ligand exchange of CO with phosphorus ligands. The structure of the complexes was studied by nuclear magnetic resonance spectroscopy, infrared spectroscopy, electrospray ionization–high-resolution mass spectroscopy, and X-ray analyses. In addition, their catalytic activity for hydrosilylation was demonstrated.

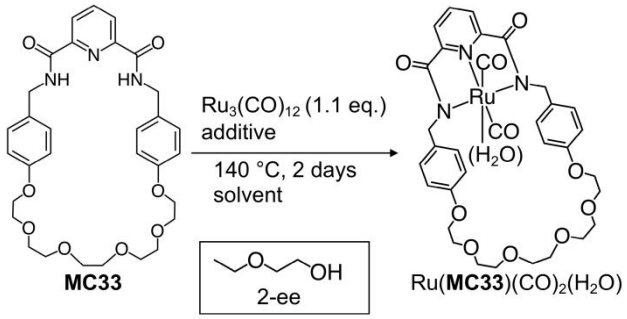
1. Introduction

The pincer-type macrocyclic complex, which has a vacant coordination site in its cavity, is of considerable interest in coordination[1] and supramolecular chemistry.[2] One of the most attractive application of this motif is the metal-templated synthesis of interlocked molecules (e.g., rotaxanes and catenanes).[3] More recently, macrocycle catalysts whose topology affects their reactivity and selectivity were reported. For example, Pd(II)-tethered pincer-type macrocycles as chemoselective catalysts were developed by our group,[4b–d] while Chaplin *et al.* reported on the selective synthesis of *gem*- and *E*-enynes catalyzed by a Rh-tethered pincer-type macrocycle.[1g] Meanwhile, Heck reaction and oxidative alkynyl-alkynyl homocoupling reaction catalyzed by *N*-heterocyclic carbene (NHC)-type macrocyclic Pd complexes was reported by Saito and coworkers.[1a] To expand the application of such a metal macrocycle, we attempted to synthesize a complex with other metal centers. Ruthenium is a group-8 member and belongs to the platinum group. It forms 6-coordinate complexes.[5] It is expected that the use of ruthenium as a macrocyclic core will improve the ease of tuning of structures by increasing the coordination numbers. For instance, many types of phosphine ligands can be utilized to realize the precise adjustment of cavity sizes in macrocyclic system. Moreover, catalytic applications are expected because many ruthenium-catalyzed reactions such as hydrosilylation, C-H arylation, and olefin metathesis are well-established. Herein, we report the synthesis, structures, and ligand-exchange behavior of novel macrocyclic ruthenium complexes. In addition, their catalytic activity for hydrosilylation is demonstrated.

2. Results and discussion

Macrocyclic ligand **MC33** was prepared in a manner similar to our previous method.[4] Briefly, it was prepared by S_N2 reaction between N^2,N^6-bis((4-hydroxyphenyl)methyl)-2,6-pyridinedicarboxamide and bis(*p*-tolylsulfonyl)pentaethylene glycol with Cs_2CO_3. We then examined the metalation of **MC33** with ruthenium precursors (Table 1). In contrast to the related precedents, the use of Ru(II) complexes with the bases failed, and no macrocyclic complex was obtained (Table S1). Meanwhile, the use of a Ru(0) carbonyl complex $Ru_3(CO)_{12}$ led

Table 1. Synthesis of Ru(**MC33**)$(CO)_2(H_2O)$



entry	solvent	additive	yield / %
1	DMF	–[a]	10
2	2-ee	–[a]	17
3	2-ee	PPh_3 (1.1 eq.[b])	trace
4	2-ee	CO (1 atm)	97

[a]No additive. [b]Equivalent to **MC33**

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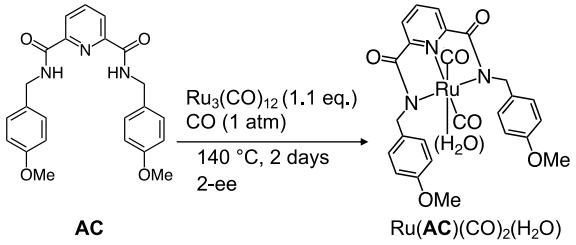
to the formation of the dicarbonyl complex Ru(**MC33**)$(CO)_2(H_2O)$ in a low yield after recrystallization from acetonitrile (Table 1, entry 1). The yield increased slightly when 2-ethoxyethanol (2-ee) was used as the solvent (entry 2). The addition of other coordinating additives such as PPh_3 completely inhibited metalation (entry 3). Finally, the yield was raised to 97% by conducting the reaction in CO atmosphere (1 atm) in 2-ee (entry 4).[6] Meanwhile, the corresponding acyclic complex Ru(**AC**)$(CO)_2(H_2O)$ was synthesized similarly with 92% yield (Scheme 1). The aqua complexes were characterized by one-dimensional (1D) and two-dimensional (2D) NMR spectroscopy (Figs S1–S4), IR (Figure S5), ionization–high-resolution mass spectrometry (ESI-HR-MS) (Figure S6) as well as by single crystal X-ray diffraction analysis. The acyclic complex Ru(**AC**)$(CO)_2(H_2O)$ was also identified in a similar manner (Figs S7–S10). Fig. 1 shows the structure of the cyclic complex. The axial carbonyl ligand was partially replaced by a dimethylformamide (DMF) molecule during recrystallization from DMF–H_2O, which resulted in the positional disorder. The *cis*-dicarbonyl geometry is in good agreement with the IR spectrum of Ru(**MC33**)$(CO)_2(H_2O)$, showing two CO absorptions at 2044 and 1971 cm^{-1} (Figure S5). We also determined the crystal structure of the acyclic complex Ru(**AC**)$(CO)_2(H_2O)$ (Fig. 2) and found that the pincer framework in Ru(**MC33**)$(CO)_2(H_2O)$ is quite similar to that in this acyclic analogue, indicating

