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An unexpected semi-hydrogenation of a ligand in the complexation of 2,7-bispyridinyl-1,8-naphthyridine with $Ru_3(CO)_{12}$†

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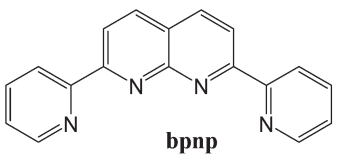
Thermal reaction of 2,7-bis(2-pyridinyl)-1,8-naphthyridine (**bpnp**) with $Ru_3(CO)_{12}$ in the presence of moisture resulted in the formation of a formate-bridged diruthenium complex [(**bpnp**-H_3)Ru_2(μ-HCOO)-$(CO)_4$] (**1**), in which the ligand was partially hydrogenated. Complex **1** was fully characterized by spectroscopic analyses and X-ray single crystal determination. Regarding the partially reduced ligand in **1**, it occurs through a water–gas shift type reduction. The bridging formate ligand can be substituted by other carboxylate ligands. Physical and chemical properties of the newly prepared complexes were investigated.

Introduction

Since the discovery of diruthenium tetracarbonyl complexes by Lewis and co-workers in 1969,[1] the diruthenium(I,I) derivatives containing a "$Ru_2(CO)_4$" backbone have appeared as an attractive class of dinuclear compounds in the study of coordination chemistry,[2a,3] catalysis,[2b–d,4] and biological activity.[2e,5] These studies clearly illustrate the importance of the bridging ligands, particularly the carboxylates, in stabilization of these complexes and in governing the catalytic activities.[2–5] However, the coordination chemistry of "$Ru_2(CO)_4$" toward 2,7-bis(2-pyridyl)-1,8-naphthyridine (**bpnp**), which is known to be a good tetradentate ligand in the stabilization of metal–metal bonding in the complexes, has not been disclosed. Since **bpnp** is a crescent shaped tetra-donor, coordination of four nitrogen donors toward a dinuclear species would in principle have both axial positions capped, which is expected to affect the properties of the resulting metal complex. We describe here the thermal reaction of **bpnp** with $Ru_3(CO)_{12}$ in the presence of moisture to yield a formate-bridged diruthenium(I,I) complex containing a partial reduction of the naphthyridine ligand.



bpnp

Results and discussion

Heating a mixture of $Ru_3(CO)_{12}$ and **bpnp** in chlorobenzene in the presence of moisture at 140 °C for 4 h gave [(**bpnp**-H_3)-Ru_2(μ-HCOO)$(CO)_4$] (**1**) in 90% yield based on the ligand. Carrying out the reaction under extreme dry conditions resulted in the formation of a mixture of complicated products, but not complex **1**, indicating that water plays an important role in the formation of this complex. Complex **1** was characterized by spectroscopic techniques and crystallographic analysis. The characteristic IR stretching at 1579 cm^{-1} is attributed to the bridging formate group. Bands appearing at 2057, 2012, 1958 and 1925 cm^{-1} are assigned to the terminal CO stretching vibrations. The most significant ^1H NMR signals for the complex are the protons corresponding to the naphthyridine framework. Due to the partial hydrogenation of the ligand, five sets of ^1H NMR signals of **1** (δ 5.13, 3.01, 2.76, 2.68 and 1.75) appear in the region of $C_{(sp3)}$–H, which is correlated to three signals (δ 69.2, 28.3 and 28.2) of ^{13}C NMR shifts. In addition, the ^{13}C NMR shift at δ 174.3 is assigned to be the carbon of the bridging formate. The detailed structure of **1** was confirmed by X-ray diffraction analysis of its single crystal.

The solid-state structure of **1** crystallized from dichloromethane and diethyl ether was determined by single crystal

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†CCDC 942976 for **1**. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt53029a

