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Synthesis and structural characterization of novel ruthenium(II) complexes featuring an *N*,*N*,*O*-scorpionate ligand: A versatile synthetic precursor for open-face scorpionatoruthenium(II) complexes

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ABSTRACT

The syntheses and characterization of novel ruthenium(II) complexes containing bis(3,5-dimethylpyrazol-1-yl)acetato (bdmpza), a new class of scorpionate ligands, are reported herein. [RuCl(bdmpza)(η^4-1,5-cyclooctadiene)] (**1**) was found to be a versatile precursor to synthesize a wide range of new ruthenium(II) complexes with the bdmpza ligand. The treatment of **1** with pyridine (py), diphenylphosphinoethane (dppe), 2,2′-bipyridyl (bpy), 1,10-phenanethroline (phen), or bispicolylamine (Hbpica) in refluxing *N*,*N*-dimethylformamide resulted in displacement of the 1,5-cyclooctadiene ligand to afford [RuCl(bdmpza)(py)$_2$] (**2**), [RuCl(bdmpza)(dppe)] (**3**), [RuCl(bdmpza)(bpy)] (**4**), [RuCl(bdmpza)(phen)] (**5**), and [Ru(bdmpza)(Hbpica)]Cl (**6**Cl) in good yields, respectively. The structures of **1**–**4**, and **6** were determined by X-ray structure analyses.

1. Introduction

The metal complexes bearing monoanionic terdentate *fac*-type ligands such as tris(pyrazol-1-yl)borato, HB(pz)$_3^-$ (Tp) [1], and cyclopentadienyl derivatives, η^5-$C_5R_5^-$ (Cp, R = H; Cp*, R = Me) [2] have been prominently studied in inorganic and organometallic chemistry because of their rich chemistry (Fig. 1). It has been widely recognized that the properties of the complexes bearing these ligands are considerably distinct in several cases [3]. In addition, a new class of this ligand type, the *N*,*N*,*O*-scorpionates, bis(pyrazol-1-yl)acetato (bpza) and bis(3,5-dimethylpyrazol-1-yl)acetato (bdmpza), has been introduced by Otero and his team in 1999 [4]. Recently Burzlaff and co-workers reported a simple and convenient synthetic method for Hbdmpza in 2001 [5].

The bpza and bdmpza ligands are isoelectronic to Tp, Cp, or Cp* but exhibit different binding properties and *trans* influences due to the carboxylate group, a less bulky and weaker σ-donor. It is of particular interest to survey the complexes of bpza and bdmpza for comparison. Thus, the chemistry of transition-metal complexes of bpza or bdmpza has been the subject of increasing attention [6,7]. Otero synthesized a series of titanium, zirconium, and niobium complexes to develop new "single site" group 4 and 5 catalyst precursors for polymerization catalysis [6b]. Burzlaff and coworkers reported their iron(II) and zinc(II) complexes to mimic the structural motif "facial 2-His-1-carboxylate triad" found in metalloenzymes [6k,6f–g]. However, ruthenium complexes featuring the *N*,*N*,*O*-scorpionate ligands are rather underdeveloped [7]. In order to extend the chemistry of mononuclear ruthenium complexes of the *N*,*N*,*O*-scorpionate ligands we describe the synthesis and characterization of the neutral complex of [RuCl(bdmpza)(η^4-cod)] (**1**) (cod = 1,5-cyclooctadiene); a versatile starting material which allows for a new synthetic route to a wide variety of ruthenium(II) complexes featuring the bdmpza ligand. A series of new ruthenium(II) complexes of the types [RuCl(bdmpza)(L1)$_2$], [RuCl(bdmpza)(L2)], and [Ru(bdmpza)(L3)]Cl (L1(monodentate) = pyridine (py), (**2**); L2 (bidentate) = 1,2-diphenylphosphinoethane (dppe), (**3**); L2 = 2,2′-bipyridyl (bpy), (**4**); L2 = 1,10-phenanethroline (phen), (**5**); L3 (terdentate) = bispicolylamine (Hbpica), (**6**) is also reported.

2. Experimental

2.1. General

The synthesis and manipulation of all metal complexes were performed under an inert atmosphere of argon using standard Schlenk techniques unless otherwise stated. Diethyl ether was

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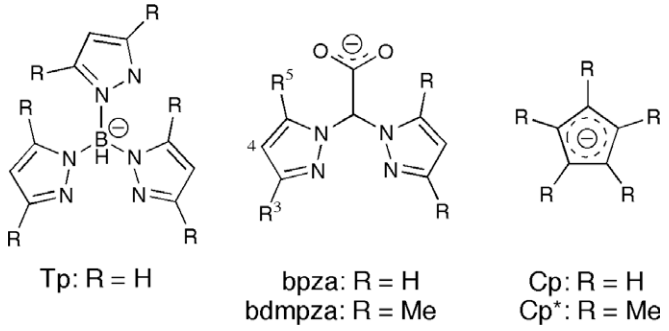


Fig. 1. Monoanionic terdentate facial-type ligands related to the chemistry described herein.

