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Stereoselective synthesis of chlorido–phosphine ruthenium complexes bearing
a pyrazole-based protic tripodal amine ligand

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ABSTRACT

Octahedral ruthenium(II) complexes bearing a tripodal amine ligand featuring three ionizable pyrazole NH groups, tris((5-mesitylpyrazol-3-yl)methyl)amine (LH₃), have been synthesized in a stereoselective manner. Treatment of the chlorido complex

$[\{\text{RuCl}(\text{LH}_3)\}_2(\mu_2\text{-Cl})]\text{Cl}$ (**1**) with triphenylphosphine in methanol and subsequent anion exchange with potassium hexafluorophosphate resulted in the clean formation of the phosphine complex $\text{cis}(\text{P},\text{N}_{\text{amine}})\text{-}[\text{RuCl}(\text{PPh}_3)(\text{LH}_3)]\text{PF}_6$ ($\text{cis}(\text{P},\text{N}_{\text{amine}})\text{-2}$), in which the phosphine ligand lies in the position *cis* to the amine nitrogen atom. Similarly, diphosphines $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ reacted with **1** under the same conditions to give the diphosphine-bridged dinuclear ruthenium complexes $\text{cis}(\text{P},\text{N}_{\text{amine}})\text{-}[\{\text{RuCl}(\text{LH}_3)\}_2\{\mu_2\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\}](\text{PF}_6)_2$ (**3a**: $n = 4$; **3b**: $n = 3$; **3c**: $n = 2$). The *cis*-selectivity is in marked contrast with the reaction in toluene, which affords the *trans* isomer exclusively (H. Yamagishi, S. Nabeya, T. Ikariya, S. Kuwata, Inorg. Chem. 54 (2015) 11584.). On the other hand, a related chlorido–(dimethyl sulfoxide) complex $\text{trans}(\text{S},\text{N}_{\text{amine}})\text{-}[\text{RuCl}(\text{Me}_2\text{SO-S})(\text{LH}_3)]\text{Cl}$ (**4**) was synthesized by the reaction of $\text{cis-}[\text{RuCl}_2(\text{Me}_2\text{SO})_4]$ with LH_3 . Detailed structures of $\text{cis}(\text{P},\text{N}_{\text{amine}})\text{-2}$, **3a**, and **4** have been determined by X-ray crystallography.

Keywords: Tripodal ligand, Pyrazole, Hydrogen bond, Crystal structure

1. Introduction

Crafting coordination spaces with tripodal ligands has been the focus of intense research to develop activation and selective transformation of substrates therein [1–8]. In

octahedral complexes bearing a C_3 -symmetric tripodal tetradentate ligand, two stereoisomers should occur if the rest two monodentate ligands are different from each other. Thus, strict control of the ligand orientation around the metal is often required to define the coordination site for the substrate molecule. In the course of our extensive studies on cooperative reactivity of metals and protic N-heterocycle ligands [9–20], we have recently communicated the synthesis of a ruthenium complex **1** having a protic tris(pyrazolylmethyl)amine ligand, tris((5-mesitylpyrazol-3-yl)methyl)amine (LH_3), and its derivatization to the mononuclear phosphine complex *trans*(P,N_{amine})-[RuCl(PPh_3)(LH_3)]Cl (*trans*(P,N_{amine})-**2**; Scheme 1) [11]. Given that the metal–ligand cooperation in activation and transformation of substrate molecules is envisaged, the tunable phosphine ligand should be installed at the position *cis* to the amine nitrogen atom to fix the substrate-binding site surrounded by the three Brønsted acidic NH groups in LH_3 . In spite of significant recent advances in the coordination chemistry of multiproton-responsive tripodal ligands [6,21–23], however, introduction of supporting monodentate ligands to the specific site in the protic secondary coordination sphere remains rarely explored. We describe here stereoselective synthesis of the desired isomer *cis*(P,N_{amine})-**2** and related compounds bearing the multiproton-responsive tripodal ligand LH_3 .