Scheme 1. Synthesis of Ru(**AC**)$(CO)_2(H_2O)$



AC Ru(**AC**)$(CO)_2(H_2O)$

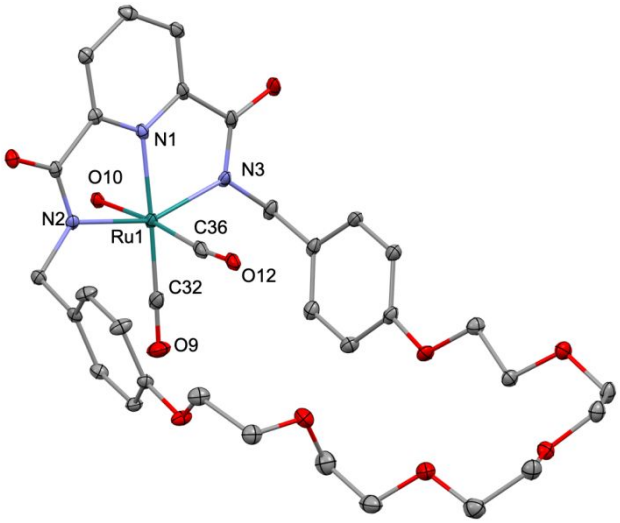


Fig. 1 ORTEP diagram of Ru(**MC33**)$(CO)_{1.35}(H_2O)(dmf)_{0.65}$. The partially occupying DMF ligand trans to the aqua ligand as well as the hydrogen atoms was omitted for clarity. Ellipsoids were drawn at the 30% probability level.

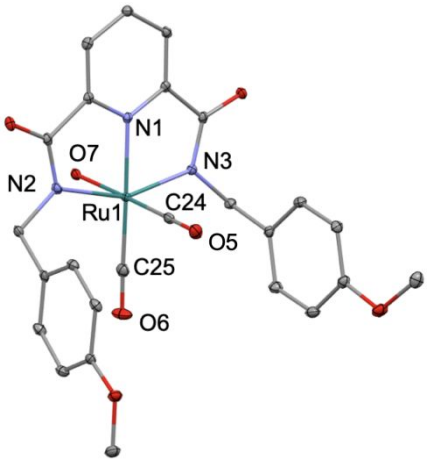


Fig. 2 ORTEP diagram of Ru(**AC**)$(CO)_2(H_2O)$. Hydrogen atoms and co-crystalized solvent were omitted for clarity. Ellipsoids were drawn at the 30% probability level.

that the macrocyclic structure does not cause any significant perturbation to the local coordination environment around the Ru atom (Tables S2 and S3). In both compounds, the amide substituents hang over toward the axial carbonyl ligand, in contrast to the previously reported Pd complex with a smaller macrocyclic structure.[4b]

Note that the NMR observation of Ru(**MC33**)$(CO)_2(H_2O)$ was fully consistent with the results of X-ray diffraction analysis that the Ru complex formed a *cis*-dicarbonyl structure. Fig. 3 shows a part of the ^1H NMR spectra of **MC33** ligand and Ru(**MC33**)$(CO)_2(H_2O)$ in DMSO-d_6. The signal of amide NH (H_c in **MC33**) disappeared after complexation, indicating the formation of the *NNN*-pincer-type coordination. The geminal benzylic protons H_c in Ru(**MC33**)$(CO)_2(H_2O)$ were separately observed at 5.50 and 3.60 ppm; this result is in agreement with the symmetry reduction through complexation. Besides, variable temperature (VT)-NMR experiments of Ru(**MC33**)$(CO)_2(H_2O)$ (Fig. S11) revealed that the signals of protons the diastereotopic H_c become much closer at 100 °C. Two set of peaks appeared at 5.52 and 3.55 ppm at 30 °C were shifted to those at 5.34 and 3.83 ppm at 100 °C. It was difficult to raise the temperature beyond 100 °C because Ru(**MC33**)$(CO)_2(H_2O)$ gradually decomposed upon heating, probably through decarboxylation. The resonances of the

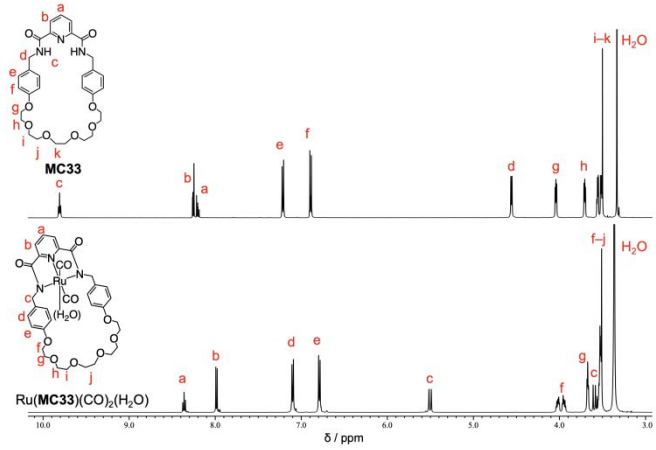


Fig. 3 The partial ^1H-NMR spectra of **MC33** and Ru(**MC33**)$(CO)_2(H_2O)$ (500 MHz, DMSO-d_6).

benzylic protons in the acyclic complex Ru(**AC**)$(CO)_2(H_2O)$ also exhibited similar shifts upon warming (Fig. S12). These observations may indicate that the rotational flexibilities of the N(amide)–C(benzyl) bonds are comparable in the cyclic and acyclic complexes.