distilled from sodium-benzophenone ketyl prior to use. Methanol and ethanol were distilled over magnesium methoxide and magnesium ethoxide, respectively. *N*,*N*-dimethylformamide (DMF) was distilled over BaO. Pyridine, $CDCl_3$ and acetonitrile were dried over CaH_2 and distilled. All solvents used in this study were degassed by three freeze-pump-thaw cycles. Bis(3,5-dimethylpyrazol-1-yl)acetic acid (Hbdmpza) [5], bispicolylamine (Hbpica) [8], and $[RuCl_2(\eta^4\text{-cod})]_n$ [9] were prepared according to the literature. All other chemicals were used without further purification unless noted. ^1H and ^{31}P spectra were recorded on a JEOL JNM-Alpha 500 spectrometer. ^1H NMR chemical shifts are referenced to residual solvent resonance or using TMS as an internal standard. ^{31}P NMR chemical shifts are referenced to external trimethylphosphite. Infrared spectra (cm^{-1}) were recorded on a JASCO FT/IR 800 spectrometer using KBr disks. Elemental analyses were performed on a J-Science Co., Ltd. JM10 equipped with an auto-sampler at the Instrumental Research Center, University of the Ryukyus. The electrospray ionization mass spectra were obtained with Waters Quattro micro API by using ESI in positive-ion (PI) mode.

2.2. X-ray crystallography

Crystal data are summarized in Table 2. Each single crystal was mounted on a glass fiber. Diffraction data were collected on a Rigaku AFC7/CCD Mercury diffractometer. The data were integrated, scaled, sorted, and averaged using CRYSTALCLEAR software [10]. Absorption corrections were applied using Multi Scan method for **1**·(H_2O), **3**, and **6**Cl·$2H_2O$ or Coppens numerical method for **2**·(H_2O)(CH_3OH) and **4**. The structures were solved using SIR97 [11] for **1**·(H_2O), **3**, and **6**Cl·$2H_2O$, SIR92 [12] for **2**·(H_2O)(CH_3OH), or SHELX97 [13] for **4**·0.5 H_2O and refined with crystals [14] using CRYSTALSTRUCTURE 3.8 [15] as a graphical interface. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located on calculated positions and refined as riding models.

2.3. Synthesis

2.3.1. Synthesis of [RuCl(bdmpza)(η^4-cod)] (**1**)

A brown suspension of $[RuCl_2(\eta^4\text{-cod})]_n$ (100 mg, 0.36 mmol) and Hbdmpza (177 mg, 0.71 mmol) in absolute ethanol (10 mL) was refluxed for 21 h. Insoluble materials were filtered off and the solvent was removed in vacuo to produce orange crystalline solids. The solids were dissolved in MeOH and allowed to stand for 1 day at room temperature to afford **1**. Yield: 70 mg (20%). Anal. Calc. for $C_{20}H_{27}ClN_4O_2Ru$: C, 48.82; H, 5.53; N, 11.39. Found: C, 48.57; H, 5.24; N, 11.38%. ^1H NMR ($CDCl_3$, 500 MHz): δ = 6.50 (s, 1H, CH), 5.95 (s, 2H, H^4), 5.43 (m, 2H, olefinic H of cod), 4.43 (m, 2H, olefinic H of cod), 2.67 (m, 2H, aliphatic H of cod), 2.58 (m, 2H, aliphatic H of cod), 2.54 (s, 6H, Me^5), 2.43 (s, 6H, Me^3), 2.19 (m, 2H, aliphatic H of cod), 2.00 (m, 2H, aliphatic H of cod). ESI-MS (+) CH_3CN (*m*/*z*) 493 [**1** + H^+]$^+$.

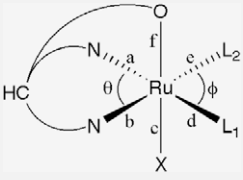
2.3.2. Synthesis of [RuCl(bdmpza)($py)_2$] (**2**)

A solution of **1** (100 mg, 0.203 mmol) and pyridine (py) (32 mg, 0.406 mmol) in DMF (10 mL) was refluxed for 8 h. The solvent was removed in vacuo. The obtained orange solids were dissolved in methanol and allowed to stand for 1 day at room temperature to afford **2**. Yield: 89 mg (81%). *Anal.* Calc. for $C_{22}H_{25}ClN_6O_2Ru$: C, 48.75; H, 4.65; N, 15.51. Found: C, 48.42; H, 4.86; N, 15.26%. ^1H NMR ($CDCl_3$, 500 MHz): δ = 9.06 (d, 4H, *J* = 5.13 Hz, H^2_{py}), 7.56 (t, 2H, *J* = 1.62 Hz, H^4_{py}), 7.14 (t, 4H, *J* = 5.13 Hz, H^3_{py}), 6.54 (s, 1H, CH), 5.95 (s, 2H, H^4), 2.56 (s, 6H, Me^5), 1.92 (s, 6H, Me^3). ESI-MS (+) CH_3CN (*m*/*z*) 543 [**2** + H^+]$^+$.

