

BCSJ Award Article

Synthesis, Structure, and Proton-Transfer Reactions of Brønsted Acidic Pyridylpyrazole Complexes of Ruthenium

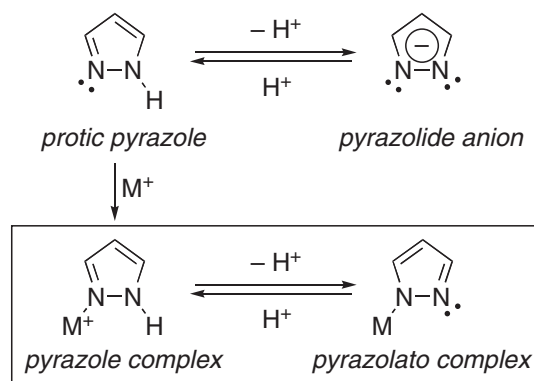
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A reaction of $[\{\text{Cp}^*\text{Ru}(\mu_3\text{-Cl})\}_4]$ (Cp^* : $\eta^5\text{-C}_5(\text{CH}_3)_5$) with 5-phenyl-3-(2-pyridyl)-1*H*-pyrazole (PhpypzH) afforded a chelating pyrazole complex $[\text{Cp}^*\text{RuCl}(\text{PhpypzH})]$ (**2**) bearing an NH proton at the β -position to the metal. Treatment of **2** with an equimolar amount of silver nitrite followed by anion exchange with KOTf (OTf: OSO_2CF_3) gave the pyrazolato–nitrosyl complex $[\text{Cp}^*\text{Ru}(\text{NO})(\text{Phpypz})](\text{OTf})$ (**3**) through a proton shift from the pyrazole ligand to the nitrite ion. In contrast, simple ligand exchange took place in the reaction of silver nitrite and $[\text{Cp}^*\text{RuCl}(\text{bipy})]$ (bipy: 2,2'-bipyridine) without the protic chelate ligand to give the nitro complex $[\text{Cp}^*\text{Ru}(\text{NO}_2\text{-}\kappa\text{N})(\text{bipy})]$ (**4**). Protonation of **4** with triflic acid led to the formation of the nitrosyl complex $[\text{Cp}^*\text{Ru}(\text{NO})(\text{bipy})](\text{OTf})_2$ (**5**). The pyrazolato complex **3** was also obtained by the reaction of $[\text{Cp}^*\text{Ru}(\text{NO})\text{Cl}_2]$ with PhpypzH and KOTf in water. Reversible protonation of **3** resulted in the formation of the dicationic pyrazole complex $[\text{Cp}^*\text{Ru}(\text{NO})(\text{PhpypzH})](\text{OTf})_2$ (**6**). The detailed structures of **2–4** and **6** have been determined by X-ray crystallography.

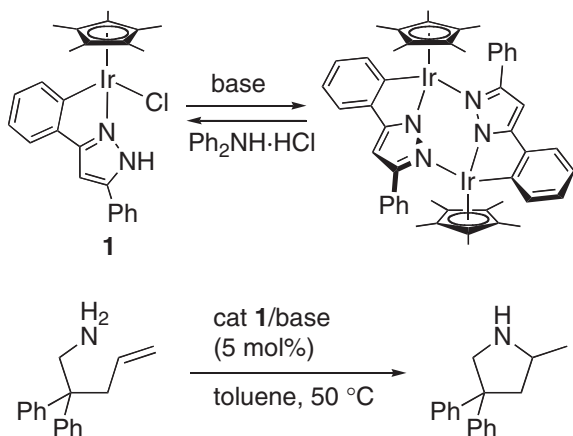
Pyrazoles have been used as versatile ligands for a variety of coordination compounds ranging from bioinorganic models¹ and antitumor agents² to materials with efficient luminescent properties.³ The Brønsted basic imino nitrogen in pyrazoles allows them to be σ -donors toward metal centers as in other *N*-heterocycles typified by pyridines.^{4,5} Provided that the NH group is not masked with substituents, such pyrazoles are amphoteric molecules with a Brønsted acidic NH group in addition to the basic imino nitrogen. Deprotonation of the protic pyrazoles affords pyrazolide anions (Scheme 1), which bind to metals with more diversified manners including the μ - $\kappa\text{N},\kappa\text{N}'$ coordination in dinuclear ligands.^{4,6} The acidity and hydrogen-bond-donating ability of protic pyrazoles are increased upon coordination,⁵ and consequently most protic pyrazole complexes are associated with intra- and intermolecular hydrogen bonds. Some poly(protic pyrazole) complexes are known as anion hosts through multiple hydrogen bonds.^{4,7} Deprotonation of coordinated protic pyrazoles with enhanced acidity is also intriguing, because it should cause significant electronic perturbation to the properties of the pyrazole complexes. In the (pyrazole)ruthenium complexes $[\text{RuCl}(\text{PzH})(\text{bipy})_2]^+$ (PzH: a protic pyrazole, bipy: 2,2'-bipyridine), for example, the two MLCT absorptions are red-shifted by 60 and 30 nm upon treatment with a base.⁸ Lam and co-workers created a molecular “pivot-hinge” composed of two square-planar (protic pyrazole)platinum units, in which the two units are flipped in response to deprotonation and reprotonation of the NH group in the ligated pyrazole.⁹ Satake and co-workers demonstrated that



Scheme 1. Reversible deprotonation of uncoordinated and ligated protic pyrazole.