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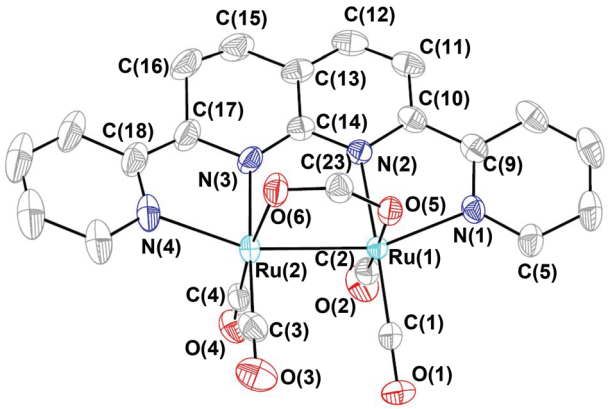
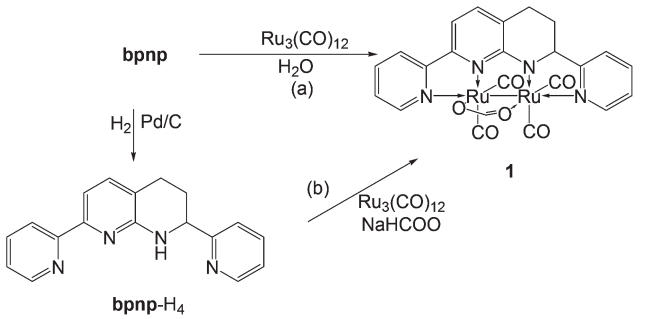


Fig. 1 ORTEP plot of **1** at the 30% probability level. Labels of some aromatic carbons are omitted for clarity.

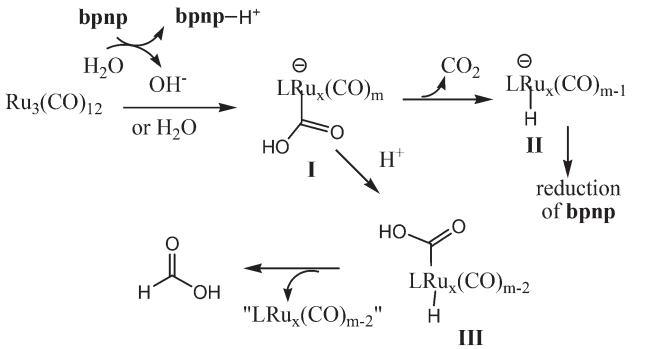
Table 1 Selected bond distances (Å) and angles (°) of **1**

Ru(1)–N(1)	2.159(2)	Ru(2)–N(3)	2.104(2)
Ru(1)–N(2)	2.118(2)	Ru(2)–N(4)	2.176(2)
Ru(1)–C(1)	1.856(3)	Ru(2)–C(3)	1.858(3)
Ru(1)–C(2)	1.838(3)	Ru(2)–C(4)	1.827(3)
Ru(1)–O(5)	2.148(2)	Ru(2)–O(6)	2.168(2)
Ru(1)–Ru(2)	2.6616(3)	N(3)–C(17)	1.476(4)
C(10)–C(11)	1.370(4)	C(11)–C(12)	1.391(5)
C(12)–C(13)	1.359(5)	C(13)–C(14)	1.452(4)
C(13)–C(15)	1.483(4)	C(16)–C(17)	1.514(5)
N(2)–C(10)	1.374(3)	N(3)–C(14)	1.325(4)
N(2)–C(14)	1.364(3)		
N(2)–Ru(1)–C(1)	177.5(1)	O(5)–Ru(1)–C(2)	176.7(1)
N(1)–Ru(1)–Ru(2)	157.36(6)	N(1)–Ru(1)–N(2)	77.49(9)
N(3)–Ru(2)–C(3)	171.79(11)	O(6)–Ru(2)–C(4)	174.1(1)
N(4)–Ru(2)–Ru(1)	160.21(7)	N(3)–Ru(2)–N(4)	77.1(1)
C(1)–Ru(1)–C(2)	88.23(13)	C(3)–Ru(2)–C(4)	91.5(1)