2.3.3. Synthesis of [RuCl(bdmpza)(dppe)] (**3**)

A solution of **1** (100 mg, 0.203 mmol) and diphenylphosphinoethane (dppe) (81 mg, 0.203 mmol) in DMF (10 mL) was refluxed for 8 h. The solvent was removed in vacuo. The remaining yellow solids were dissolved in MeOH and allowed to stand for 1 day at room temperature to afford **3** as yellow crystals. Yield: 130 mg (84%). *Anal.* Calc. for $C_{38}H_{39}ClN_4O_2P_2Ru$: C, 58.35; H, 5.03; N, 7.16%. Found: C, 58.39; H, 4.95; N, 7.33%. ^1H NMR ($CDCl_3$, 500 MHz): δ = 8.00 (s, 4H, Ph), 7.37–7.11 (m, 16H, Ph), 6.23 (s, 1H, CH), 5.76 (s, 2H, H^4), 2.77 (m, 2H, CH_2), 2.38 (m, 2H, CH_2), 2.33 (s, 6H, Me^5), 2.24 (s, 6H, Me^3). ^{13}P NMR ($CDCl_3$, 202.3 MHz): δ = 40.0. ESI-MS (+) CH_3CN (*m*/*z*) 783 [**3** + H^+]$^+$.

Table 1
Pertinent bond distances (Å) and angles (°) for **1**–**4**, and **6**.

		1	**2**	**3**	**4A** **4B**	**6**
	*a* (Å)	2.146(2)	2.070(4)	2.1509(17)	2.119(4) 2.110(4)	2.155(2)
	b (Å)	2.151(2)	2.078(3)	2.1655(17)	2.098(4) 2.102(5)	2.105(1)
	c (Å)	2.4095(7)	2.4082(8)	2.4131(5)	2.3975(15) 2.3962(12)	2.139(2)
	d (Å)		2.065(4)	2.2748(5)	2.027(4) 2.019(4)	2.031(2)
	e (Å)		2.101(3)	2.2869(5)	2.019(4) 2.035(4)	2.045(2)
	f (Å)	2.1178(18)	2.115(2)	2.1128(14)	2.090(3) 2.103(3)	2.0876(18)
	θ (°)	84.94(8)	87.98(14)	85.10(7)	83.99(16) 85.36(18)	86.04(8)
	φ (°)		91.42(14)	81.21(2)	79.12(18) 78.54(19)	89.82(8)

*2.3.4. Synthesis of [RuCl(bdmpza)(bpy)] (**4**)*

A solution of **1** (100 mg, 0.203 mmol) and 2,2′-bipyridyl (bpy) (32 mg, 0.203 mmol) in DMF (10 mL) was refluxed for 8 h. The solvent was removed in vacuo to give a purple solid. The product was recrystallized by layered solvent diffusion of diethyl ether into a concentrated solution of **4** in MeOH at room temperature. Yield: 91 mg (83%). Anal. Calc. for $C_{22}H_{25}ClN_6O_3Ru$ (as **4**·H_2O): C, 47.35; H, 4.52; N, 15.06. Found: C, 47.15; H, 4.57; N, 14.90%. ^{1}H NMR ($CDCl_3$, 500 MHz): d = 8.81 (br, 2H, H^3_{py})), 8.07 (d, 2H, J = 7.56 Hz, H^6_{py})), 7.63 (t, 2H, J = 8.10 Hz, H^5_{py})) 7.26 (m, 2H, H^4_{py})), 6.56 (s, 1H, CH), 6.14 (s, 2H, H^4), 2.69 (s, 6H, Me^5), 2.59 (s, 6H, Me^3). ESI-MS (+) CH_3CN (m/z) 541 [**4** + H^+]$^+$.

*2.3.5. Synthesis of [RuCl(bdmpza)(phen)] (**5**)*

A solution of **1** (100 mg, 0.203 mmol) and 1,10-phenanethroline (phen) (40 mg, 0.203 mmol) in DMF (10 mL) was refluxed for 20 h. Removal of the solvent in vacuo afforded deep purple solids which were dissolved in MeOH followed by Et_2O diffusion at room temperature to generate **5** as deep purple crystals. Yield: 103 mg (90%). *Anal.* Calc. for $C_{24}H_{27}ClN_6O_4Ru$ (as **5**·$2H_2O$): C, 48.04; H, 4.54; N, 14.01%. Found: C, 48.30; H, 4.43; N, 14.03%. ^{1}H NMR ($CDCl_3$, 500 MHz): d = 9.35 (d, 2H, J = 5.67 Hz, H^2_{phen}), 8.13 (d, 2H, J = 7.29 Hz, H^4_{phen}), 7.89 (s, 2H, H^6_{phen}), 7.59 (q, 2H, H^3_{phen}), 6.54 (s, 1H, CH), 6.21 (s, 2H, H^4), 2.81 (s, 6H, Me^5), 2.57 (s, 6H, Me^3). ESI-MS (+) CH_3CN (m/z) 565 [**5** + H^+]$^+$.