We next assessed the effect of the macrocyclic structure by performing ligand substitution. A suspension of Ru(**MC33**)$(CO)_2(H_2O)$ and two equivalent of phosphine or phosphite ligands (PPh_3 (**P1**) or $P(OEt)_3$ (**P2**)) was allowed to reflux in 1,4-dioxane for 3 min in a sealed tube (Fig. 4). When PPh_3 was employed, a mono(phosphine) complex Ru(**MC33**)$(CO)_2$(**P1**), whose structure was confirmed by X-ray analysis (Fig. 5a), was obtained as the major product. The incoming phosphine ligand binds at the axial position opposite to the looping chain, which appears to prevent the coordination of the second phosphine molecule. There was no significant change in monitoring the ^{1}H NMR spectra even the reaction time was prolonged from 3 min to 60 min. The ^{1}H and ^{13}C NMR spectra of the PPh_3 complex show C_s symmetric patterns similar to those in the spectra of the starting complex Ru(**MC33**)$(CO)_2(H_2O)$ (Figs 4, S13, and S14). The chemical shift of 21.9 ppm in the ^{31}P NMR corresponds to the typical value for a Ru(II)-PPh_3 complex (Fig. S15).[5d] In addition to the fully matched ESI-HR-MS data (Fig. S16), the two CO absorption peaks (2060 and 1977 cm^{-1}) observed in the IR spectrum were in agreement with the *cis*-orientation of the carbonyl ligands (Fig. S17). On the other hand, when using $P(OEt)_3$, the bis(phosphite) complex Ru(**MC33**)(CO)(**P2**)$_2$ was cleanly obtained. The X-ray analysis revealed a *trans*-bis(phosphite) structure that was formed by exchanging the solvent and one of the CO ligand on the Ru(**MC33**)$(CO)_2(H_2O)$ by two $P(OEt)_3$ (Figure 5b). Meanwhile, the ^{1}H-NMR spectrum, especially, the signal of the proton H_d observed as a singlet, showed increased symmetry of the product (Figs 4 and S18). The ^{13}C-NMR spectrum (Fig. S19) was fully assignable as a bis(phosphite) structure. Further, a single signal in the ^{31}P-NMR spectrum (113.8 ppm, Fig. S20), the exact matching of the MS analysis data (Fig. S21), and a single CO absorption in the IR spectrum (1959 cm^{-1}, Fig. S22) fully supported the formulation. The difference in the stoichiometry and geometry between the Ru(**MC33**)$(CO)_2$(**P1**) and Ru(**MC33**)(CO)(**P2**)$_2$ can be explained by the difference in the steric bulkiness of the phosphorous ligands. The same ligand substitution reaction was examined with acylic complex Ru(**AC**)$(CO)_2(H_2O)$ (Schemes S1 and S2). In the presence of two