a cationic (π -allyl)palladium–pyrazole complex is an excellent precatalyst for cyclopropanation of ketene silyl acetals with allylic acetates.¹⁰ However, chemical transformations promoted by reversible proton transfer from pyrazole complexes still remain unexplored¹¹ in spite of increasing research activities on protic pyrazole complexes.^{2,4–16} In addition, detailed structural comparison between pyrazole complexes and the conjugate base, κN -pyrazolato (also termed pyrazolido or pyrazolyl) complexes, has rarely been performed.¹²

We have demonstrated that late transition metal bifunctional complexes with chelating primary amine ligands catalyze both reductive and oxidative transformations as well as C–C bond-



Scheme 2. Reversible dehydrochlorination of protic pyrazole complex **1** and intramolecular hydroamination of ω -aminoalkene catalyzed by **1**.

forming reactions.¹⁷ The notable catalytic performance results from the cooperation of the metal center and the neighboring protic amine ligand at the α -position to the metal. We thus envisioned that the protic pyrazole complexes bearing an NH group at the β -position to the metal would also serve as such metal–ligand bifunctional catalysts. As part of our research program focusing on β -protic cooperating ligands,^{18,19} we have recently demonstrated that the half-sandwich iridium complex **1** bearing C–N chelate protic pyrazole ligand undergoes reversible dehydrochlorination and catalyzes intramolecular hydroamination of unactivated alkenes (Scheme 2).²⁰ We describe here the synthesis, structures, and proton-transfer reactions of the isoelectronic N–N chelate pyrazole complexes of ruthenium.

Experimental

General. All manipulations were performed under an atmosphere of argon using standard Schlenk technique unless otherwise specified. Solvents were dried by refluxing over sodium benzophenone ketyl (THF, diethyl ether, and hexane), P₂O₅ (acetonitrile), CaH₂ (dichloromethane), and distilled before use. Water and 1,2-dichloroethane were degassed by bubbling with argon. 5-Phenyl-3-(2-pyridyl)-1*H*-pyrazole (PhppyzH),¹³ [$\text{Cp}^*\text{Ru}(\mu_3\text{-Cl})_4$],²¹ [$\text{Cp}^*\text{Ru}(\text{NO})\text{Cl}_2$],²² and [$\text{Cp}^*\text{RuCl}(\text{bipy})$]²³ were prepared according to the literature. ¹H NMR spectra (300.40 and 399.78 MHz) were obtained on a JEOL JNM-LA300 and JNM-ECX400 spectrometer. Infrared spectra were recorded on a JASCO FT/IR-610 spectrometer. Elemental analyses were performed by the Analytical Facility at the Research Laboratory of Resources Utilization, Tokyo Institute of Technology or on a Perkin-Elmer 2400II CHN analyzer.

Synthesis of [$\text{Cp}^*\text{RuCl}(\text{PhppyzH})$] $\cdot$ 0.5THF (2** $\cdot$ 0.5THF).** To a solution of [$\text{Cp}^*\text{Ru}(\mu_3\text{-Cl})_4$] (170.6 mg, 0.1569 mmol) in CH₃CN (16 mL) was added PhppyzH (139.2 mg, 0.6291 mmol), and the solution was stirred for 16 h at room temperature. After removal of the solvent under reduced pressure, the resulting solid was recrystallized from THF–hexane (3 mL/18 mL) to give dark brown crystals. The crystals were rinsed with acetone and dried in vacuo (126.9 mg, 0.2399 mmol,

38%). ¹H NMR (CD₃CN): δ 1.67 (s, 15H, Cp*), 7.27 (s, 1H, aryl), 7.39–7.51 (m, 4H, aryl), 7.89 (m, 2H, aryl), 8.13 (m, 2H, aryl), 9.06 (m, 1H, aryl), 12.76 (br, 1H, NH). Found: C, 58.82; H, 5.76; N, 7.60%. Calcd for C₂₆H₃₀ClN₃O_{0.5}Ru: C, 59.03; H, 5.72; N, 7.94%.

Synthesis of [$\text{Cp}^*\text{Ru}(\text{NO})(\text{Phppyz})$](OTf) (3**).** **From 2:** A mixture of **2** (111.0 mg, 0.210 mmol) and AgNO₂ (36.0 mg, 0.234 mmol) in CH₃CN (5 mL) was stirred for 4 h at room temperature. The resultant suspension was filtered, and KOTf (212.0 mg, 1.13 mmol) was added to the filtrate. After stirring for 3 h, the mixture was evaporated to dryness and dissolved in CH₂Cl₂ (4 mL). The solution was washed with water (3 mL $\times$ 2). Removal of the solvent from the separated organic layer afforded **3** (93.6 mg, 0.147 mmol, 70%). ¹H NMR (CD₃CN): δ 1.86 (s, 15H, Cp*), 7.32 (m, 1H, aryl), 7.44 (m, 4H, aryl), 7.94 (m, 2H, aryl), 8.05, 8.19, 8.38 (m, 1H each, aryl). IR (KBr): 1799 cm^{−1} (ν_{NO}). Found: C, 47.16; H, 3.97; N, 8.81%. Calcd for C₂₅H₂₅F₃N₄O₄RuS: C, 47.24; H, 3.96; N, 8.81%.

From [$\text{Cp}^*\text{Ru}(\text{NO})\text{Cl}_2$]: A mixture of [$\text{Cp}^*\text{Ru}(\text{NO})\text{Cl}_2$] (54.9 mg, 0.163 mmol) and PhppyzH (36.1 mg, 0.163 mmol) in H₂O (5 mL) was stirred for 15 h at 50 °C. To the resultant solution was added KOTf (153.0 mg, 0.813 mmol). After stirring the mixture for 3 h at room temperature, the resultant brown solution was extracted with CH₂Cl₂ (3 mL $\times$ 6). Evaporation of the extract and recrystallization from CH₃CN–diethyl ether (7 mL/20 mL) afforded red crystals of **3** (76.5 mg, 0.120 mmol, 74%).