*2.3.6. Synthesis of [Ru(bdmpza)(Hbpica)]Cl (**6**Cl)*

A solution of **1** (100 mg, 0.203 mmol) and bispicolylamine (Hbpica) (40.4 mg, 0.203 mmol) in DMF (10 mL) was refluxed for 12 h. The solvent was removed in vacuo. The isolated solid was dissolved in MeOH and followed by diffusion of diethyl ether yielded brown crystals suitable for X-ray analysis. Yield: 61 mg (49%). *Anal.* Calc. for $C_{24}H_{32}ClN_7O_4Ru$ (as **6**Cl•$2H_2O$): C, 46.56; H, 5.21; N, 15.84. Found: C, 46.82; H, 5.28; N, 15.75%. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.96 (d, 2H, J = 2.97 Hz, H^2_{py}), 7.54 (m, 2H, H^4_{py}), 7.26–7.23 (m, 2H, H^5_{py}), 7.06–7.04 (m, 2H, H^3_{py}), 6.43 (s, 1H, CH), 5.92 (s, 2H, H^4), 5.25 (dd, 2H, J = 7.50 Hz, CH_2), 4.05 (d, 2H, J = 9.0 Hz, CH_2), 2.46 (s, 6H, Me^5), 1.93 (s, 6H, Me^3). ESI-MS (+) CH_3CN (m/z) 549 [**6** – Cl^-]$^+$.

3. Results and discussion

*3.1. Synthesis and structure of [RuCl(bdmpza)(η^4-cod)] (**1**)*

[RuCl(bdmpza)(η^4-cod)] (**1**) was successfully obtained by the reaction of Hbdmpza with $[RuCl_2(\eta^4\text{-cod})]_n$ in ethanol. Complex **1** is stable to air and moisture in both the solid state and in solution. A ν_{as} (COO^-) absorption was observed at 1671 cm^{-1} in the IR spectrum (KBr). The two pyrazolyl groups in **1** are equivalent showing only one set of signals in the ^{1}H NMR spectrum: δ = 5.95 (s, 2H, H^4), 2.54 (s, 6H, Me^5), and 2.43 (s, 6H, Me^3). The structure of **1** was unequivocally determined by X-ray crystallography as depicted in Fig. 2 along with the selected bond lengths and angles. A water molecule (not shown in Fig. 2) is bound by hydrogen-bonding to O1 with a distance of 2.798 Å. The Cl ligand is *trans* to the carboxylate group. The complex is approximately octahedral with respect to Ru. The cod ligand coordinates to Ru with the average Ru–C distance of 2.223(15) Å, no significant difference with that of [RuBrTp(η^4-cod)] (Ru–C, 2.213(2) Å) [16]. Note that two of methylene groups (C19 and C20) of the cod ligand were disordered and atoms with higher occupancies are shown in the figure. The average Ru–N distance is 2.149(3) Å while the Ru1–Cl1 and Ru1–O2 distances are 2.4095(7) Å and 2.1177(18) Å, respectively. The angles N2–Ru1–O2, N4–Ru1–O2, N(2)–Ru1–Cl1, and N4–Ru1–Cl1 are, 84.94(8)°, 86.36(8)°, 83.33(7)°, 86.59(6)°, and 85.61(6)°, respectively, which are slightly distorted from 90°. The Cl1–Ru1–O2 angle is 166.28(5)°.

Complex **1** is a versatile precursor to obtain a wide range of ruthenium(II) complexes of the bdmpza ligand as discussed vide infra.

Table 2
XRD experimental details.

	1·(H_2O)	**2**·(H_2O)(CH_3OH)	**3**	**4**·0.5 H_2O	**6**Cl·$2H_2O$
Formula	$C_{20}H_{29}ClN_4O_3Ru$	$C_{23}H_{31}ClN_6O_4Ru$	$C_{38}H_{39}ClN_4O_2P_2Ru$	$C_{22}H_{24}ClN_6O_{2.5}Ru$	$C_{24}H_{32}ClN_7O_4Ru$
Formula weight	509.99	592.06	782.19	548.99	619.08
T (K)	200(2)	193(2)	200(2)	200(2)	200(2)
Crystal system	monoclinic	triclinic	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a (Å)	13.445(2)	8.3315(8)	7.8530(3)	10.1339(16)	11.2600(17)
b (Å)	11.2466(14)	10.2038(9)	25.4696(10)	14.9377(18)	17.440(3)
c (Å)	15.666(2)	16.703(2)	17.7904(7)	16.296(3)	13.410(2)
α (°)	90	97.056(10)	90	71.536(9)	90
β (°)	113.626(4)	101.007(12)	93.8644(18)	87.762(13)	95.600(3)
γ (°)	90	112.831(9)	90	74.603(10)	90
V (Å^3)	2170.3(5)	1253.8(2)	3550.2(2)	2253.2(6)	2620.8(7)
Crystal size	0.30 × 0.30 × 0.17	0.35 × 0.15 × 0.05	0.38 × 0.20 × 0.20	0.30 × 0.10 × 0.03	0.25 × 0.10 × 0.05
Z	4	2	4	4	4
D_{calc} (g cm^{-3})	1.561	1.568	1.463	1.618	1.569
μ (cm^{-1})	8.740	7.736	6.470	8.495	7.450
Maximum and minimum transmission	0.8656 and 0.7795	0.962 and 0.821	0.8815 and 0.7911	0.975 and 0.831	0.805 and 0.963
Reflections collected	20 664	12 086	26 612	22 043	25 137
Independent reflections (R_{int})	4929 (0.032)	5368 (0.029)	7787 (0.0231)	9720 (0.056)	5896 (0.054)
Data/parameter	4929/380	5368/347	7787/440	9720/634	5896/462
Final R indicates [$I > 2\sigma(I)$]	R_1 = 0.0374, wR_2 (all data) = 0.0845[a]	R_1 = 0.0483, wR_2 (all data) = 0.1480[a]	R_1 = 0.0302,wR_2 (all data) = 0.0692[a]	R_1 = 0.0566wR_2 (all data) = 0.1111[a]	R_1 = 0.0330,wR_2 (all data) = 0.0741[a]
Goodness –of-fit (GOF) on F^2	1.000	1.002	1.000	1.005	1.013
Largest difference peak and hole (eA^{-3})	0.664 and −0.567	1.96 and −1.16	0.410 and −0.609	2.19 and −1.78	0.71 and −0.75