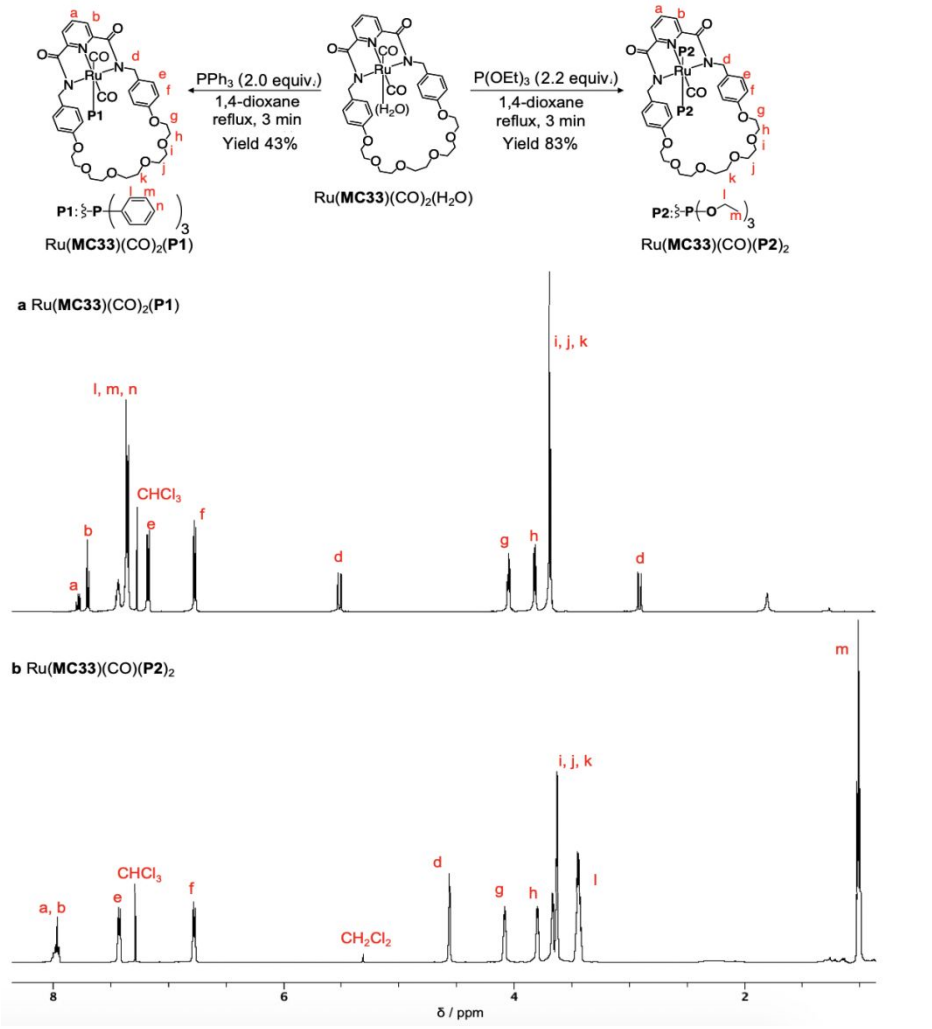


Fig. 4 Synthesis and ^{1}H-NMR spectra of Ru(**MC33**)$(CO)_2$(**P1**) and Ru(**MC33**)(CO)(**P2**)$_2$ (500 MHz, $CDCl_3$, r.t.).

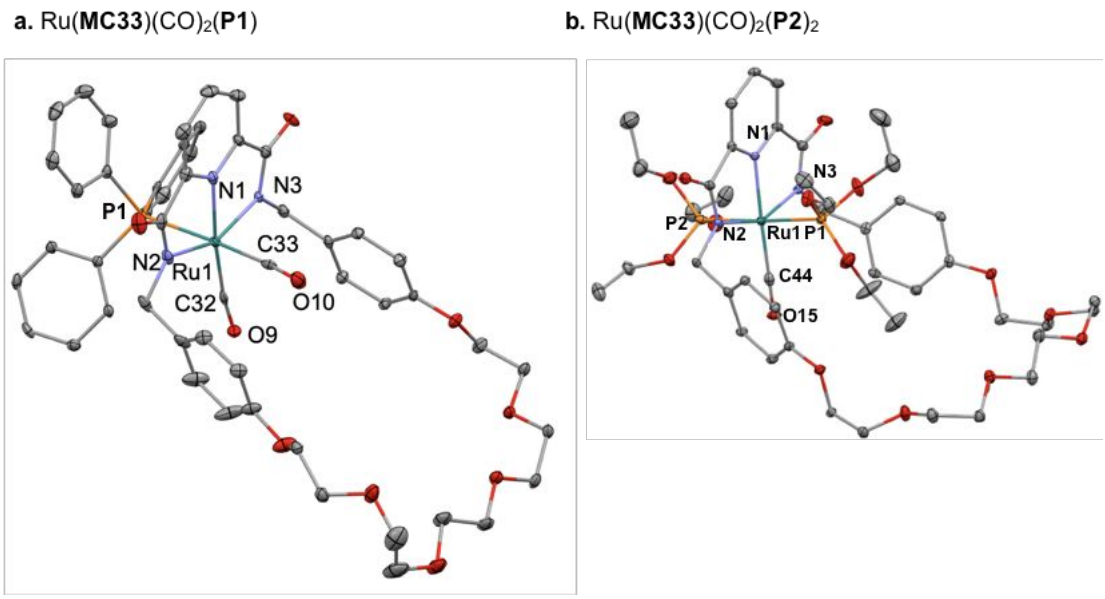
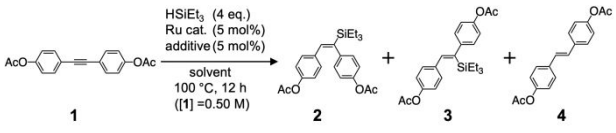


Fig. 5 ORTEP diagrams of (a) Ru(**MC33**)$(CO)_2$(**P1**) and (b) Ru(**MC33**)(CO)(**P2**)$_2$. Hydrogen atoms and co-crystalized solvent were omitted for clarity. Ellipsoids were drawn at the 30% probability level. For the letter, one of the two crystallographically independent molecules was omitted.

equivalent of **P2**, bis(phosphite) complex Ru(**AC**)(CO)(**P2**)$_2$ was formed in a similar manner to the macrocyclic one (Figs S26–S29). Although an acyclic complex Ru(**AC**)$(CO)_2$(**P1**) was similarly formed with the use of **P1**, it was difficult to be isolated from by-products, whose formation would be enhanced by the absence of the glycol chain (Figs S23–25). The less sterically hindered Ru(**AC**)$(CO)_2(H_2O)$ had higher reactivity and was difficult to control the reaction precisely at this condition. We also measured the UV–vis spectra of these Ru complexes and found that the absorbance peak of Ru(**MC33**)$(CO)_2$(**P1**) was almost identical to that of Ru(**MC33**)$(CO)_2(H_2O)$; however, the spectrum of Ru(**MC33**)(CO)(**P2**)$_2$ was different possibly due to the increased number of phosphorous ligands (Fig. S30).