Synthesis of [$\text{Cp}^*\text{Ru}(\text{NO}_2\text{-}\kappa\text{N})(\text{bipy})$] $\cdot$ CH₂Cl₂ (4** $\cdot$ CH₂Cl₂).** A mixture of [$\text{Cp}^*\text{RuCl}(\text{bipy})$] (296.5 mg, 0.6929 mmol) and AgNO₂ (111.0 mg, 0.721 mmol) in THF (35 mL) was stirred at room temperature for 12 h. The reaction mixture was filtered, and the filtrate was evaporated to dryness. The resultant dark brown powder was recrystallized from CH₂Cl₂–hexane (15 mL/50 mL) to afford **4** $\cdot$ CH₂Cl₂ (245.9 mg, 0.4698 mmol, 68%) as red crystals. ¹H NMR (C₆D₆): δ 1.58 (s, 15H, Cp*), 6.58 (m, 2H, aryl), 6.83 (m, 2H, aryl), 7.10 (m, 2H, aryl), 9.12 (m, 2H, aryl). IR (KBr): 1321, 1280 cm^{−1} (ν_{NO}). The presence of solvated dichloromethane was confirmed by ¹H NMR spectroscopy and a preliminary X-ray analysis. Satisfactory analytical data could not be obtained by partial loss of the solvated molecule. Found: C, 49.26; H, 4.89; N, 8.29%. Calcd for C₂₁H₂₅Cl₂N₃O₂Ru: C, 48.19; H, 4.81; N, 8.03%. Single crystals of **4** suitable for X-ray analysis were obtained as a monohydrate by recrystallization from wet 1,2-dichloroethane–hexane.

Protonation of 4. To a solution of **4** $\cdot$ CH₂Cl₂ (34.1 mg, 0.0651 mmol) in THF (5 mL) was added triflic acid (=trifluoromethanesulfonic acid; 16.0 μ L, 0.18 mmol) at −78 °C. The mixture was warmed to room temperature over the course of 12 h. After removal of the solvent in vacuo, the resultant yellow powder was extracted with CH₃CN (5 mL). Recrystallization of the extract from CH₃CN–diethyl ether (2 mL/20 mL) afforded [$\text{Cp}^*\text{Ru}(\text{NO})(\text{bipy})$](OTf)₂ (**5**; 36.5 mg, 0.0507 mmol, 78%)²⁴ as yellow microcrystals.

Synthesis of [$\text{Cp}^*\text{Ru}(\text{NO})(\text{PhppyzH})$](OTf)₂ $\cdot$ CH₃CN (6** $\cdot$ CH₃CN).** **From 3:** To a solution of **3** (26.5 mg, 0.0417 mmol) in CH₂Cl₂ (4 mL) was added triflic acid (3.7 μ L, 0.042 mmol) at −78 °C, and the mixture was slowly warmed to room

Table 1. X-ray Crystallographic Data for **2**•0.5THF, **3**, **4**•H₂O, and **6**•CH₃CN

	2 •0.5THF	3	4 •H ₂ O	6 •CH ₃ CN
Formula	C ₂₆ H ₃₀ ClN ₃ O _{0.50} Ru	C ₂₅ H ₂₅ F ₃ N ₄ O ₄ RuS	C ₂₀ H ₂₅ N ₃ O ₃ Ru	C ₂₈ H ₂₉ F ₆ N ₅ O ₇ RuS ₂
Fw	529.07	635.62	456.51	826.75
Space group	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> 2 ₁ / <i>n</i> (No. 14)
Crystal color	dark brown	orange	dark brown	orange
Crystal dimension/mm ³	0.4 × 0.3 × 0.2	0.6 × 0.2 × 0.1	0.5 × 0.4 × 0.3	0.3 × 0.2 × 0.2
<i>a</i> /Å	11.467(4)	7.719(2)	8.952(3)	13.845(8)
<i>b</i> /Å	12.894(5)	23.019(7)	10.518(4)	16.479(8)
<i>c</i> /Å	17.482(8)	14.602(5)	11.184(4)	16.432(10)
α /°	82.633(16)	90	88.587(10)	90
β /°	77.049(15)	93.428(4)	89.850(12)	119.331(7)
γ /°	75.449(16)	90	67.918(6)	90
<i>V</i> /Å ³	2431.1(17)	2589.9(14)	975.5(6)	3268(3)
<i>Z</i>	4	4	2	4
<i>T</i> /K	193	193	193	93
<i>D</i> _{calcd} /g cm ⁻³	1.445	1.630	1.554	1.680
μ (Mo K α)/cm ⁻¹	7.75	7.47	8.29	6.95
Reflections measured	22488	23256	8611	29342
No. of unique reflections	10581	5861	4197	7454
Transmission factors	0.771–0.856	0.796–0.928	0.712–0.780	0.544–0.870
No. of variables	574	368	196	507
<i>R</i> _{int}	0.037	0.088	0.022	0.106
<i>R</i> 1 [<i>I</i> > 2 σ (<i>I</i>)]	0.065	0.043	0.050	0.069
<i>wR</i> 2 (all data)	0.168	0.136	0.136	0.192
Goodness-of-fit	1.002	1.000	1.004	1.006
Residual electron density/e Å ⁻³	1.35, –1.01	0.79, –0.72	1.52, –0.97	2.66, –1.50

temperature with stirring. After 18 h, the mixture was evaporated to dryness. Subsequent recrystallization from CH₃CN–diethyl ether (1 mL/15 mL) afforded **6**•CH₃CN as orange crystals (29.2 mg, 0.0353 mmol, 85%). ¹H NMR (CD₃CN): δ 1.88 (s, 15H, Cp*), 7.60 (m, 3H, aryl), 7.70 (s, 1H, aryl), 7.76 (m, 1H, aryl), 7.89 (m, 2H, aryl), 8.39 (m, 2H, aryl), 8.56 (m, 1H, aryl), 13.27 (s, 1H, NH). IR (KBr): 1828 cm⁻¹ (ν_{NO}). Found: C, 40.60; H, 3.58; N, 8.33%. Calcd for C₂₈H₂₉F₆N₅O₇RuS₂: C, 40.68; H, 3.54; N, 8.47%.