analysis. An ORTEP diagram of the molecular structure of **1** is shown in Fig. 1 and relevant bond distances and angles are collected in Table 1. The structure of this newly prepared diruthenium(I,I) displays a dinuclear core of "$Ru_2(CO)_4$", similar to that in previously reported compounds.[6] Two ruthenium centers are *cis*-bridged by the **bpnp**-H_4 ligand and a formate. Two axial sites of the diruthenium core are capped by the pyridinyl nitrogen atoms of **bpnp**-H_4. Each ruthenium center in **1** is in an octahedral coordination geometry with two carbonyl groups occupying it in a *cis* fashion. A slightly distorted eclipsed conformation is adopted about the Ru(1)–Ru(2) bond as evidenced by the torsional angle: N(2)–Ru(1)–Ru(2)–N(3) 10.54(9)° and C(2)–Ru(1)–Ru(2)–C(4) 17.96(13)°. The Ru–C distances *trans* to nitrogen donors are slightly longer (1.856(3)–1.858(3) Å) than those *trans* to oxygen donors (formate) (1.827(3)–1.838(3) Å) due to the *trans* influence. Analysis of bond distances along the naphthyridine rings (Table 1) tells one of naphthyridine rings remaining as an aromatic system, but not the other, consistent with the spectroscopic data. Both bite angles of the bipyridinyl fragment toward the metal centers [N(1)–Ru(1)–N(2) 77.49(9)° and N(3)–Ru(2)–N(4) 77.1(1)°] deviate from 90°, which are quite similar to those of



Scheme 1 Formation of diruthenium complex **1**.



Scheme 2 Pathway for the formation of the metal-hydride and the formate ligand.

bipyridine metal complexes. No significant discrepancies in the other bond lengths and angles are noticed in complex **1**. It was noticed that the Ru–Ru distance (2.6616(3) Å) is relatively shorter than that of complexes with "$Ru_2(CO)_4$",[4] indicating that geometrically constraining this tetradentate ligand shortens the metal–metal bond.

Notably, complex **1** could be prepared from the hydrogenated ligand directly (Scheme 1). Thus, with Pd/C as a catalyst, hydrogenation of **bpnp** gave the partially reduced compound **bpnp**-H_4 in 83% yield, which when treated with $Ru_3(CO)_{12}$ in the presence of formic acid provided **1** in practically quantitative yield. Apparently, the formation of **1** from **bpnp** requires the addition of H_2. The addition of hydrogen to **bpnp** resulting in the formation of complex **1** is believed to occur *via* ruthenium-catalyzed transfer hydrogenation. This was proved by a separate experiment. Treatment of **bpnp** with isopropanol and Cs_2CO_3 in the presence of [$RuCl_2(THF)(CO)_3$] (5 mol%) as the catalyst under refluxing conditions readily yielded **bpnp**-H_4 in 75% yield.

As illustrated in the crystal structure, a formate ligand acts as a bridging ligand in complex **1**. Quite likely, the formate is formed by the deprotonation of formic acid, which is generated from CO and H_2O under the reaction conditions. Nakahara and co-workers disclosed that formic acid is an intermediate in the water–gas-shift process as evidenced by the NMR study.[8] A mechanistic rationalization is illustrated in Scheme 2. The initial step involves the nucleophilic attack of

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water or hydroxide to the coordinated carbonyl ligand. It is known that the carbonyl carbon center of "$Ru(CO)_n$" is susceptible to nucleophilic attack,[4a,7] which leads to the formation of the hydroxycarbonyl species **I**. Elimination of the hydroxycarbonyl ligand generates the metal-hydride species **II** accompanied by the formation of carbon dioxide. Indeed, the generation of CO_2 from the reaction was identified. This process is in agreement with the typical pathway for a WGS reaction catalyzed by transition-metal complexes.[9] The ligand **bpnp** was partially reduced by the metal-hydride followed by the protonation. Replacement of water with D_2O gave the deuterated product **1**, clearly confirming the hydrogen atoms from H_2O molecules. Protonation of the ruthenium hydroxycarbonyl may give the intermediate **III**. Subsequently, the reductive elimination of hydride and hydroxycarbonyl ligands results in the formation of formic acid, acting as a bridging ligand for the di-ruthenium core (Scheme 2).

The oxidation and reduction potentials of **1** were determined by cyclic voltammetry in acetonitrile (Fig. 2). The cyclic voltammogram of complex **1** exhibits two $1e^-$ irreversible ligand-based oxidations at −0.7, 0.65 and 1.25 V, whereas the free **bpnp**-H_4 shows irreversible oxidation potentials at −0.86 and −1.6 V. This irreversible behaviour is different from the related "$Ru_2(CO)_4$" species coordinated by other 1,8-naphthyridine-based ligands.[6]

The electronic spectra of complexes and **bpnp**-H_4 were recorded in acetonitrile in the range of 200–700 nm. The λ_{max} values of all compounds are given in Table 2. Three major transitions that appeared for complex **1** in acetonitrile are at 290, 372 and 455 nm with the extinction coefficients of 2240, 4680 and 19 950, respectively. The intra-ligand transition ($\pi\rightarrow\pi^*$) is observed at 372 nm, which is red-shifted (*ca.* 30 nm) compared with the free ligand **bpnp**-H_4. The broad absorption