2. Experimental

2.1. 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 (toluene and diethyl ether), CaH_2 (dichloromethane), and $\text{Mg}(\text{OMe})_2$ (methanol), and distilled before use. Tris((5-mesitylpyrazol-3-yl)methyl)amine (LH_3) and **1** [11] as well as *cis*- $[\text{RuCl}_2(\text{Me}_2\text{SO})_4]$ [24] were synthesized according to the literature. ^1H (399.8 MHz) and ^{31}P (161.8 MHz) NMR spectra were obtained on a JEOL JNM-ECX-400 spectrometer. ^1H NMR shifts are relative to the residual CHDCl_2 (δ 5.32) and CHCl_3 (δ 7.26), while ^{31}P shifts are referenced to phosphoric acid (δ 0.0), respectively. *J* values are given in Hz. Infrared spectra were recorded on a JASCO FT/IR-6100 spectrometer. Electrochemical measurements were made with a VersaSTAT 4 electrochemical analyzer using a glassy carbon working electrode, a platinum wire auxiliary electrode, and an Ag/AgCl reference electrode. Potentials were measured in dichloromethane–0.1 M *n*Bu₄NPF₆. UV-vis spectra were recorded on a JASCO V-630 spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400II CHN analyzer.

2.2 Synthesis

2.2.1. *cis*(P,N_{amine})-[RuCl(PPh₃)(LH₃)]PF₆ (*cis*(P,N_{amine})-**2**)

A mixture of **1** (66.2 mg, 0.0422 mmol) and triphenylphosphine (63.2 mg, 0.241 mmol) in methanol (5 mL) was stirred at 60 °C for 12 h. After cooling to room temperature, potassium hexafluorophosphate (46.2 mg, 0.251 mmol) was added, and the mixture was stirred for additional 1 h. After removal of the solvent in vacuo, the residue was extracted with dichloromethane (3 mL × 2). Addition of diethyl ether (18 mL) to the concentrated extract (ca. 1.5 mL) afforded orange crystals of *cis*(P,N_{amine})-**2** (72.6 mg, 0.0628 mmol, 74%). ¹H NMR (400 MHz, CD₂Cl₂): 1.84 (s, 12H, *o*-Me), 1.97, 2.30 (s, 6H each, *o*- and *p*-Me), 2.31 (s, 3H, *p*-Me), 3.63, 4.10 (d, 2H each, ²J_{HH} = 14.7, NCH₂Pz), 4.16 (s, 2H, NCH₂Pz), 6.13 (d, 1H, ⁴J_{HH} = 1.4, CH of pyrazole), 6.18 (d, 2H, ⁴J_{HH} = 1.8, CH of pyrazole), 6.91 (s, 4H, C₆H₂Me₃), 6.94 (s, 2H, C₆H₂Me₃), 7.31–7.35, 7.61–7.66 (m, 6H each, PPh₃), 7.39–7.43 (m, 3H, PPh₃), 10.88 (br, 2H, NH), 11.57 (br, 1H, NH). ³¹P{¹H} NMR (162 MHz, CD₂Cl₂): δ 45.3 (s). UV-vis (CH₂Cl₂) λ_{max}, nm (ε, L mol⁻¹ cm⁻¹): 239 (20700), 307 (7400). *Anal.* Calc. for C₅₇H₆₀ClF₆N₇P₂Ru: C, 59.24; H, 5.23; N, 8.48. Found: C, 59.03; H, 5.36; N, 8.31%. Crystals suitable for X-ray analysis was obtained by recrystallization from dichloromethane–toluene with a drop of methanol.

2.2.2. $[{\{RuCl(LH_3)\}_2(\mu_2-dppb)}](PF_6)_2$ (**3a**)