From [Cp*Ru(NO)Cl₂]: A mixture of [Cp*Ru(NO)Cl₂] (55.9 mg, 0.166 mmol) and AgOTf (85.2 mg, 0.332 mmol) in CH₃CN (5 mL) was stirred for 3 h at room temperature. The reaction mixture was filtered, and PhpyzH (36.7 mg, 0.166 mmol) was added to the filtrate. After stirring for 16 h at room temperature, the mixture was filtered. Evaporation of the filtrate and recrystallization from CH₃CN–diethyl ether afforded **6**•CH₃CN as orange solid (88.6 mg, 0.107 mmol, 64%).

Deprotonation of 6 to Give 3. A mixture of **6**•CH₃CN (29.1 mg, 0.0352 mmol) and K₂CO₃ (4.9 mg, 0.035 mmol) in CH₂Cl₂ (2.5 mL) was stirred for 17 h at room temperature. The reaction mixture was filtered, and the filtrate was evaporated to dryness. Recrystallization from CH₃CN–diethyl ether (1 mL/15 mL) afforded red crystals of **3** (20.0 mg, 0.0315 mmol, 89%).

X-ray Diffraction Studies. Diffraction experiments were performed on a Rigaku Saturn CCD area detector with graphite monochromated Mo K α radiation ($\lambda = 0.71070$ Å). Single crystals suitable for X-ray analyses were mounted on glass fibers. Intensity data were corrected for Lorentz-polarization

effects and for absorption. Details of crystal and data collection parameters are summarized in Table 1.

Structure solution and refinements were carried out by using the CrystalStructure program package.²⁵ The heavy-atom positions were determined by a Patterson method program (DIRDIF99 PATTY;²⁶ for **2**•0.5THF) or direct methods program (SIR92;²⁷ for **3**, **4**•H₂O, and **6**•CH₃CN) and remaining non-hydrogen atoms were found by subsequent Fourier syntheses. The non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques based on *F*². Because both of the two crystallographically independent Cp* groups in **2**•0.5THF were severely disordered, these groups were included in the refinements as follows. The methyl carbon atoms in one Cp* group (C(6)–C(10)) in **2**•0.5THF were refined with isotropic thermal parameters. The other Cp* group was located at two disordered positions with 70% and 30% occupancies, and the minor component was treated as a rigid group with isotropic thermal parameters. The C and O atoms in the solvating THF molecule in **2**•0.5THF were refined with fixed isotropic thermal parameters. For **4**•H₂O, the Cp* ligand was located at two disordered position with 50% occupancies and refined isotropically as rigid groups. For **6**•CH₃CN, the triflate anion uninvolved in the hydrogen bond with the cation was located at two disordered positions with 55% and 45% occupancies. The hydrogen atoms in the solvated water molecule in **4**•H₂O were found in the difference Fourier map and all the other hydrogen atoms except for those in the disordered Cp* groups were placed at calculated positions; these hydrogen atoms were included in the refinements with a riding model. Crystallographic data have been deposited with

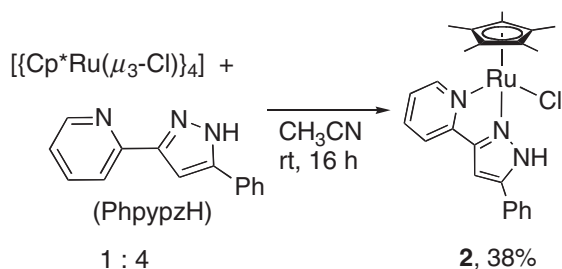
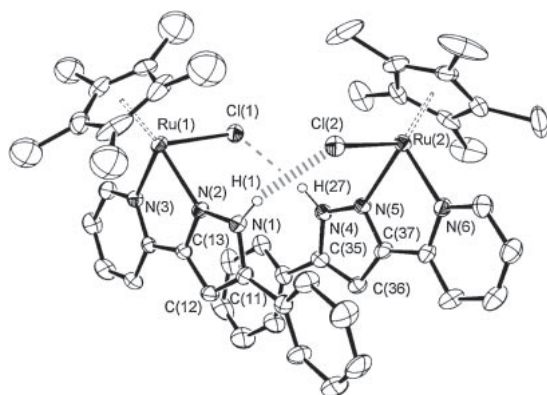
Scheme 3. Synthesis of protic pyrazole complex **2**.

Figure 1. Crystal structure of **2**·0.5THF with thermal ellipsoids at the 30% probability level. A pair of two crystallographically independent molecules is shown. Hydrogen atoms except for the NH protons, the minor component of the disordered Cp* ligand, and the solvated THF molecule are omitted for clarity.

the Cambridge Crystallographic Data Centre: Deposition numbers CCDC-802114, CCDC-802115, CCDC-802116, and CCDC-802117 for compounds **2**·0.5THF, **3**, **4**·H₂O, and **6**·CH₃CN, respectively. 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, U.K.; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Results and Discussion

Synthesis and Structure of Pyrazole–Chlorido Complex **2**.