[a] $wR_2 = [\sum(w(F_0^2 - F_c^2)^2)/\sum w(F_0^2)^2]^{1/2}$.

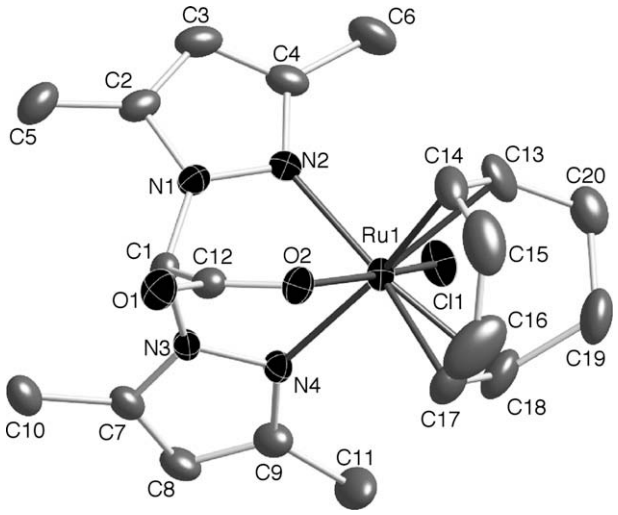


Fig. 2. Perspective view of [RuCl(bdmpza)(η^4-cod)] (**1**). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Ru1–O2, 2.1177(18); Ru1–N2, 2.146(2); Ru1–N4, 2.151(2); Ru1–C13, 2.229(3); Ru1–C14, 2.201(3); Ru1–C17, 2.218(3); Ru1–C18, 2.242(3); Ru1–Cl1, 2.4095(7); Cl1–Ru1–O1, 166.28(5); N2–Ru1–N4, 84.94(8).

*3.2. Reactivity of complex **1** towards N- or P-donor ligands: Synthesis and characterization of [RuCl(bdmpza)(L1)$_2$], [RuCl(bdmpza)(L2)], or [Ru(bdmpza)(L3)]Cl (L1 = py, **2**; L2 = dppe, **3**; bpy, **4**; phen, **5**; L3 = Hbpica, **6**)*

The cod ligand in **1** can be replaced with other ligands. Reactions of **1** with L1 (monodentate), L2 (bidentate), or L3 (terdentate) such as py, dppe, bpy, phen, or Hbpica in refluxing DMF produced **2**–**6** in good yield, respectively. Complexes **2**–**6** are also stable to air and moisture in both the solid state in solution. Kirchner et al. reported that the reactions of [RuClTp(η^4-cod)] with $Ph_2PCH_2PPh_2$ (dppm), $Ph_2PCH_2CH_2NMe_2$ (pn), $Me_2NCH_2CH_2NMe_2$ (tmeda), py, or 3-methylpyridine (3-Mepy) in refluxing DMF generated two types of [RuClTp(L1)$_2$] or [RuClTp(L2)] complexes [16]. As described by Kirchner, the replacement of the cod ligand in **1** is also substitutionally rather inert due to the presence of the bdmpza ligand, contrasting sharply to the case of the Cp-type ligands [17] (see Scheme 1).

The molecular structures of **2**–**4**, and **6** were determined by X-ray crystallography. (The pertinent bond distances and angles are summarized in Table 1, and the crystallographic information is in Table 2.) Structural data were further provided by NMR and IR spectroscopy, elemental analysis, and electrospray ionization (ESI) mass spectrometry.

Treatment of **1** with two equivalents of pyridine in refluxing DMF produced **2**. Fig. 3 shows the structure of **2** in which the geometry around the Ru is octahedral and two pyridine ligands are positioned *trans* to the pyrazolyl groups. A ν_{as} (COO^-) absorption was observed at 1640 cm^{-1} in the IR spectrum (KBr). The two pyridine ligands in **2** are equivalent showing only one set of signals in the ^1H NMR spectrum: δ = 9.06 (d, 4H, H^2_{py}), 7.56 (t, 4H, H^4_{py}), and 7.14 (t, 4H, H^3_{py}). The distances of Ru–$N^{pyridine}$ in **2** (Ru1–N5 is 2.101(13) Å and Ru1–N6 is 2.065(4) Å) are significantly longer than those in **4** and **6** (see Table 1), indicating two pyridines coordinate to Ru more weakly.

The reaction of **1** with one equivalent of dppe gave **3** in 84% yield. The structure of **3** is shown in Fig. 4. The geometry around Ru is approximately octahedral and the Cl ligand positioned *trans* to the carboxylato group. A ν_{as} (COO^-) absorption was observed at 1657 cm^{-1} in the IR spectrum (KBr).