A mixture of **1** (156.8 mg, 0.100 mmol) and 1,4-bis(diphenylphosphino)butane (43.7 mg, 0.102 mmol) in methanol (10 mL) was stirred at 60 °C for 16 h. After cooling to room temperature, potassium hexafluorophosphate (82.9 mg, 0.450 mmol) was added, and the mixture was stirred for additional 1 h. After removal of the solvent in vacuo, the residue was extracted with dichloromethane (2 mL $\times$ 2). Addition of diethyl ether (18 mL) to the concentrated extract (ca. 2 mL) afforded orange crystals of **3** $\cdot$ 2H₂O (181.0 mg, 0.0805 mmol, 81%). ¹H NMR (400 MHz, CD₂Cl₂): δ 0.99, 2.15 (brs, 4H each, CH₂ of dppb), 1.79 (s, 24H, *o*-Me), 1.92, 2.29 (s, 12H each, *o*- and *p*-Me), 2.30 (s, 6H, *p*-Me), 3.33, 4.05 (d, 4H each, ²J_{HH} = 14.4, NCH₂Pz), 4.10 (s, 4H, NCH₂Pz), 6.09 (d, 2H, ⁴J_{HH} = 1.8, CH of pyrazole), 6.13 (d, 4H, ⁴J_{HH} = 1.9, CH of pyrazole), 6.89 (s, 8H, C₆H₂Me₃), 6.92 (s, 4H, C₆H₂Me₃), 7.33–7.38 (m, 8H, PPh₂), 7.45–7.49 (m, 12H, PPh₂), 10.37 (d, 2H, ⁴J_{HH} = 1.9, NH), 11.36 (d, 4H, ⁴J_{HH} = 1.8, NH). ³¹P{¹H} NMR (162 MHz, CD₂Cl₂): δ 42.2 (s). UV-vis (CH₂Cl₂) λ_{max} , nm (ϵ , L mol⁻¹ cm⁻¹): 239 (37200), 309 (13700). Anal. Calc. for C₁₀₆H₁₁₈Cl₂F₁₂N₁₄P₄Ru₂ $\cdot$ 2H₂O: C, 56.61; H, 5.47; N, 8.72. Found: C, 56.65; H, 5.40; N, 8.99%. Crystals suitable for X-ray analysis was obtained by recrystallization from dichloromethane–toluene with a drop of methanol.

2.2.3. $[\{RuCl(LH_3)\}_2\{\mu_2-Ph_2P(CH_2)_nPPh_2\}](PF_6)_2$ (**3b**, $n = 3$; **3c**, $n = 2$)

The title compounds were synthesized from **1** and 1,3-bis(diphenylphosphino)propane (for **3b**) or 1,2-bis(diphenylphosphino)ethane (for **3c**) by using a procedure similar to that used for **3a**. Data for **3b**: yield, 73%. 1H NMR (400 MHz, CD_2Cl_2): δ 1.32 (brs, 2H, $CH_2CH_2CH_2$), 1.89 (s, 24H, *o*-Me), 1.96, 2.23 (s, 12H each, *o*- and *p*-Me), 2.08 (brs, 4H, PCH_2), 2.33 (s, 6H, *p*-Me), 3.49, 4.98 (d, 4H each, $^2J_{HH} = 14.6$, NCH_2Pz), 4.08 (s, 4H, NCH_2Pz), 6.10 (d, 2H, $^4J_{HH} = 1.9$, CH of pyrazole), 6.13 (d, 4H, $^4J_{HH} = 1.9$, CH of pyrazole), 6.90 (s, 8H, $C_6H_2Me_3$), 6.92 (s, 4H, $C_6H_2Me_3$), 7.11–7.19 (m, 16H, PPh_2), 7.30–7.34 (m, 4H, PPh_2), 10.64 (brs, 4H, NH), 11.42 (d, 2H, $^4J_{HH} = 1.9$, NH). $^{31}P\{^1H\}$ NMR (162 Hz, CD_2Cl_2): δ 41.7 (s). Data for **3c**: yield, 47%. 1H NMR (400 MHz, CD_2Cl_2): δ 1.89 (s, 24H, *o*-Me), 1.95, 2.28 (s, 12H each, *o*- and *p*-Me), 2.31 (s, 6H, *p*-Me), 2.32 (d, 4H, $^2J_{PH} = 14.0$, PCH_2), 3.28, 3.97 (d, 4H each, $^2J_{HH} = 14.5$, NCH_2Pz), 4.01 (s, 4H, NCH_2Pz), 6.07 (d, 2H, $^4J_{HH} = 1.8$, CH of pyrazole), 6.10 (d, 4H, $^4J_{HH} = 2.3$, CH of pyrazole), 6.92 (s, 8H, $C_6H_2Me_3$), 6.94 (s, 4H, $C_6H_2Me_3$), 7.16–7.21 (m, 16H, PPh_2), 7.30–7.33 (m, 4H, PPh_2), 10.65 (brs, 4H, NH), 11.38 (d, 2H, $^4J_{HH} = 1.8$, NH). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ 43.3 (s).