The protic pyrazole complex of ruthenium [Cp*RuCl(PhpypzH)] (**2**) was obtained by the stoichiometric reaction of [Cp*Ru(μ₃-Cl)₄] with PhpypzH in acetonitrile, as shown in Scheme 3. The ¹H NMR spectrum of **2** exhibits a low-field broad singlet assignable to the pyrazole proton. The Brønsted acidity of this proton was inferred from a facile H–D exchange with D₂O in a ¹H NMR experiment. Figure 1 depicts the molecular structure of **2** determined by a single-crystal X-ray structural analysis; selected bond distances and angles are listed in Table 2. Complex **2** has a three-legged piano-stool structure, in which the Brønsted acidic NH group and Brønsted basic chlorido ligand point to totally different directions with averaged intramolecular NH...Cl distances of 4.21 Å. As a consequence, **2** forms a hydrogen-bonded dimer in the solid state with an approximate C₂-symmetry as shown in Figure 1. Similar intermolecular hydrogen bonds are observed for the isoelectronic C–N chelate iridium complex **1**²⁰ and cationic

Table 2. Selected Interatomic Distances (Å) and Angles (°) for **2**·0.5THF

Molecule A		Molecule B	
Ru(1)–Cl(1)	2.4728(17)	Ru(2)–Cl(2)	2.4888(17)
Ru(1)–N(2)	2.114(3)	Ru(2)–N(5)	2.105(3)
Ru(1)–N(3)	2.136(4)	Ru(2)–N(6)	2.139(4)
N(1)–N(2)	1.349(5)	N(4)–N(5)	1.365(5)
N(1)–C(11)	1.365(6)	N(4)–C(35)	1.361(6)
C(11)–C(12)	1.376(7)	C(35)–C(36)	1.372(6)
C(12)–C(13)	1.412(6)	C(36)–C(37)	1.405(7)
N(2)–C(13)	1.336(6)	N(5)–C(37)	1.333(6)
N(1)···Cl(2)	3.264(4)	N(4)···Cl(1)	3.197(4)
H(1)···Cl(2)	2.37	H(27)···Cl(1)	2.30
N(2)–Ru(1)–N(3)	74.55(14)	N(5)–Ru(2)–N(6)	74.54(15)
Ru(1)–N(2)–N(1)	136.1(3)	Ru(2)–N(5)–N(4)	135.1(3)
Ru(1)–N(2)–C(13)	116.9(2)	Ru(2)–N(5)–C(37)	117.9(3)
N(1)–N(2)–C(13)	106.4(3)	N(4)–N(5)–C(37)	106.1(3)
N(2)–N(1)–C(11)	111.2(3)	N(5)–N(4)–C(35)	110.2(3)
N(1)–C(11)–C(12)	106.9(3)	N(4)–C(35)–C(36)	107.8(4)
C(11)–C(12)–C(13)	105.5(4)	C(35)–C(36)–C(37)	105.2(4)
N(2)–C(13)–C(12)	110.1(4)	N(5)–C(37)–C(36)	110.6(4)

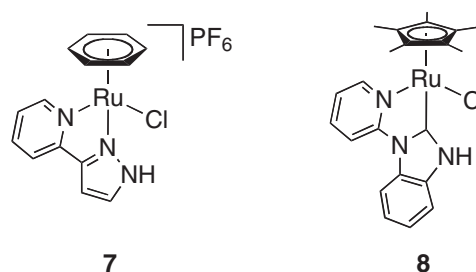
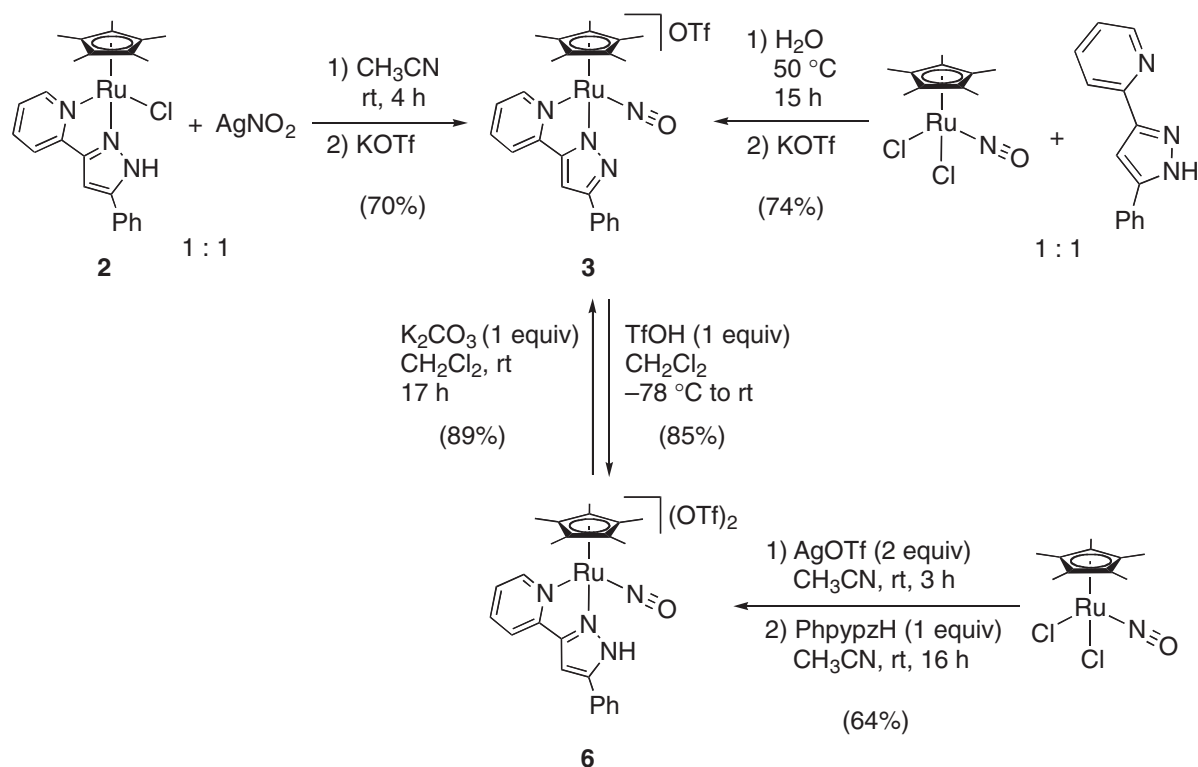