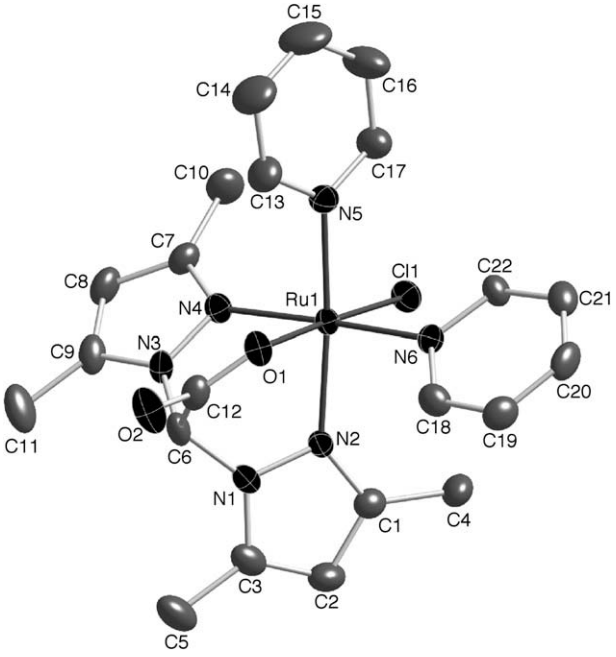
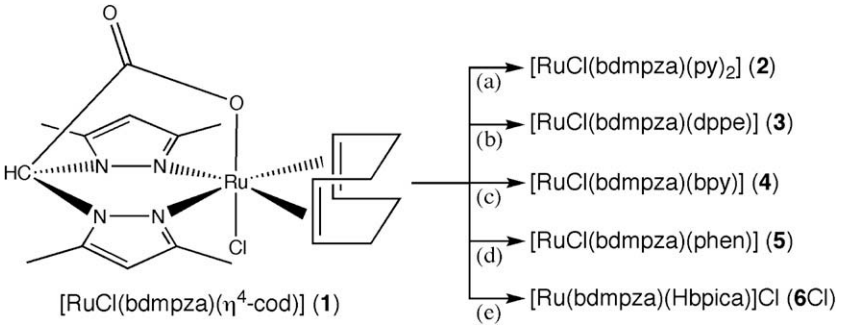


Fig. 3. Perspective view of [RuCl(bdmpza)(py)$_2$] (**2**). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Ru1–O1, 2.115(2); Ru1–N2, 2.078(3); Ru1–N4, 2.070(4); Ru1–N5, 2.101(3); Ru1–N6, 2.065(4); Ru1–Cl1, 2.4082(8). Cl1–Ru1–O1, 177.61(5); N2–Ru1–N4, 87.98(14); N5–Ru1–N6, 91.42(14).



Scheme 1. Summary of the reactions to prepare complexes **2**–**6**. Reagents and conditions: (a) 2 equiv of pyridine, DMF, reflux for 8 h, yield 81%; (b) 1 equiv of diphenylphosphinoethane (dppe), DMF, reflux for 8 h, yield 84%; (c) 1 equiv. of 2,2'-bipyridyl (bpy), DMF, reflux for 8 h, yield 83%; (d) 1 equiv. of 1,10-phenanethroline (phen), DMF, reflux for 20 h, yield 90%; (e) 1 equiv. of bispicolylamine (Hbpica), DMF, reflux for 12 h, yield 49%.

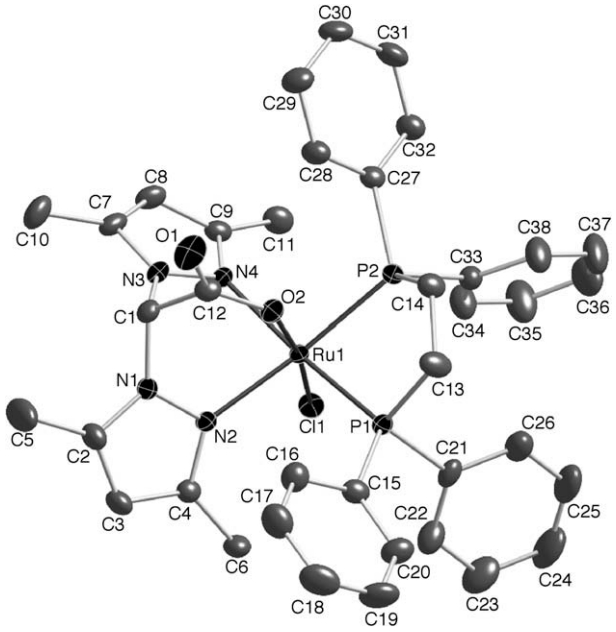


Fig. 4. Perspective view of [RuCl(bdmpza)(dppe)] (**3**). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles(°): Ru1–O2, 2.1128(14); Ru1–2, 2.1655(17); Ru1–N4, 2.1509(17); Ru1–P1, 2.2748(5); Ru1–P2, 2.2869(5); Ru1–Cl1, 2.4131(5), Cl1–Ru1–O2, 171.60(4); N2–Ru1–N4, 85.10(7); P1–Ru1–P2, 81.21(2).