Finally, we elucidated the catalytic activity of Ru(**MC33**)$(CO)_2(H_2O)$ for the hydrosilylation of 4,4'-bis(acetoxy)phenylacetylene (**1**) (Table 2). We previously reported that Pd catalysts with a macrocyclic ligand exhibited characteristic chemoselectivity for the Suzuki–Miyaura cross-coupling of 2,6-dibromopyridine compared to acylic analogues.[4c] Considering these results, the Ru complexes developed in this study were also expected to show unique catalytic activity. The treatment of **1** with $HSiEt_3$ (4 equiv) and Ru(**MC33**)$(CO)_2(H_2O)$ (5 mol%) in 1,4-dioxane yielded a mixture of *cis*- (**2**) and *trans*-vinylsilane (**3**) as the hydrosilylation products and *trans*-semihydrogenation product (**4**) (entry 1). Addition of PPh_3 (5 mol%) to the catalyst improved the *cis*-selectivity (entry 2). The results may suggest that the external bulky ligand masks the less hindered axial position and switches the reaction site to the inside of the macrocycle. Changing the solvent from dioxane to 1,3-dimethyl-2-imidazolidinone (DMI) slightly increased the selectivity of **2**. DMI was used because both **1** and Ru(**MC33**)$(CO)_2(H_2O)$ were well soluble in this solvent. It would be coordinated to the Ru catalyst which might positively affect to increase the selectivity. Meanwhile, the acyclic analogue Ru(**AC**)$(CO)_2(H_2O)$ exhibited the highest chemoselectivity under identical conditions. It should still be emphasized that the difference in the selectivities of the macrocyclic and acyclic catalyst systems indicates a large potential to exhibit the beneficial catalytic activity for the hydrosilylation owing to the topological effect of Ru(**MC33**)$(CO)_2(H_2O)$. Further optimization of the reaction conditions and mechanistic study and elucidation of the macrocyclic topological effect are currently under investigation.

Table 2 Hydrosilylation of diarylacetylene **1** catalyzed by Ru(**MC33**)$(CO)_2(H_2O)$



entry	Ru cat.	additive	solvent	yield[b] /% 2	3	4
1	Ru(**MC33**)$(CO)_2(H_2O)$	–[a]	dioxane	20	27	20
2	Ru(**MC33**)$(CO)_2(H_2O)$	PPh_3	dioxane	61	6	24
3	Ru(**MC33**)$(CO)_2(H_2O)$	PPh_3	DMI	56	0	12

3. Conclusions

In summary, we synthesized a pincer-type ruthenium macrocycle Ru(**MC33**)$(CO)_2(H_2O)$ with a coordination site in a cavity from a macrocyclic pyridine bis(amide) ligand and $Ru_3(CO)_{12}$. Ligand exchange of this complex with phosphine and phosphite ligands yielded mainly a mono(phosphine) complex Ru(**MC33**)$(CO)_2$(**P1**) and a bis(phosphite) complex Ru(**MC33**)(CO)(**P2**)$_2$, respectively, depending on the bulkiness of the entering phosphorous ligands. These macrocycle complexes were characterized by NMR, IR, HRMS,

and X-ray diffraction analyses. The cavity of the macrocycle lies around the axial coordination site, in contrast to that of the corresponding Pd macrocycle (equatorial).[4b] Since the cavity of the Ru-macrocycle can be tuned by phosphine coordination, these complexes can be used for molecular recognition and catalytic reaction with unique selectivity.

4. Experimental section

Materials and methods

All solvents were distilled or dried before use according to the general purification procedure. Commercially available reagents including $Ru_3(CO)_{12}$ (Aldrich), 2-ethoxyethanol (Tokyo Chemical Industry Co., Ltd.), *N*,*N*-dimethylformamide (DMF, Kanto Chemical Co., Inc), triphenylphosphine (Tokyo Chemical Industry Co., Ltd.) triethylphosphite (Tokyo Chemical Industry Co., Ltd.), triethylsilane (Tokyo Chemical Industry Co., Ltd.), 1,4-dioxane (Tokyo Chemical Industry Co., Ltd.) and acetonitrile (Kanto Chemical Co., Inc.) were used without further purification unless otherwise noted. **MC33** was prepared *via* S_N2 reaction between N^2,N^6-bis((4-hydroxyphenyl)methyl)-2,6-pyridinedicarboxamide and bis(*p*-tolylsulfonyl)pentaethylene glycol with Cs_2CO_3, according to our previous work.[4b,4c)] All reactions were carried out under inert atmosphere of argon. Silica gel column chromatography was performed using silica gel 60 (spherical, grain size 40–50 μm) (Kanto Chemical Co. Inc., Tokyo, Japan). The ^{1}H-, ^{13}C- and ^{31}P-NMR spectra were measured on a BRUKER Biospin AVANCE III HD 500 spectrometer at 500, 125 and 202 MHz, respectively. ^{1}H-NMR shifts were expressed in parts per million relative to the internal standard Me_4Si (δ, 0.00), $(CH_3)_2SO$ (δ, 2.49) and C_6D_6 (δ, 7.16). ^{13}C-NMR shifts were referenced to the solvent of $CDCl_3$ (δ, 77.0), DMSO-d_6 (δ, 39.5) and C_6D_6 (δ, 128.1). VT-NMR spectra were measured on a BRUKER Biospin AVANCE DPX 300 spectrometer at 300 MHz. HR-MS were measured on a BRUKER micrOTOFII spectrometer using ESI-TOF method and elemental analyses were performed on a J-SCIENCE LAB MICRO CORDER JM10. These measurements were conducted by National University Corporation, Tokyo Institute of Technology Center for Advanced Material Analysis, on request. UV-vis spectra were measured on a JASCO V-550 UV-vis spectrometer. Recycling preparative GPC was performed by JAI LC-9210NEXT system with $CHCl_3$ eluent. IR spectra were recorded on a JASCO FT/IR-460 plus spectrometer.