Chart 1.

[(arene)Ru] complex **7**¹⁴ as well as the closely related protic N-heterocyclic carbene complex **8** (Chart 1),¹⁸ though the hydrogen-bonded dimers of **1** and **7** are not C₂-symmetric but centrosymmetric. The Ru–N(pyrazole) distance of 2.110 Å (mean) is comparable with that in the isoelectronic complex **7** (2.0511(17) Å).¹⁴

Synthesis and Structure of Pyrazolato–Nitrosyl Complex **3.** Although half-sandwich complexes with chelating protic pyrazole ligands such as **2** are not unprecedented,^{14,15,20} little is known about their proton-donating ability. We therefore examined dehydrative conversion of nitrite ion to nitrosyl ligand on **2**, which would be triggered by proton migration from the chelate pyrazole ligand in **2** to nitrite ion.¹⁸ Treatment of the pyrazole–chlorido complex **2** with an equimolar amount of silver nitrite followed by anion exchange with KOTf resulted in the formation of the pyrazolato–nitrosyl complex [Cp*Ru(NO)(Phpypz)](OTf) (**3**) as shown in Scheme 4. The IR spectrum of **3** exhibits a strong absorption assignable to an NO stretching band at 1799 cm^{−1}, indicating the formation of a linear nitrosyl ligand. The detailed structure of **3** has been determined by X-ray crystallography (Figure 2a); selected bond distances and angles are listed in Table 3. The nitrosyl ligand is essentially linear with the Ru–N–O angle of 164.3(3)°. In contrast to the pyrazole complex **2**, the uncoordinated nitrogen atom in the chelate (N(1)) is far from the



Scheme 4. Synthesis and reversible protonation of pyrazolato-nitrosyl complex **3**.

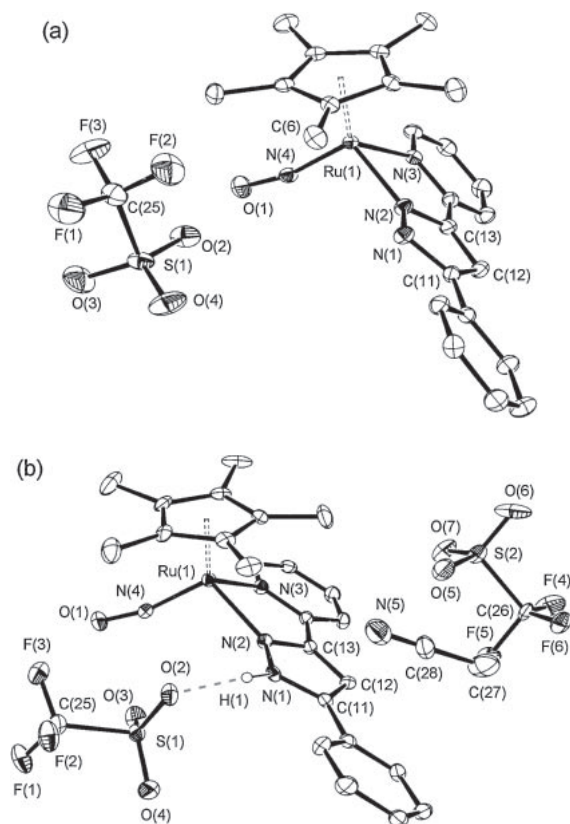
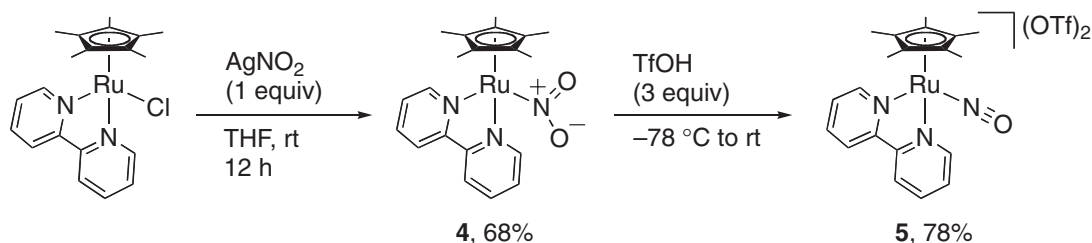


Figure 2. Crystal structures of **3** (a) and **6**·CH₃CN (b) with thermal ellipsoids at the 30% probability level. Hydrogen atoms except for the NH proton as well as the minor components of the disordered triflate anion are omitted for clarity.