2.2.4. $[Ru(dppm)(LH_3)]Cl_2$ (**3d**)

A mixture of **1** (141.3 mg, 0.0901 mmol) and bis(diphenylphosphino)methane (69.3 mg, 0.180 mmol) in methanol (10 mL) was stirred at 60 °C for 18 h. After removal

of the solvent in vacuo, recrystallization from 1,2-dichloroethane–methanol–diethyl ether (2 mL/0.5 mL/18 mL) afforded **9** as a yellow powder (103.5 mg, 0.0886 mmol, 49%). ^1H NMR (400 MHz, CD_2Cl_2): δ 1.97 (s, 12H, *p*-Me), 1.90, 2.30 (s, 6H each, *o*- and *p*-Me), 2.26 (s, 3H, *p*-Me), 4.19 (d, 2H each, $^2J_{\text{HH}} = 14.5$, NCH_2Pz), 4.48 (t, 2H, $^2J_{\text{PH}} = 10.3$, PCH_2P), 4.73 (s, 2H, NCH_2Pz), 5.50 (brd, 2H, $^2J_{\text{HH}} = 14.5$, NCH_2Pz), 5.95 (s, 1H, CH of pyrazole), 6.42 (s, 2H, CH of pyrazole), 6.85 (s, 2H, $\text{C}_6\text{H}_2\text{Me}_3$), 6.90 (s, 4H, $\text{C}_6\text{H}_2\text{Me}_3$), 7.02–7.07, 7.75–7.80 (m, 4H each, PPh_2), 7.25–7.33 (m, 8H, PPh_2), 7.37–7.41, 7.48–7.52 (m, 2H each, PPh_2), 11.25 (brs, 2H, NH), 14.09 (s, 1H, NH). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2): δ 0.9, 8.7 (d, 1P each, $^2J_{\text{PP}} = 56.5$).

2.2.5. $[\text{RuCl}(\text{Me}_2\text{SO}-S)(\text{LH}_3)]\text{Cl}$ (**4**)

A mixture of *cis*- $[\text{RuCl}_2(\text{dmsO})_4]$ (48.5 mg, 0.100 mmol) and $\text{LH}_3 \cdot 0.5\text{H}_2\text{O}$ (65.5 mg, 0.106 mmol) in dimethyl sulfoxide (2 mL) was stirred at 100 °C for 15 h. Removal of the solvent in vacuo and subsequent recrystallization from methanol–diethyl ether (1 mL/20 mL) afforded **4**·3MeOH as orange crystals (67.7 mg, 0.0707 mmol, 71%). ^1H NMR (400 MHz, CDCl_3): δ 1.93, 2.27 (s, 12H each, *o*- and *p*-Me), 1.96 (s, 12H, *o*-Me), 2.30 (s, 3H, *p*-Me), 2.60 (s, 6H, Me_2SO), 4.597 (s, 2H, NCH_2Pz), 4.604, 5.72 (d, 2H each, $^2J_{\text{HH}} = 13.7$, NCH_2Pz), 5.89 (d, 2H, $^4J_{\text{HH}} = 1.8$, CH of pyrazole), 6.22 (d, 2H, $^4J_{\text{HH}} = 1.5$, CH of pyrazole), 6.80 (s, 2H, $\text{C}_6\text{H}_2\text{Me}_3$), 6.86 (s, 4H, $\text{C}_6\text{H}_2\text{Me}_3$), 11.68 (br, 1H, NH), 12.57 (br, 2H, NH). IR (KBr, cm^{-1}): 1032 (SO). UV-vis (CH_2Cl_2) λ_{max} , nm (ϵ , $\text{L mol}^{-1} \text{cm}^{-1}$): 237

(28600), 325 (10100). *Anal.* Calc. for $C_{41}H_{51}Cl_2N_7ORuS \cdot 3CH_3OH$: C, 55.16; H, 6.63; N, 10.23. Found: C, 54.86; H, 6.88; N, 10.29%.