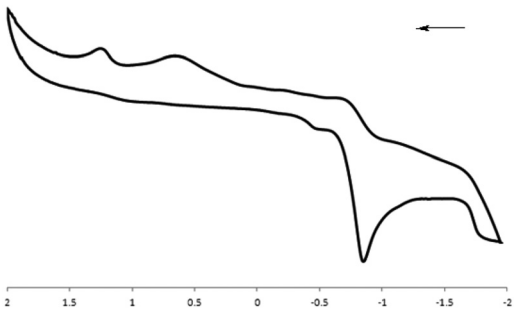


Fig. 2 Cyclic voltammogram for **1** with 0.1 M $[Bu_4N][PF_6]$ as the supporting electrolyte at a scanning rate of 100 mV s^{-1}.

Table 2 UV-vis data for complexes **1–2** and **bpnp**-H_4

Compound	λ_{max}/nm (log ε)[a]
bpnp-H_4	339 (3.86), 250 (4.16), 218 (4.16)
1	455 (3.35), 372 (3.67), 290 (4.3)
2a	455 (3.36), 368 (3.75), 286 (4.35)
2b	455 (3.75), 372 (3.67), 287 (4.37), 231 (4.61)

[a] In CH_3CN, at 25 °C.

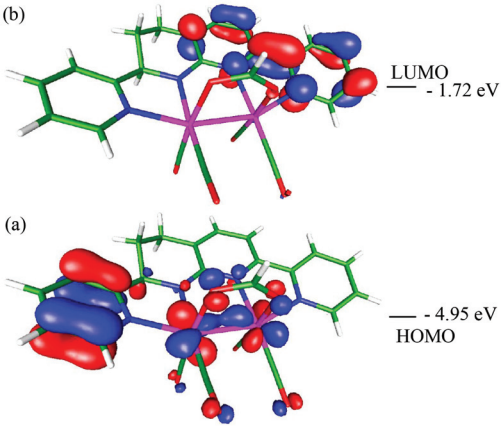
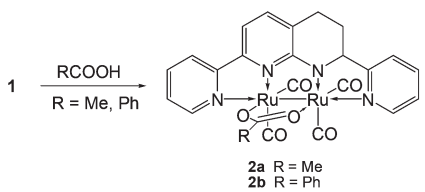


Fig. 3 HOMO (a) and LUMO (b) calculated for complex **1**.

in the visible region at 455 nm is assigned as a metal–ligand to ligand charge transfer band.

We have carried out a DFT calculation based on the X-ray crystal structure. This shows that the HOMO (highest occupied molecular orbital) is located mostly along the Ru–Ru vector and one of the pyridinyl rings within the complex (Fig. 3a). On the other hand, the LUMO (lowest unoccupied molecular orbital) is located in the unsaturated part of naphthyridine and the other pyridinyl ring (Fig. 3b). The calculated absorption for the HOMO–LUMO transition is at 464.5 nm, which is in agreement with the experimental data.

In order to understand the coordination chemistry of the diruthenium complex, ligand substitutions of **1** toward various donors were investigated. Treatment of **1** with an equimolar amount of triphenylphosphine gave a mixture of various substituted products as evidenced by a complicated ^{31}P NMR spectrum, indicating that the substitution is not regio-selective. However, reaction of **1** with excess of triphenylphosphine readily caused decomposition of **1** to give the free ligand **bpnp**-H_4. The bidentate dppe (dipehenylphosphinoethane) also did the similar reaction. These observations indicate that the chelation stabilization of **bpnp**-H_4 toward "$Ru_2(CO)_4$" is not comparable to that of the phosphine ligands. On the other hand, the bridging formate was replaced by other carboxylates (eqn (1)). Complex **1** was treated with excess acetic acid in acetone at 50 °C to give the acetate bridged complex **2a**, whereas benzoic acid provided the substituted product **2b** accordingly. Both complexes **2a** and **2b** were characterized by NMR, UV-Vis and elemental analysis. ^1H-NMR shifts of the tetradentate in both **2a** and **2b** are quite similar to those in **1**, whereas the absorption spectra for **2a** and **2b** are also similar to that of **1** (Table 2).