Synthesis of Ru(MC33)(CO)$_2$(H$_2$O)

A mixture of **MC33** (139 mg, 0.24 mmol) and $Ru_3(CO)_{12}$ (58 mg, 0.09 mmol) in 2-ee (2.0 mL) was degassed by freeze-pump-thaw cycling in three times, and stirred at 140 °C under a CO atmosphere for 2 days. The mixture was cooled to room temperature to give a yellow solid. The resultant yellow solid was filtrated and washed with CH_3OH, CH_3CN and CH_2Cl_2. The solid was dried *in vacuo* to give Ru(**MC33**)$(CO)_2(H_2O)$ (176 mg, 97% yield) as a yellow solid.
^{1}H-NMR δ (500 MHz, DMSO-d_6, r.t.): 8.36 (t, 1H, *J* = 10 Hz), 7.98 (d, 2H, *J* = 10 Hz), 7.10 (d, 4H, *J* = 10 Hz), 6.79 (d, 4H, *J* = 10 Hz), 5.50 (d, 2H, *J* = 10 Hz), 4.06-3.91 (m, 4H), 3.72-3.64 (m, 4H), 3.63-3.50 (m, 12H) ppm. ^{13}C-NMR δ (125 MHz, DMSO-d_6, r.t.): 200.3, 190.6, 167.5, 157.1, 153.6, 140.5, 133.4, 129.3, 123.8, 113.9, 70.2, 70.1, 69.9, 67.0, 52.9 ppm. IR(KBr): 3066, 3033, 2929, 2044, 1971, 1612, 1583, 1564, 1510, 1444, 1244 cm^{-1}. HRMS (ESI-TOF-MS, positive) (*m*/*z*) for $C_{33}H_{35}N_3NaO_{10}Ru$ ([M-H_2O+Na]$^+$): Calculated 758.1267; Found 758.1259. Note that H_2O was dissociated from complex during MS measurement. Anal. Calcd. for $C_{33}H_{37}N_3O_{11}Ru$: C, 52.66; H, 4.95; N, 5.58, Found: C, 51.13; H, 4.33; N, 5.47.

Synthesis of Ru(AC)(CO)$_2$(H$_2$O)

A mixture of **AC** (195 mg, 0.48 mmol) and $Ru_3(CO)_{12}$ (112 mg, 0.18 mmol) in 2-ee (4.0 mL) was degassed by freeze-pump-thaw cycling in three times, and stirred at 140 °C under a CO atmosphere for 2 days. The mixture was cooled to room temperature to give a yellow solid. The resultant yellow solid was filtrated and washed with CH_3OH, CH_3CN and CH_2Cl_2. The solid was dried *in vacuo* to give Ru(**AC**)$(CO)_2(H_2O)$ (255 mg, 92% yield).
^{1}H-NMR δ (300 MHz, DMSO-d_6): 8.35 (t, 1H, *J* = 7.7 Hz), 7.97 (d, 2H, *J* = 7.7 Hz), 7.15 (d, 4H, *J* = 8.3 Hz), 6.82 (d, 4H, *J* = 8.5 Hz), 5.04 (d, 2H, *J* = 13.4 Hz), 4.03 (d, 2H, *J* = 13.4 Hz), 3.69 (s, 6H). ^{13}C-NMR δ (125 MHz, DMSO-d_6, r.t.): 200.1, 190.9, 167.6, 157.8, 153.6, 140.4, 133.3, 129.3, 123.7, 113.3, 54.9, 53.2 ppm. IR (KBr): 2870, 2046, 1977, 1920, 1612, 1585, 1510, 1442, 1244 cm^{-1}. HRMS (ESI-TOF-MS, positive) (*m*/*z*) for $C_{25}H_{21}N_3NaO_6Ru$ ([M–H_2O+Na]$^+$): Calculated 584.0373; Found 584.0382.

Synthesis of Ru(MC33)(CO)$_2$(P1)