2.3. 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-K α radiation ($\lambda = 0.710\ 70\ \text{\AA}$). Intensity data ($6^\circ < 2\theta < 55^\circ$) 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 direct methods program (SIR92 [26]) and remaining non-hydrogen atoms were found by subsequent Fourier syntheses. The chloride counteranion in **4**·3MeOH was placed at two disordered positions with 85% and 15% occupancies. The solvating dichloromethane molecule in **3**·2(toluene)·6MeOH·CH₂Cl₂ was partially disordered and refined with restraint geometries. One of the solvating methanol molecules was also disordered; the disordered oxygen atoms were refined isotropically while the carbon atom was included in the refinements with fixed isotropic thermal parameter and restraint geometries. The rest non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques based on F^2 . The methanol OH hydrogen atoms in **2**·2MeOH and **4**·3MeOH (except for

the one lying near the disordered chloride anion) were found in the final difference Fourier map and included in the refinements with a riding model, while the rest OH hydrogen atoms were not included in the refinements. The rest hydrogen atoms were placed at calculated positions and included in the refinements with a riding model. The atomic scattering factors were taken from ref [27], and anomalous dispersion effects were included; the values of $\Delta f'$ and $\Delta f''$ were taken from ref [28].

3. Results and discussion

3.1. Stereoselective synthesis of chlorido–phosphine complexes **2**

As illustrated in Scheme 1, we have previously revealed that the reaction of the chlorido-bridged diruthenium(II) complex **1** with triphenylphosphine in toluene leads to exclusive formation of the chlorido–phosphine complex *trans*(P,N_{amine})-**2**, wherein the incoming phosphine ligand lies in the position *trans* to the amine nitrogen atom in the tripodal ligand LH₃ [11]. The result sharply contrasts with the reaction of a related aprotic tripodal ligand, tris(pyridylmethyl)amine (TPA), with [RuCl₂(PPh₃)₃], which affords a mixture of *cis*(P,N_{amine})- and *trans*(P,N_{amine})-[RuCl(PPh₃)(tpa)]⁺ [29]. The notable difference in the product selectivity prompted us to further investigate the reaction of the protic LH₃ ligand, which led to the finding that use of methanol as the solvent completely switches the product selectivity to the *cis* isomer. The ¹H NMR spectrum of this complex, confirming the C_s symmetry in solution, exhibits no remote coupling between the

phosphorus nuclei and the methylene protons in the tripodal ligand [11], in agreement with the *cis*-orientation of the phosphine ligand and the amine nitrogen atom. Subsequent anion exchange to hexafluorophosphate resulted in isolation of the *cis*(P,N_{amine})-**2** as crystals. X-ray analysis substantiated the orientation of the monodentate ligands in *cis*(P,N_{amine})-**2** (Fig. 1). Selected bond distances and angles are listed in Table 2. The pyrazole NH groups are engaged in hydrogen bonds with the solvating methanols (H(1)⋯O(1), 1.95; N(1)⋯O(1), 2.872(4); H(2)⋯O(2), 1.94; N(3)⋯O(2), 2.851(4) Å) and the chlorido ligand (H(3)⋯Cl(1), 2.68; N(5)⋯Cl(1), 3.163(3) Å). The latter intramolecular interaction appears to cause significant deformation of the octahedral configuration of the metal with the small Cl(1)–Ru(1)–N(6) and Cl(1)–Ru(1)–N_{amine} angles of 85.17(8) and 164.27(7)°. The corresponding angles in *trans*(P,N_{amine})-**2** are 103.41(6) and 176.68(6)° [11]. The Ru(1)–Cl(1) distance of 2.4351(10) Å is comparable with that in the *trans* isomer (2.4312(7) Å), while the Ru(1)–P(1) distance is increased (2.3288(10) versus 2.2863(7) Å), possibly due to the steric repulsion with the LH₃ ligand [11].