2a R = Me
2b R = Ph

(1)

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To highlight the application of the formation of a formate, we set out to catalytically prepare formic acid from CO and H_2O. Quite disappointingly, complex **1** did not show any catalytic activity towards this preparation. However, with the use of an *in situ* generated catalytic system from **bpnp** and $Ru_3(CO)_{12}$, reactions of water under pressurized CO (100 psi) gave formic acid in a turnover number of 98 (mol of product per mol of catalyst), indicating that some intermediates from the complexation of **bpnp** with $Ru_3(CO)_{12}$ might play the role of catalysts.

Conclusions

In summary, we have reported the synthesis and the characterization of the carboxylate-bridged diruthenium complex [(**bpnp-H$_3$**)Ru_2(μ-HCOO)$(CO)_4$] that resulted from the complexation of $Ru_3(CO)_{12}$ with **bpnp**. The structure of **1** was confirmed by X-ray single crystal analyses. Interestingly, the ligand was partially hydrogenated during the complexation. This study provides an insight into the ligand effect on "$Ru_2(CO)_4$" complexes, particularly for the species with both axial positions capped. Studies on the catalytic reactivity of these complexes are currently under investigation.

Experimental

General information

All reactions and manipulation steps were performed under a dry nitrogen atmosphere. Tetrahydrofuran was distilled under nitrogen from sodium benzophenone ketyl. Dichloromethane and chlorobenzene were dried over CaH_2 and distilled under nitrogen. Other chemicals and solvents were of analytical grade and were used after degassing (degassed process). Nuclear magnetic resonance spectra were recorded in $CDCl_3$ on a Bruker AVANCE 400 spectrometer. Chemical shifts are given in parts per million relative to Me_4Si for ^1H and ^{13}C NMR. Infrared spectra were measured on a Varian 640-IR spectrometer. The ligand **bpnp** was prepared according to a reported procedure.[10]

Preparation of complex 1

Method a. To a mixture of **bpnp** (28.4 mg, 0.1 mmol) and $Ru_3(CO)_{12}$ (57.5 mg, 0.09 mmol) was added chlorobenzene (1.0 mL) and H_2O (0.1 mL) under nitrogen. The mixture was heated at 140 °C with stirring for 4 h. During the reaction, the gas generated was bubbled into a solution of $CaCl_2$ and a white solid of $CaCO_3$ was formed. The reaction solution was then cooled to room temperature, filtered through Celite, and washed with EtOAc and acetone. The solution was recovered and concentrated and the residue was recrystallized from dichloromethane and toluene to give **1** as orange solids (58.1 mg, 0.09 mmol, 90%). ^1H NMR (400 MHz, d_6-acetone): δ 8.99 (d, J = 5.2 Hz, 1 H), 8.95 (d, J = 4.4 Hz, 1 H), 8.17 (d, J = 8.4 Hz, 1 H), 8–8.05 (m, 2 H), 7.8 (s, 1 H, *H*-COO), 7.73 (d, J = 8 Hz, 1 H), 7.57 (t, J = 6.4 Hz, 1 H), 7.5 (t, J = 6.4 Hz, 1 H), 7.05 (d, J = 6.4 Hz, 1 H), 6.99 (d, J = 6.4 Hz, 1 H), 5.13 (m, 1 H), 3.01 (m, 1 H), 2.76 (m, 1 H), 2.68 (m, 1 H), 1.75 (m, 1 H); ^{13}C NMR (200 MHz): δ 207.6, 206.6, 205.3, 202.1, 174.3, 166.8, 165.7, 158, 153.6, 152.3, 152.2, 138.8, 138.7, 133.3, 125.9, 124.5, 124.2, 122.5, 106.8, 69.2, 28.3, 28.2. ESI-MS (TOF): m/z calcd for $[M - HCOO]^+$ = 602.92, found 603.10. Anal. calcd for $C_{23}H_{16}N_4O_6Ru_2$: C, 42.73; H, 2.49; N, 8.67. Found: C, 42.43; H, 2.38; N, 8.43.

Chlorobenzene containing 1% water as the solvent gave **1** in 90% yield. A solution of chlorobenzene saturated with water also provided a similar result.