Table 3. Selected Interatomic Distances (Å) and Angles (°) for **3** and **6**·CH₃CN

	3	6 ·CH ₃ CN
Ru(1)–N(2)	2.044(3)	2.086(6)
Ru(1)–N(3)	2.136(3)	2.139(6)
Ru(1)–N(4)	1.775(3)	1.802(4)
N(4)–O(1)	1.162(4)	1.145(6)
N(1)–N(2)	1.350(4)	1.353(6)
N(1)–C(11)	1.347(5)	1.368(9)
C(11)–C(12)	1.416(5)	1.398(9)
C(12)–C(13)	1.377(5)	1.380(9)
N(2)–C(13)	1.356(5)	1.341(9)
N(1)···O(2)	—	2.810(7)
H(1)···O(2)	—	1.92
N(2)–Ru(1)–N(3)	76.03(13)	75.3(2)
Ru(1)–N(2)–N(1)	130.1(2)	133.4(5)
Ru(1)–N(2)–C(13)	119.0(2)	118.5(3)
N(1)–N(2)–C(13)	110.8(3)	106.5(5)
N(2)–N(1)–C(11)	106.0(3)	110.5(5)
N(1)–C(11)–C(12)	110.6(3)	106.5(5)
C(11)–C(12)–C(13)	104.1(3)	105.7(6)
N(2)–C(13)–C(12)	108.5(3)	110.8(5)
Ru(1)–N(4)–O(1)	164.3(3)	161.6(7)

hydrogen-bond acceptors, with the shortest N(1)···O(triflate) distance of 4.541(5) Å. Loss of the NH proton is further evidenced by the ¹H NMR spectrum of **3**, which displays no NH signals. The reaction would involve the initial formation of the nitro-pyrazole complex [Cp*₂Ru(NO₂-κN)(PhpypzH)], which undergoes proton transfer from the pyrazole ligand to the nitro ligand to give **3**, as observed in protonation and protonolysis to nitro complexes with external Brønsted acid.²⁸



Scheme 5. Synthesis and protonation of nitro complex 4.

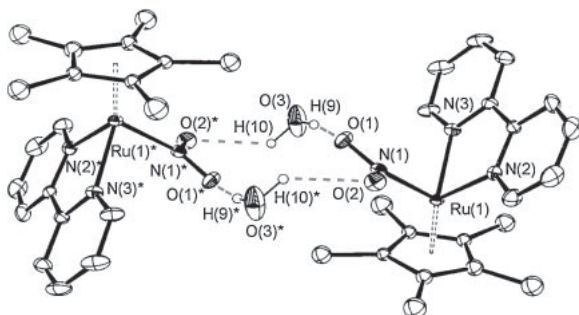


Figure 3. Crystal structure of **4**·H₂O with thermal ellipsoids at the 30% probability level. Only one of the two conformers of the disordered Cp* ligand is shown. Hydrogen atoms except for those in the solvated water molecule are omitted for clarity. Asterisks denote atomic position determined by crystallographic inversion center.

The pyrazolato–nitrosyl complex **3** was also obtained by the ligand substitution of the nitrosyl complex [Cp*Ru(NO)Cl₂] with PhppzH in water (Scheme 4). Notably, the pyrazole proton is lost spontaneously under this synthetic condition, suggesting the strong Brønsted acidity of the dicationic species [Cp*Ru(NO)(PhppzH)]²⁺, which may be formed transiently.

To gain more insight into the role of the protic pyrazole ligand in **2** in the conversion of **2** to **3**, we carried out the reaction of the bipyridine complex [Cp*RuCl(bipy)] without a Brønsted acidic proton in the chelate ligand under similar conditions.²⁹ The reaction led to the formation of the nitro complex **4** as shown in Scheme 5. Although a number of nitro complexes have been known so far, organometallic nitro complexes are rather scarce.^{28,30} The IR spectrum of **4** exhibits the NO stretching bands at 1321 and 1280 cm^{−1}, indicating the coordination of nitrite ion.^{28,31} An X-ray analysis of **4**·H₂O established that the nitrite ion binds to the metal through the nitrogen atom rather than the oxygen atom (Figure 3 and Table 4). The metric parameters around the nitro ligand are unexceptional,³¹ and the two N–O distances in the nitro ligand are almost identical to each other. The nitro oxygen atoms are linked with the solvated water molecule by a hydrogen bond to form a dimeric structure of **4** in the crystal, suggesting that these oxygen atoms have proton-accepting ability. In fact, the nitro ligand in **4** undergoes facile protonation and protonolysis to afford the dicationic nitrosyl complex **5**²⁴ in good yield. The sequential transformations shown in Scheme 5 are consistent with the transient formation of the nitro–pyrazole complex [Cp*Ru(NO₂-κN)(PhppzH)] in the reaction of the pyrazole–chlorido complex **2** and nitrite. Dehydrative conversion of nitrite ion under neutral conditions is thus achieved by the

Table 4. Selected Interatomic Distances (Å) and Angles (°) for **4**·H₂O

(a) Distances			
Ru(1)–N(1)	2.074(3)	O(1)···O(3)	2.870(4)
Ru(1)–N(2)	2.111(3)	O(1)···H(9)	2.06
Ru(1)–N(3)	2.106(4)	O(2)···O(3)*	2.932(6)
N(1)–O(1)	1.248(4)	O(2)···H(10)*	2.21
N(1)–O(2)	1.253(4)		
(b) Angles			
N(2)–Ru(1)–N(3)	75.77(13)	Ru(1)–N(1)–O(2)	121.0(2)
Ru(1)–N(1)–O(1)	123.0(2)	O(1)–N(1)–O(2)	116.0(3)

cooperation of the metal center and the neighboring pyrazole ligand that supplies a proton.