A mixture of Ru(**MC33**)$(CO_2)(H_2O)$ (49 mg, 0.06 mmol) and triphenylphosphine (**P1**, 31 mg, 0.12 mmol) in 1,4-dioxane (4.0 mL) was vigorously refluxed with stirring for 3 min. The mixture was cooled to room temperature, and extracted with $CHCl_3$. After concentration under reduced pressure, the residue was purified by silica gel column chromatography (CH_2Cl_2/CH_3OH = 20/1) to give Ru(**MC33**)$(CO)_2$(**P1**) (28 mg, 43% yield) as a red solid.
^{1}H-NMR δ (500 MHz, $CDCl_3$, r.t.): 7.79 (t, 1 H. *J* = 10 Hz), 7.69 (d, 2H, *J* = 10 Hz), 7.49-7.31 (m, 15 H), 7.17 (d, 4H, *J* = 10 Hz), 6.77 (d, 4H, *J* = 10 Hz), 5.50 (d, 2H, *J* = 10 Hz), 4.05 (t, 4H, *J* = 5 Hz), 3.82 (t, 4H, *J* = 5 Hz), 3.75-3.64 (m, 8H), 2.89 (d, 2H, *J* = 10 Hz) ppm. ^{13}C-NMR δ (125 MHz, $CDCl_3$, r.t.): 200.5 (d, *J*= 13 Hz), 185.1 (d, *J*= 113 Hz), 168.6, 158.0, 153.8, 139.3, 133.5 (d, *J*= 13 Hz), 133.0, 130.9, 130.3, 128.9 (d, *J*= 10 Hz), 128.2 (d, *J*= 41 Hz), 125.0, 114.6, 71.0, 70.8 (d, *J*= 6 Hz), 69.7, 67.4, 53.2 ppm. ^{31}P-NMR δ (202 MHz, $CDCl_3$, r.t.): 21.9 ppm. IR (NaCl): 3066, 3055, 3028, 3001, 2952, 2931, 2908, 2834, 2060, 1977, 1583, 1510, 1435, 1248 cm^{-1}. HRMS (ESI-TOF-MS, positive) (*m*/*z*) for $C_{51}H_{50}N_3NaO_{10}PRu$ ([M+Na]$^+$): Calculated 1020.2184; Found 1020.2177.

Synthesis of Ru(MC33)(CO)(P2)$_2$

A mixture of Ru(**MC33**)$(CO)_2(H_2O)$ (28 mg, 0.037 mmol) and triethylphosphite (**P2**, 12.8 μL, 0.075 mmol) in 1,4-dioxane (1.0 mL) was stirred at vigorously reflux temperature for 3 min. The

mixture was cooled to room temperature, and extracted with CH_2Cl_2. After concentration under reduced pressure, the residue was purified by preparative TLC ($CHCl_3$/CH_3CN = 80/20 then $CHCl_3$/CH_3OH = 95/5) to give Ru(**MC33**)(CO)(**P2**)$_2$ (32 mg, 83% yield) as a yellow solid.

^{1}H-NMR δ (500 MHz, $CDCl_3$, r.t.): 8.03-7.93 (m, 3H), 7.42 (d, 4H, *J* = 10 Hz), 6.76 (d, 4H, *J* = 10 Hz), 4.60-4.52 (m, 4H), 4.14-4.04 (m, 4H), 3.84-3.74 (m, 4H), 3.71-3.57 (m, 14H), 3.49-3.48 (m, 12H), 1.03-0.97 (m, 18H) ppm. ^{13}C-NMR δ (125 MHz, $CDCl_3$, r.t.): 203.9 (t, *J* = 13 Hz), 168.3, 157.5, 155.6, 138.4, 133.9, 132.2, 123.2, 113.7, 71.2, 70.8, 70.7, 69.8, 67.8, 61.2, 54.5, 16.2 ppm. ^{31}P-NMR δ (202 MHz, $CDCl_3$, r.t.): 113.0 ppm. IR (NaCl): 2981, 2927, 2906, 2870, 1959, 1610, 1579, 1510, 1441, 1244, 1026 cm^{-1}. HRMS (ESI-TOF-MS, positive) (*m*/*z*) for $C_{44}H_{65}N_3NaO_{15}P_2Ru$ ([M+Na]$^+$): Calculated 1062.2839; Found 1062.2821.

Synthesis of Ru(AC)(CO)$_2$(P1)

A mixture of Ru(**AC**)(CO_2)(H_2O) (7.2 mg, 0.012 mmol) and triphenylphosphine (**P1**, 6.9 mg, 0.025 mmol) in 1,4-dioxane (0.6 mL) was vigorously refluxed with stirring for 30 min. The mixture was cooled to room temperature, and extracted with CH_2Cl_2. After concentration under reduced pressure, the residue was purified by silica gel column chromatography (CH_2Cl_2/CH_3OH = 95/5) to give Ru(**AC**)(CO)$_2$(**P1**) with a small amount of by-products (7 mg, 71% crude yield).

^{1}H-NMR δ(500 MHz, C_6D_6, r.t.): 7.77-7.70 (m, 1H), 7.62 (d, 2H, *J* = 10 Hz), 7.56 (d, 4H, *J* = 10 Hz), 7.49-7.42 (m, 6H), 6.95-6.90 (m, 9H), 6.70 (d, 4H, *J* = 10 Hz), 6.09 (d, 2H, *J* = 15 Hz), 3.21 (d, 2H, *J* = 15 Hz), 3.15 (s, 6H) ppm. ^{31}P-NMR δ(202 MHz, C_6D_6, r.t.): 23.2 ppm. IR (NaCl): 3068, 3027, 2952, 2931, 2908, 2835, 2060, 1977, 1583, 1510, 1435, 1248 cm^{-1}.

Synthesis of Ru(AC)(CO)(P2)$_2$.