The *cis* and *trans* complexes **2** hardly isomerized to each other at least under their synthetic conditions. When isolated *cis*(P,N_{amine})-**2** was heated in toluene at 100 °C for 20 h, only 11% of the complex was converted to the cation of *trans*(P,N_{amine})-**2** on the ¹H NMR criteria. On the other hand, isomerization of *trans*(P,N_{amine})-**2** to the *cis* isomer was not observed in methanol at 60 °C for 20 h. These results suggest that the selective formation of *cis*- and *trans*(P,N_{amine})-**2** does not involve the solvent-dependent

isomerization of **2**. Although we currently have no conclusive evidence for the selective formation of **2**, a possible explanation is illustrated in Scheme 2. In the reaction of **1** and triphenylphosphine in methanol, a postulated intermediate $[\text{RuCl}_2(\text{LH}_3)]$ may form a hydrogen-bonding network (Scheme 2, left) involving a less-distorted octahedral metal center owing to the participation of the solvent molecules. Such non-covalent interactions in the second coordination sphere would inhibit the substitution of the chlorido ligand *trans* to the amine nitrogen atom and lead to selective formation of *cis*(P,N_{amine})-**2**. Szymczak and co-workers estimated the strength of such multiple hydrogen bonds between the chloride and a tripodal protic ligand, illustrated in Scheme 2 (right), by DFT calculations and alluded to the suppression of chloride dissociation by the noncovalent interactions [30]. On the other hand, the intramolecular hydrogen bond between the pyrazole NH group and chlorido ligand would be less effective to suppress the dissociation due to the structural distortion around the ruthenium (*vide infra*); hence, the strong *trans* influence of the σ -donating central amine in LH₃ would facilitate the formation of the *trans*(P,N_{amine})-**2** in toluene, which is incapable of making a hydrogen bond with the chlorido ligand.

Unlike the chlorido-bridged dinuclear complex **1** [11], the mononuclear complex *cis*(P,N_{amine})-**2** did not react with 1,2-diphenylhydrazine at room temperature. The inertness may be ascribed to the steric hindrance of the phosphine ligand in *cis*(P,N_{amine})-**2**.

3.2. Synthesis of diphosphine-bridged dinuclear complexes **3**

Appropriate accumulation of mononuclear complexes bearing protic groups in their second coordination sphere would give a redox-active multimetallic site surrounded by multiple proton-delivering functional groups, which is attractive for multielectron-coupled multielectron transfer reactions. With a synthetic protocol to introduce a phosphine ligand to selective positions in the Ru(LH₃) moiety in hand, we thus attempted to link two Ru(LH₃) units by a diphosphine, with maintaining *syn*-orientation of the three NH groups and chlorido ligand as in *cis*(P,N_{amine})-**2**. When the chlorido complex **1** was treated with an equimolar amount of 1,4-bis(diphenylphosphino)butane (DPPB) and hexafluorophosphate anion in methanol, the diphosphine-bridged dinuclear complex [$\{\text{RuCl}(\text{LH}_3)\}_2(\mu_2\text{-dppb})](\text{PF}_6)_2$ (**3a**) was obtained in good yield (Eq. (1)). The structure of **3a**, with a crystallographic inversion center on the bridging diphosphine ligand, was unambiguously characterized by X-ray analysis (Fig. 2 and Table 2). The coordination geometry with the *cis* orientation of the phosphine and amine donors is almost superimposable with that in the monophosphine complex *cis*(P,N_{amine})-**2**. Unfortunately, the two Ru–Cl units point to opposite directions, and the intramolecular Ru···Ru distance is as far as 10.6 Å. The ³¹P{¹H} NMR spectrum demonstrated that the symmetrical structure of **3a** is preserved even at –30 °C. The cyclic voltammogram of **3a** displayed only one reversible oxidation wave (+0.33 V vs Fc^{0/+}), indicating the absence of intramolecular electronic interaction between the two Ru(LH₃) centers.

To place the two ruthenium centers in closer positions, we also examined smaller spacers in a similar manner. When 1,3-bis(diphenylphosphino)propane (DPPP) or 1,2-bis(diphenylphosphino)ethane (DPPE) was treated with **1**, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the product exhibited only one ^{31}P singlet (δ 41.7 (DPPP, **3b**), 43.3 (DPPE, **3c**)) in agreement with the formation of the diphosphine-bridged dinuclear complexes corresponding to **3**. In contrast, the reaction with a much smaller diphosphine, 1,2-bis(diphenylphosphino)methane (DPPM), gave a mixture of a mononuclear chelate complex $[\text{Ru}(\text{dppm})(\text{LH}_3)]\text{Cl}_2$ (**3d**) showing two ^{31}P doublets at δ 0.9 and 8.7 along with an equimolar amount of unreacted **1**. As expected, addition of one more equivalent of DPPM led to complete conversion of **1** to **3d**.