Reversible Protonation of Pyrazolato Complex 3 to Give Pyrazole Complex 6. The pyrazolato complex **3** proved to undergo protonation at the uncoordinated β-nitrogen atom in the pyrazole ring. When **3** was treated with an equimolar amount of triflic acid, the dicationic pyrazole–nitrosyl complex **6** was obtained as shown in Scheme 4. The ¹H NMR spectrum of **6** displays the NH resonance at 13.27 ppm, which disappeared upon treatment with D₂O. The ν(NO) value of 1828 cm^{−1} observed for **6** is higher than that for **3** (1799 cm^{−1}), being consistent with the reduced back donation to the nitrosyl ligand in the dicationic complex **6**. Furthermore, the structure of **6** has been confirmed by an X-ray analysis (vide infra). Complex **6** was also obtained by the reaction of the chlorido complex [Cp*Ru(NO)Cl₂] with two equiv of silver triflate and subsequent treatment with PhppzH (Scheme 4), possibly through the triflate complex [Cp*Ru(NO)(OTf)₂].³² The Brønsted acidity of the dicationic pyrazole complex **6** may be estimated to be stronger than hydrochloric acid but weaker than triflic acid, considering the isolation of the monocationic pyrazolato complex **3** from the reaction without pretreatment with silver triflate. As expected, the reaction of **6** with potassium carbonate regenerated the pyrazolato complex **3** as illustrated in Scheme 4.

The structure of the pyrazole complex **6** has been determined by X-ray crystallography, as shown in Figure 2b and Table 3. The short contact between the NH group and an oxygen atom in one of the two triflate counter anion indicates the presence of the hydrogen bond. Having acquired both pyrazolato and pyrazole complexes **3** and **6** with exactly the same ancillary ligand set, we compared the structures of **3** and **6** as well as the chlorido complex **2** in detail (Table 3 and Figure 4). The Ru(1)–N(2) distance in the pyrazolato complex **3** (2.044(3) Å),

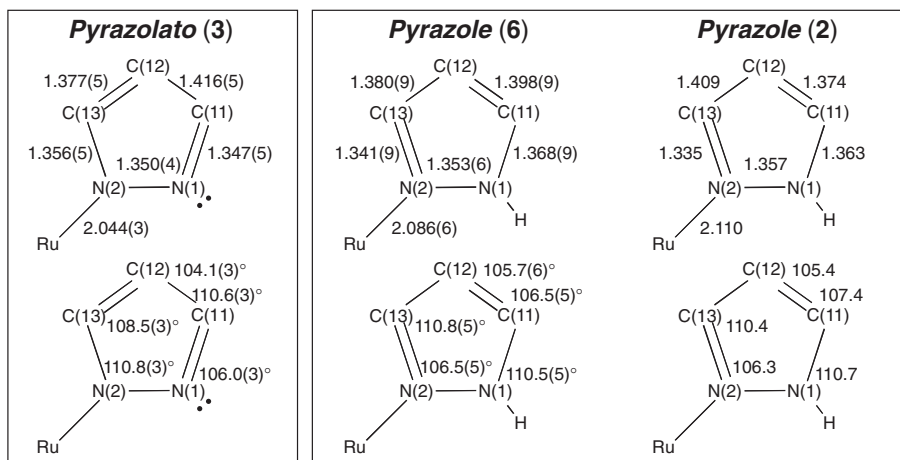


Figure 4. Bond distances (Å) and interior angles (deg) in the pyrazole ring of pyrazolato complex **3** and pyrazole complexes **6** and **2**. The values for **2** are averages of the two crystallographically independent molecules.

wherein the coordinated pyrazole is formally classified in an anionic X-type ligand, is shorter than that in the dative (L-type) pyrazole complexes **6** (2.086(6) Å) and **2** (2.110 Å, mean). The double bonds in the pyrazole ring are delocalized in both pyrazolato and pyrazole complexes; exceptionally, the C(11)–C(12) bond in the pyrazolato complex **3** and the C(12)–C(13) bond in the pyrazole–chlorido complex **2** are slightly longer than the other bonds in agreement with their canonical structures. The coordinated pyrazole nitrogen atom is almost planar in both protonated and deprotonated forms with the angle sum around the nitrogen atom of 358.4–359.9°. The N(1)–N(2)–C(13) angle in the pyrazolato complex **3** (110.8(3)°) is meaningfully larger than those in the pyrazole complexes **2** and **6** (106.3 (mean) and 106.5(5)°). On the contrary, the adjacent Ru(1)–N(2)–N(1) and N(2)–N(1)–C(11) angles in **3** are smaller than those in **2** and **6**. Similar trend is observed in pyrazolato and pyrazole complexes without the chelate arm¹² as well as the related protic *N*-heterocyclic carbene complex **8** and the deprotonated form, imidazolyl complex.¹⁸ The dihedral angle between the Cp* ligand and N–N chelate planes in the pyrazolato complex **3** (50.0(2)°) is much larger than that in the pyrazole complex **6** (29.1(3)°). The resultant short N(1)···C(6) contact of 3.151(6) Å in the pyrazolato complex **3** may suggest the presence of an attractive CH···N interaction.³³

Conclusion

We have synthesized the chelate-stabilized protic pyrazole complexes **2** and **6** and revealed their proton-transfer reactions. In the reaction of the chlorido complex **2** and silver nitrite, proton transfer from the protic pyrazole ligand to the coordinated nitrite led to the dehydrative conversion of nitrite ion under neutral conditions. The reactions using the bipyridine complexes substantiated the necessity of the β -protic ligand in this transformation. On the other hand, the dicationic pyrazole–nitrosyl complex **6** underwent reversible deprotonation, which allowed us detailed structural comparison between the interconvertible couples of pyrazole and pyrazolato complexes **6** and **3**. Further studies on the bifunctional catalysis with these protic pyrazole complexes involving reversible deprotonation of the β -NH group as a key step are now under way.

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