Method b. A mixture of **bpnp**-H_4 (57 mg, 0.2 mmol), $Ru_3(CO)_{12}$ (130 mg, 0.18 mmol) and formic acid (0.08 ml, 1.7 mmol) in benzene (1.0 mL) was placed in a reaction tube. The resulting mixture was stirred at 100 °C for 12 h. The reaction mixture was then cooled to room temperature, and filtered through Celite with the eluent of EtOAc–acetone. The filtrate was concentrated and the residue was re-precipitated from CH_2Cl_2–toluene to give pure **1** as orange solids (0.18 mmol, 91%).

Preparation of bpnp-H_4

Method a. A solution of **bpnp** (0.12 g, 0.42 mmol) and Pd/C (20 mg) in ethanol (10 mL) was placed in an autoclave. Hydrogen gas (100 psi) was pressurized. The mixture was heated at 100 °C for 24 h. The mixture was filtered through Celite, and washed with acetone and methanol. The filtrate was concentrated to give the pure compound as yellow solids (0.11 g, 0.35 mmol, 83%). ^1H (400 MHz, d_6-acetone): δ 8.57–8.60 (m, 2 H), 8.37 (d, J = 8 Hz, 1 H), 7.67–7.84 (m, 3 H), 7.54 (d, J = 7.6 Hz, 1 H), 7.46 (d, J = 8 Hz, 1 H), 7.24–7.41 (m, 2 H), 6.45 (s, 1 H), 4.77–4.8 (m, 1 H), 2.77–2.84 (m, 1 H), 2.56–2.63 (m, 1 H), 2.14–2.28 (m, 1 H), 2.08–2.12 (m, 1 H). ^{13}C (100 MHz, $CDCl_3$): δ 162.3, 156.6, 155.2, 152.6, 149.2, 148.9, 136.9, 136.7, 136.6, 122.9, 122.2, 120.6, 120.4, 116.5, 110.8, 56.7, 27.8, 24.6. Anal. calcd for $C_{18}H_{16}N_4$: C, 74.98; H, 5.59; N, 19.43. Found: C, 74.47; H, 5.39; N, 19.18.

Method b. In a sealed tube was placed a mixture of **bpnp** (20 mg, 0.07 mmol), $RuCl_2(THF)(CO)_3$ (3 mg) and Cs_2CO_3 (10 mg, 0.03 mmol) in isopropanol (1 mL). This mixture was heated at 110 °C with stirring for 12 h. After cooling, the mixture was filtered through Celite to remove metal salt and the filtrate was concentrated to give the desired product (15.2 mg, 75%).

Preparation of complex 2a

A solution of complex **1** (20 mg, 0.031 mmol) and acetic acid (0.31 mmol) in acetone (1.0 mL) was heated at 50 °C for 12 h. The reaction mixture was cooled, filtered through Celite, and washed with acetone. The combined organic solutions were dried over anhydrous Na_2SO_4 and concentrated. The residue was re-precipitated from methanol–ether to give the product as a red solid (16.5 mg, 80%): ^1H NMR (400 MHz, acetone-d_6): δ 8.97 (d, J = 4.4 Hz, 1 H), 8.93 (d, J = 6 Hz, 1 H), 8.17 (d, J = 8.4 Hz, 1 H), 7.97–8.03 (m, 2 H), 7.7 (d, J = 7.6 Hz, 1 H), 7.54

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(t, J = 7.6 Hz, 1 H), 7.5 (t, J = 6.8 Hz, 1 H), 7.02 (d, J = 7.2 Hz, 1 H), 6.97 (d, J = 7.2 Hz, 1 H), 5.15–5.19 (m, 1 H), 3.01–3.08 (m, 1 H), 2.8–2.87 (m, 1 H), 2.74–2.79 (m, 1 H), 1.65–1.73 (m, 1H), 1.47 (s, 3 H, –Me); ^{13}C NMR (100 MHz): δ 207.5, 206.5, 205.6, 197.87, 183.5, 166.6, 165.3, 157.8, 153.4, 152.1, 152, 138.6, 138.4, 133.1, 125.7, 124.3, 123.9, 122.4, 122.3, 106.6, 69.3, 28.6, 28.4, 23.3. Anal. calcd $C_{24}H_{18}N_4O_6Ru_2$: C, 43.64; H, 2.75; N, 8.48. Found: C, 43.34; H, 2.48; N, 8.13.