A mixture of Ru(**AC**)(CO_2)(H_2O) (12 mg, 0.02 mmol) and triethylphosphite (**P2**, 6.7 μL, 0.04 mmol) in 1,4-dioxane (1.0 mL) was stirred at vigorously reflux temperature for 3 min. The mixture was cooled to room temperature, and extracted with CH_2Cl_2. After concentration under reduced pressure, the residue was purified by preparative TLC ($CHCl_3$/CH_3CN = 80/20 then CH_2Cl_2/CH_3OH = 95/5) to give Ru(**AC**)(CO)(**P2**)$_2$ (15 mg, 84% yield) as a yellow solid.

^{1}H-NMR δ(500 MHz, C_6D_6, r.t.): 8.09 (d, 2H, *J* = 10 Hz), 7.92 (d, 4H, *J* = 10 Hz), 7.25 (t, 1H, *J* = 5 Hz), 6.84 (d, 4H, *J* = 10 Hz), 4.97 (s, 4H), 3.38-3.30 (m, 18H), 0.85 (t, 18H, *J* = 5 Hz) ppm. ^{13}C-NMR δ(125 MHz, C_6D_6, r.t.): 204.9 (t, *J* = 13 Hz), 169.2, 158.9, 156.1, 138.5, 134.8, 132.6, 123.3, 113.4 61.3, 56.8, 54.8, 16.2 ppm. ^{31}P-NMR δ(202 MHz, C_6D_6, r.t.): 113.8 ppm. IR (NaCl): 3066, 2979, 2929, 2906, 2856, 2044w, 1608, 1576, 1510, 1441, 1248, 1026 cm^1.

Ru-catalyzed hydrosilylation of 4,4'-bis(acetoxyphenyl)acetylene (1) with HSiEt$_3$.

To a solution of 4,4'-bis(acetoxyphenyl)acetylene (**1**, 147 mg, 0.5 mmol), Ru(**MC33**)(CO_2)(H_2O) (16 mg, 0.025 mmol) and PPh_3 (7 mg, 0.025 mmol) as an additive in 1,4-dioxane (2.0 mL) was degassed by freeze-pump-thaw cycling in three time. The mixture added triethylsilane (0.3 mL, 2.0 mmol) at 100 °C for 12 h. The mixture was cooled to room temperature, and extracted with $CHCl_3$. After concentration under reduced pressure, the yields of **2**, **3** and **4** were determined by ^{1}H-NMR using 1,1,2,2-tetrachloroethane as an internal standard.*cis*-Vinylsilane **2**: ^{1}H-NMR[7] δ (500 MHz, $CDCl_3$, r.t.): 7.04 (d, 2H, *J*= 10 Hz), 6.98 (d, 2H, *J*= 10 Hz), 6.96 (d, 2H, *J*= 10 Hz), 6.83 (d, 2H, *J*= 8.0 Hz), 6.74 (s, 1H), 2.30 (s, 3H), 2.24 (s, 3H), 0.95 (t, 9H, *J*= 10 Hz), 0.64 (q, 6H, *J* = 10 Hz) ppm.

trans-Vinylsilane **3**: ^{1}H NMR δ(500 MHz, $CDCl_3$, r.t.): 7.30 (d, 2H, *J*= 10 Hz), 7.27 (s, 1H), 7.16 (d, 2H, *J*= 10 Hz) 7.06 (d, 2H, *J*=10 Hz), 7.03 (d, 4H, *J*= 10 Hz), 2.32 (s, 3H), 2.30 (s, 3H), 0.80 (t, 9H, 7.16 (d, 4H, *J*= 10 Hz), 0.49 (q, 6H, *J*= 10, 15 Hz) ppm.

trans-Stilbene **4:** ^{1}H-NMR[7] δ (500 MHz, $CDCl_3$, r.t.): 7.50 (d, 4H, *J*= 10 Hz), 7.09 (d, 4H, *J* = 10 Hz), 7.03 (s, 2H) 2.30 (s, 6H) ppm.

Crystallography

Single crystals suitable for X-ray analyses were mounted on a fiber loop. Diffraction experiments were performed on a Rigaku Saturn CCD area detector with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Intensity data (6° < 2θ < 55°) collected at 93 K were corrected by Lorentz polarization effects and absorption. Structure solution and refinements were carried out by using the CrystalStructure program package.[8] The heavy-atom positions were determined by a direct method program (SIR92[9]) and the remaining non-hydrogen atoms were found by subsequent Fourier syntheses and refined by full-matrix least-squares techniques against F^2 using the SHELXL-2014/7 program.[10] In the crystal of Ru(**MC33**)(CO_2)(H_2O), a DMF ligand derived from the crystallization solvent exists in place of the axial carbonyl ligand with a partial occupancy. The occupancies of the two axial ligands were refined, and the carbonyl ligand was refined with restraint geometries and atom displacement parameters. The hydrogen atoms in the aqua ligands and co-crystallized water were found in the difference Fourier map and included in the refinements with constraint geometries. The rest hydrogen atoms were included in the refinements with a riding model. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC 1981319 (Ru(**MC33**)(CO)$_{1.35}$(H_2O)(dmf)$_{0.65}$), CCDC 1981320[(Ru(**MC33**)(CO)$_2$(**P1**) (**P1** = PPh_3)], CCDC 1981321 [Ru(**MC33**)(CO)(**P2**)$_2$ (**P2** = P(OEt)$_3$)] and CCDC 1981322 (Ru(**AC**)(CO)$_2$(H_2O)). Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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Conflicts of interest

The authors have no conflicts of interest to declare for this communication.

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