The Ru1–Cl1 and Ru1–O2 distances are 2.4131(5) Å and 2.1128(14) Å, respectively. The Ru–P distances in **3** are 2.2748(5) Å and 2.2869(5) Å. The Ru–N distances are 2.166(2) Å and 2.151(2) Å, longer than those of **1**, due to the *trans* influence of dppe. In [RuCl(bdmpza)(PPh_3)$_2$] (Fig. 5), the two PPh_3 ligands reside *trans* to the pyrazolyl group with the Ru–P distances of 2.3555(17) Å and 2.3688(18) Å and with the Ru–N distances of 2.199(4) Å and 2.173(4) Å. Thus, the Ru–P and Ru–N distances in **3** are appreciably shorter than those of [RuCl(bdmpza)(PPh_3)$_2$] [7a]. It is noteworthy to point out that, as mentioned above, **3** is stable to air and moisture in both the solid state and in solution, while [RuCl(bdmpza)(PPh_3)$_2$] is rather sensitive due to the steric hindrance of the two PPh_3 groups residing *trans* to the dimethylpyrazolyl groups [7a]. In the analogous complex [RuCl(bpza)(PPh_3)$_2$], (Fig. 5) in which bpza is less sterically hindered, one PPh_3 resides *trans* to the carboxylato group, the Ru–P (*trans* to the carboxylato group) and Ru–N (*trans* to Cl) distances are 2.360(3) Å and 2.100(6) Å, respectively. The remaining Ru–P and Ru–N distances are 2.378(4) Å and 2.157(6) Å, respectively.

The complex **1** reacted with one equivalent of bpy in refluxing DMF to afford **4** in 83% yield. The asymmetric unit contains two crystallographic independent molecules (**4A** and **4B**). As they are not significantly different in terms of bond distances and angles, one of them, **4A** is depicted in Fig. 6. The bpy ligand binds to Ru in a bidentate fashion and resides *trans* to the two pyrazolyl groups. The bite angles of the bpy ligand in **4A** and **4B** are 79.12(18) Å and 78.54(19) Å, respectively. The overall geometry about the Ru center can be described as a slightly distorted octahedral in both **4A** and **4B**. As expected, distances of Ru–$N^{pyridyl}$ (2.019(4) Å, 2.027(4) Å in **4A** and 2.035(4) Å, 2.019(4) Å in **4B**) in **4** are significantly shorter than those in **2** and **6**. This may be caused by synergistic bonding between Ru(II) t_{2g} orbitals and the π^* orbitals in the planar bpy ligand. The crystallographic results are consistent with the ^{1}H NMR data: the two pyrazolyl groups in **4** are equivalent showing only one set of signals at δ = 6.14, 2.69 and 2.59. In addition, the signals at δ = 8.81, 8.12, 7.63, and 7.26 are assigned to the bpy ligand. A ν_{as} (COO^-) absorption was observed at 1655 cm^{-1} in the IR spectrum (KBr).

The complex **5** was obtained in 82% yield by the reaction of **1** and phen, thoroughly characterized by NMR, IR spectroscopy, elemental analysis, and ESI-mass spectrometry. The two pyrazolyl groups in **5** are also equivalent because only one set of signals at δ = 6.21, 2.81, and 2.57 was observed in the ^{1}H NMR spectrum. In addition, the signals at δ = 9.35, 8.13, 7.89, and 7.59 are attributed to the phen ligand indicating that the phen ligand coordinates to the Ru center in a bidentate fashion similar to the bpy in **4**. A ν_{as} (COO^-) absorption was observed at 1660 cm^{-1} in the IR spectrum (KBr). It is concluded that the structure of **5** is essentially identical with that of **4**.

Shown in Fig. 7 is the structure of **6**, which has a distorted octahedral geometry around the Ru center with bdmpza and Hbpica acting as a terdentate ligand in a facial arrangement. A ν_{as} (COO^-) absorption was observed at 1620 cm^{-1} in the IR spectrum (KBr). The number of reports on Ru(II) complexes bearing Hbpica is surprisingly limited, to the best of our knowledge, there are only two previous reports [18]. The Ru–N^{amino} distance (2.139(2) Å) is longer than the distances of Ru–$N^{pyridine}$ (2.045(2) and 2.031(2) Å) which are relatively shorter than those in **2** with the pyridine ligand (Ru1–N5 is 2.101(13) Å and Ru1–N6 is 2.065(4) Å). The ^{1}H NMR spectrum of **6**Cl indicated that the pyridyl groups are equivalent. One of the diastereotopic methylene protons appeared as a doublet of doublets centered at δ = 5.25 (two protons) due to a coupling with an NH proton and a doublet at δ = 4.05 (two protons). A broad singlet at δ = 8.13 was assigned to the NH proton because this signal was not observed after the treatment of the solution of **6**Cl in $CDCl_3$ in a NMR tube with one drop of D_2O. A ν(NH) and absorption was observed at 2900 cm^{-1} in the IR spectrum.

4. Conclusion

A novel ruthenium(II) complex [RuCl(bdmpza)(η^4-1,5-cyclooctadiene)] (**1**) with a *N*,*N*,*O*-scorpionate ligand was synthesized and fully characterized. Complex **1** is a promising precursor for the formation of a number of new ruthenium(II) complexes with the bdmpza ligand.