Preparation of complex 2b

The procedure was similar to that for **2a**. ^{1}H NMR (400 MHz, acetone-d_6): δ 9.11 (d, J = 5.2 Hz, 1 H), 9.06 (d, J = 4.8 Hz, 1 H), 8.17 (d, J = 8.4 Hz, 1 H), 8.04–8.08 (m, 2 H), 7.74 (d, J = 7.6 Hz, 1 H), 7.63 (t, J = 5.6 Hz, 1 H), 7.57 (t, J = 6.4 Hz, 1 H), 7.45 (d, J = 7.6 Hz, 2 H), 7.3 (t, J = 7.6 Hz, 1 H), 7.12 (t, J = 7.6 Hz, 2 H), 6.97 (d, J = 7.6 Hz, 1 H), 6.9 (d, J = 6.8 Hz, 1 H), 5.2–5.24 (m, 1 H), 2.98–3.01 (m, 1 H), 2.84–2.87 (m, 1 H), 2.73–2.77 (m, 1 H), 1.63–1.67 (m, 1H); ^{13}C NMR (100 MHz): δ207.5, 206.6, 205.8, 205.3, 178.4, 166.7, 165.4, 157.9, 153.5, 152.2, 138.7, 138.5, 134.8, 133.1, 132.6, 131.7, 130.3, 129.7, 128.3, 125.8, 124.4, 123.9, 122.3, 106.6, 69.3, 28.6, 28.3. Anal. calcd $C_{29}H_{20}N_4O_6Ru_2$: C, 48.20; H, 2.79; N, 7.75. Found C 47.89; H, 2.65; N, 7.43.

Crystallography

Crystals suitable for X-ray determination were obtained for **1** by recrystallization from dichloromethane and toluene at room temperature. Cell parameters were determined using a Siemens SMART CCD diffractometer. Crystal data of **1**: $C_{23}H_{16}N_4O_6Ru_2$, M_w = 646.54, monoclinic, space group $P2(1)/n$; a = 9.3648(5) Å, b = 15.1336(7) Å, c = 16.4997(11) Å, α = 90°, β = 104.020(6)°, γ = 90°; V = 2268.7(2) Å^3; Z = 4; $\rho_{calcd.}$ = 1.893 Mg m^{-3}; F(000) = 1272; crystal size: 0.20 × 0.15 × 0.10 mm^3; reflections collected: 14 611; independent reflections: 5061 [R(int) = 0.0224]; θ range 2.88 to 27.50°; goodness-of-fit on F^2 1.013; final R indices [$I > 2\sigma(I)$] R_1 = 0.0277, wR_2 = 0.0641; R indices (all data) R_1 = 0.0335, wR_2 = 0.0679. The structure was solved using the SHELXS-97 program[11] and refined using the SHELXL-97 program[12] by full-matrix least-squares on F^2 values.

Physical measurement

Infrared spectra were recorded on a Varian 640-IR spectrometer on KBr pellets. Electronic absorptions were measured on a Shimatzu PC 2100 spectrometer. Cyclic voltammograms were obtained in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as the supporting electrolyte. A glassy carbon disk was used as the working electrode and a platinum wire functioned as the auxiliary electrode. All voltammograms were recorded *versus* a Ag/AgCl electrode at a scanning rate of 100 mV s^{-1}.

Computation

Calculations on the electronic states of all title complexes were carried out using the density functional theory (DFT) with B3LYP hybrid functional.[13] Restricted and unrestricted formalisms were adopted in the singlet and triplet geometry optimization, respectively. A "double-ζ" quality basis set consisting of Hay and Wadt's effective core potentials (LANL2DZ)[14] was employed for the Ru metal atom, and a 6-31G* basis set[15] for the rest of the atoms. Time-dependent DFT (TDDFT) calculations using the B3LYP functional were then performed based on the optimized structures at ground states.[16]

Production of formic acid

A mixture of **bpnp** (0.02 mmol), $Ru_3(CO)_{12}$ (0.02 mmol) and water (5 mmol) in C_6H_5Cl (1 mL) was placed in a 20 mL autoclave. The system was flashed with nitrogen three times, and then pressurized with CO (100 psi). The mixture was heated at 100 °C for 24 h. The reaction mixture was cooled to 4 °C with an ice-water bath. After releasing all gases, the solution was analysed by ^{1}H NMR and GC.

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