3.3. Synthesis of chlorido–(dimethyl sulfoxide) complex **4**

We have also explored potential precursors other than the dinuclear chlorido complex **1** for the synthesis of $\text{Ru}(\text{LH}_3)$ complexes with diverse co-ligands. The reaction of *cis*- $[\text{RuCl}_2(\text{Me}_2\text{SO})_4]$ with an equimolar amount of LH_3 in dimethyl sulfoxide at 100 °C gave rise to exclusive formation of the mononuclear chlorido–(dimethyl sulfoxide) complex *trans*($\text{S}, \text{N}_{\text{amine}}$)- $[\text{RuCl}(\text{Me}_2\text{SO}-\text{S})(\text{LH}_3)]\text{Cl}$ (**4**) as shown in Eq. (2). The related TPA complex $[\text{RuCl}(\text{Me}_2\text{SO}-\text{S})(\text{tpa})]^+$ is known to form both *cis*($\text{S}, \text{N}_{\text{amine}}$) and *trans*($\text{S}, \text{N}_{\text{amine}}$) isomers [31–35]. Interestingly, the former is thermodynamically less stable and isomerizes to the *cis*($\text{S}, \text{N}_{\text{amine}}$) isomer when heated in dimethyl sulfoxide at 100 °C [31], in

sharp contrast to **4**.

Fig. 3 depicts the crystal structure of **4**. The **S-bound** sulfoxide ligand, which lies *trans* to the amine nitrogen atom, is engaged in intramolecular hydrogen bonding with one of the pyrazole arms in LH₃ with the H(3)···O(1) and N(5)···O(1) distances of 2.02 and 2.756(2) Å [12,36]. The interaction may rationalize the thermodynamic stability of **4** over the *cis*(S,N_{amine}) isomer. The S–O distance (1.4940(15) Å) is almost comparable with those in the related aprotic tpa complexes without intramolecular hydrogen bond (1.479(3)–1.492(2) Å) [31,35]. The rest NH groups also form hydrogen bonds with the chloride counteranion and solvating methanol molecules in the second coordination sphere.

4. Conclusions

We have demonstrated solvent-dependent stereoselective synthesis of *cis*(P,N_{amine})- and *trans*(P,N_{amine})-[RuCl(PPh₃)(LH₃)]⁺ bearing a pyrazole-based multiproton-responsive tripodal amine ligand LH₃. The synthetic method was successfully applied to the preparation of the diphosphine-bridged dinuclear **complexes 3a-c**. We have also prepared the chlorido–(dimethyl sulfoxide) complex **4** in a stereoselective manner. Owing to the rigid framework of the protic tripodal ligand LH₃, the multiple hydrogen bonds in the second coordination sphere are regulated rigorously. Complexes **2–4** would be common synthetic precursors for a variety of Ru(LH₃) complexes and useful in development of their metal–ligand cooperative reactivities.

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Table and Figure captions

Table 1. Crystal data for *cis*(P,N_{amine})-**2**·2MeOH, **3a**·2(toluene)·6MeOH·CH₂Cl₂, and **4**·3MeOH.

Table 2. Selected interatomic distances (Å) and angles (°) for **2–4**.

Fig. 1. Crystal structure of the cationic part of *cis*(P,N_{amine})-**2**·2MeOH. The CH hydrogen atoms as well as the counteranion are omitted for clarity. Asterisks and number signs denote atoms generated by a symmetry operation ($1 - x$, $1 - y$, $1 - z$). Thermal ellipsoids are drawn at the 30% level.

Fig. 2. Crystal structures of the cationic part of **3a**·2(toluene)·6MeOH·CH₂Cl₂. Hydrogen atoms except for those in the NH groups as well as the counteranions and solvating molecules are omitted for clarity. Asterisks and number signs denote atoms generated by a symmetry operation ($2 - x$, $1 - y$, $2 - z$). Thermal ellipsoids are drawn at the 30% level.

Fig. 3. Crystal structure of **4**·3MeOH. Hydrogen atoms except for those in the NH groups as well as the minor component of disordered chloride counteranion are omitted for clarity. Thermal ellipsoids are drawn at the 30% level.