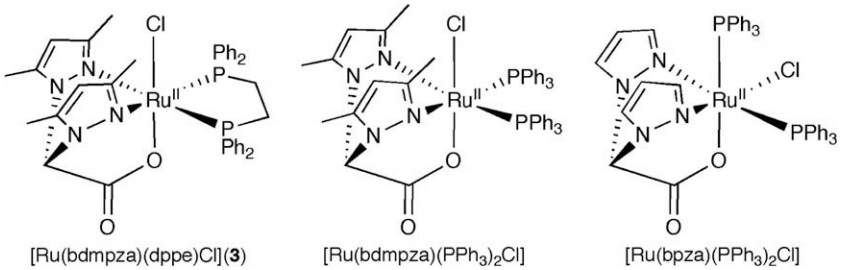


Fig. 5. Molecular structures of **3** (this work), [RuCl(bdmpza)(PPh_3)$_2$], and [RuCl(bpza)Cl(PPh_3)$_2$].

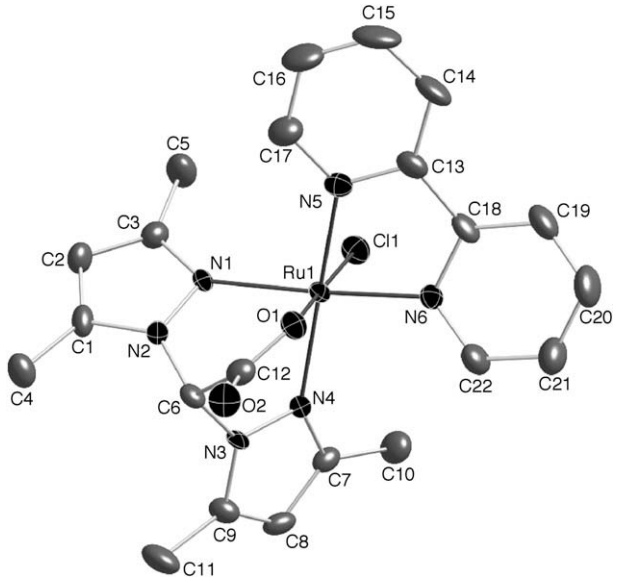


Fig. 6. Perspective view of one of the crystallographically independent molecules, [RuCl(bdmpza)(bpy)] (**4A**). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°) for **4A**: Ru1–O1, 2.090(3); Ru1–N1, 2.098(4); Ru1–N4, 2.119(4); Ru1–N5, 2.019(4), Ru1–N6, 2.027(4); Ru1–Cl1, 2.3975(15); Cl1–Ru1–O1, 176.53(10), N1–Ru1–N4, 83.99(16); N5–Ru1–N6, 79.12(18). For **4B**: Ru2–O3, 2.103(3); Ru2–N8, 2.110(4); Ru2–N10, 2.102(5); Ru2–N11, 2.035(4); Ru2–N12, 2.109(4); Ru2–Cl2, 2.3962(12); Cl2–Ru–O3, 177.70(11); N8–Ru2–N10, 85.36(18); N11–Ru2–N12, 78.54(19).

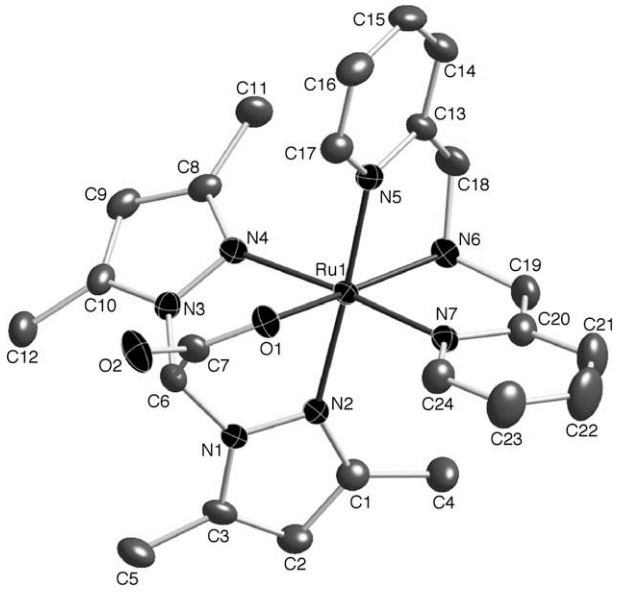


Fig. 7. Perspective view of $[Ru(bdmpza)(Hbpica)]^+$ (**6**). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Ru1–O1, 2.0876(18); Ru1–N2, 2.105(2); Ru1–N4, 2.155(2); Ru1–N5, 2.045(2); Ru1–N7, 2.031(2); Ru1–N6, 2.139(2); N6–Ru1–O1, 167.34(8); N2–Ru1–N4, 89.82(8); N5–Ru1–N6, 86.04(8).

5. Supplementary Data

Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition numbers CCDC-749388 for **1**·(H_2O), 749385 for **2**·(H_2O)(CH_3OH), 749387 for **3**, 749386 for **4**·0.5H_2O, and 749384 for **6**Cl·2H_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; email: deposit@ccdc.cam.ac.uk).

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