Equations

Scheme 1. Synthesis of chlorido–phosphine complexes **2** bearing a pyrazole-based protic tripodal ligand LH₃.

Scheme 2. Regulation of chloride dissociation by hydrogen bonding interactions with proton-responsive ligands, LH₃ (left) and tris(6-hydroxypyrid-2-ylmethyl)amine (right).

Table 1

Crystal data for *cis*(P,N_{amine})-**2**·2MeOH, **3a**·2(toluene)·6MeOH·CH₂Cl₂, and **4**·3MeOH.

	<i>cis</i> (P,N _{amine})- 2	3a	4
Formula	C ₅₉ H ₆₈ ClF ₆ N ₇ O ₂ P ₂ Ru	C ₁₂₇ H ₁₆₀ Cl ₄ F ₁₂ N ₁₄ O ₆ P ₄ Ru ₂	C ₄₄ H ₆₃ Cl ₂ N ₇ O ₄ RuS
<i>M</i>	1219.69	2674.58	958.06
Cryst. system	monoclinic	triclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	13.662(4)	12.392(2)	12.6929(4)
<i>b</i> (Å)	28.363(9)	14.022(2)	20.2225(7)
<i>c</i> (Å)	15.348(5)	20.251(3)	18.6596(6)
α (°)	90	99.822(3)	90
β (°)	98.648(3)	91.013(3)	97.702(2)
γ (°)	90	103.440(2)	90
<i>V</i> (Å ³)	5880(3)	3366.2(10)	4746.4(3)
<i>T</i> (K)	93	93	93
<i>Z</i>	4	1	4
μ (Mo-K α) (mm ⁻¹)	0.433	0.424	0.534
<i>D</i> _c (g cm ⁻³)	1.378	1.319	1.341
Limiting indices	$-17 \leq h \leq 17$ $-36 \leq k \leq 36$ $-19 \leq l \leq 19$	$-16 \leq h \leq 16$ $-13 \leq k \leq 18$ $-26 \leq l \leq 20$	$-16 \leq h \leq 16$ $-26 \leq k \leq 26$ $-24 \leq l \leq 24$
No. of unique reflection	13393	14880	10845
<i>R</i> _{int}	0.0667	0.0408	0.0314
No. variables	771	843	604
<i>R</i> 1 [<i>I</i> > 2 σ (<i>I</i>)]	0.0690	0.0610	0.0402
w <i>R</i> 2 (all data)	0.1553	0.1836	0.1149
Goodness of fit	1.000	1.000	1.000

Table 2Selected interatomic distances (Å) and angles (°) for **2**–**4**

	<i>cis</i> (P,N _{amine})- 2	<i>trans</i> (P,N _{amine})- 2	3a	4
Ru(1)–X ^a	2.3288(10)	2.2863(7)	2.3113(10)	2.2076(5)
Ru(1)–Cl(1)	2.4351(10)	2.4312(7)	2.4349(13)	2.4265(5)
Ru(1)–N(2)	2.073(3)	2.072(2)	2.075(4)	2.0667(16)
Ru(1)–N(4)	2.084(3)	2.076(2)	2.061(4)	2.0695(16)
Ru(1)–N(6)	2.083(3)	2.051(3)	2.081(3)	2.0051(18)
Ru(1)–N(7)	2.151(3)	2.1683(18)	2.143(4)	2.1567(17)
N(2)–Ru(1)–Y ^b	100.25(8)	103.85(5)	98.03(12)	103.21(5)
N(4)–Ru(1)–Y ^b	101.68(8)	100.72(6)	103.00(11)	98.78(5)
N(6)–Ru(1)–Y ^b	85.17(8)	103.41(6)	87.47(11)	96.24(5)
N(7)–Ru(1)–Y ^b	164.27(7)	176.68(6)	166.51(9)	175.53(5)
Cl(1)–Ru(1)–X ^a	92.54(4)	88.48(3)	89.94(4)	90.522(19)
ref	This work	[11]	This work	This work

^a X = P(1) (except for **4**) or S(1) (**4**). ^b Y = Cl(1) (*cis*(P,N_{amine})-**2** and **3a**), P(1) (*trans*(P,N_{amine})-**2**) or S(1) (**4**)

fig 2

fig 3

scheme 1

scheme 2