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TiO₂ Modified with A Ru(II)–N'NN' 8-Hydroxyquinolyl Complex for Efficient Gaseous Photoreduction of CO₂

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New Rigid neutral Ru(II) pincer complex [Ru(N'NN')(ONO)] was synthesized from cationic [Ru(N'NN')(MeCN)₂CI]CI (N'NN', 2,6-bis(N-benzyl-benzimidazol-2-yl)pyridine) and 4,8-dihydroxyquiniline-2-carboxylic acid (ONO). The X-ray diffraction analysis indicates that the Ru(II) center adopts a slightly distorted octahedral geometry, in which the two benzyl moieties of N'NN' ligand are located in the same side of the coordination plane defined by three N atoms of N'NN' and the Ru(II) center, and the dihedral angels of the benzyl group and the Ru(II)–N'NN' plane are 89.1 ° and 74.9 °, respectively. Upon loading onto TiO₂ nanoparticles (P25), this Ru(II) complex exhibits efficient CO₂ photoreduction ability with CO/CH₄ production activities of 26.6/17.2 μ mol g⁻¹ h⁻¹ in a gaseous photocatalytic system containing CO₂ and H₂O vapor, which is much better than that of the pristine TiO₂ nanoparticles. This result gives an good example of loading Ru(II) pincer complex onto TiO₂ nanoparticles acting as a heterogeneous photocatalytic CO₂ reduction system, which would facilitate the development of more feasible artificial photosynthesis system.

Keywords: Gaseous CO₂ photoreduction; rigid Ru(II) pincer complex; TiO₂; CO/CH₄ production

Introduction

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Carbon dioxide (CO₂) as fertile C1 source and generally produced by the combustion of fossil fuels and respiration of organism. Due to the relatively inert nature of CO₂ molecule, reduction of CO₂ to form useful chemicals or new energy source is a challenging task, which normally requires appropriate catalysts and energy input. In this context, photoreduction of CO₂ to high energy products, such as CO/CH₄ or methanol, may provide a promising procedure to solve the problem of the shortage about fossil fuels and global warming.^{1,2} Since the first CO₂ photoreduction catalyst was reported by Lehn and co-workers,³ various types of transition metal complexes based on Rh,⁴ Ni,^{5,6} Ru⁷⁻¹¹ and Co¹²⁻¹⁴ were reported as catalysts, which combining with a suitable photosensitizer displayed high efficiency for CO₂ reduction in homogeneous system.

From the view of large-scale application and efficient solar energy utilization, semiconductor-based heterogeneous photocatalysts have more advantages than homogeneous catalysts with their superior oxidation/reduction ability and potential recyclability.¹⁵ In the past decade, heterogeneous

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system for photocatalytic CO₂ reduction have been gradually developed.^{16–19} However, the search for cheaper heterogeneous photocatalysts with sufficient activity and high stability remains challenge in chemistry.^{1,2} Until now, the best catalyst performed only with turnover numbers (TONs) of ~1000 and apparent quantum yields (AQYs) of ~5%.²⁰

Ru(II) pincer complexes bearing pyridyl-based N'NN' ligands or quinolinyl-based ONO ligands have the rigid framework, high thermal and light stability, and versatile but easily modified structure with adjustable UV-vis absorption band, which might be good candidates as photosensitizers or photocatalysts for CO_2 reduction through an artificial photosynthesis process. Herein, we report a rare example of Ru(II) pincer complex bearing both N'NN' and ONO ligands each, which displays efficient photocatalytic CO_2 reduction ability to produce CO/CH_4 after combining with TiO₂ nanoparticles (P25) in a gas/solid system.

Results and discussion

Synthesis and characterization of Ru(II) pincer complex

Ligand 4,8-dihydroxyquinoline-2-carboxylic acid (ONO) was prepared according to the literature with slightly modification.^{21,22} Complex [RuCl(N'NN')(CH₃CN)₂]·Cl was prepared from [RuCl₂(p-cymene)]₂ with 2,6-bis(N-benzylbenzimidazol-2-yl)pyridine (N'NN') through the procedure reported group.23 Upon refluxing bv our of [RuCl(N'NN')(CH₃CN)₂]·Cl and one equivalent of ligand ONO with two equivalents of LiOH in methanol, the neutral complex [Ru(N'NN')(ONO)] was obtained in good yield (Scheme 1). The ¹H NMR spectrum of Ru(II) pincer complex shows one singlet

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signal with the integration of four protons at 6.10 ppm, which can be assigned to the two CH₂ groups of N'NN' ligand. The lack of any signal between 1.7~4.0 ppm in ¹HNMR of Ru(II) pincer complex clearly indicates the two acetonitrile ligands in [RuCl(N'NN')(CH₃CN)₂]·Cl were extracted by ONO pincer ligand. The IR spectrum (Fig. S1[†]) of Ru(II) pincer complex also displays a strong absorption at 1650 cm⁻¹, indicating the existence of coordinated carboxylate moiety of ONO ligand. Moreover, the Ru(II) pincer complex was also characterized by MALDI TOF-MS (Fig. S2⁺), elemental analysis, UV-vis and fluorescence spectra as described below.



For further investigation of the structure of the Ru(II) pincer complex, single crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether into the concentrated solution of the Ru(II) pincer complex in Nmethyl-2-pyrrolidinone (NMP). The crystal structure of the Ru(II) pincer complex crystallizes in a monoclinic space group P21/n (Table 1). The selected bond distances and angles are listed in Fig. 1. Although there exists the disorder of ONO ligand around the Ru(II)-N'NN' plane, the structure of the Ru(II) pincer complex still clearly displays the metal centre adopting a slightly distorted octahedral geometry which is configured by three N atoms of N'NN' ligand and two O atoms and one N atom of the ONO ligand (Fig. 1). The ONO ligand is perpendicular to the coordination plane defined by Ru(II)-N'NN' (the dihedral angel is 89.53 °). Due to the stronger coordination ability of the pyridine N atom than that of benzimidazole N atom to Ru centre, the bond distance of Ru-N(1) (pyridyl, 2.004(6) Å) is shorter than that of Ru-N(2) (imidazole, 2.037(8) Å) and Ru-N(4) (imidazole, 2.063(8) Å), which is consistent to the literature.²⁴ The bond distances of Ru(II)-N_{py} and Ru(II)-N_{bimz} in the Ru(II) pincer complex match well with the reported analogous Ru(II) complexes.²⁵⁻³¹ It is noted that the two benzyl groups of N'NN' ligand are located in the same side of the Ru(II)-N'NN' plane with the dihedral angels between the benzyl and the N'NN' framework at 89.01 $^\circ$ and 74.87°, respectively.

Table 1 Crystallographic data and structure refinement parameters for the Ru(II) pincer complex

Empirical formula	$C_{43}H_{29}N_6O_4Ru$
Formula weight	794.79
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 12.139(9) Å α= 90°; b=
	15.53 (1) Å β= 98.77 (1)°; c =
	24.30 (2) Å γ = 90°
	24.30 (2) A $\gamma = 90^{\circ}$

Volume 4528(6) Å³ View Article Online 4, 1.166 Mg/m3.1039/C8CY00158H Z, Density (calculated) Absorption coefficient 0.389 mm⁻¹ F(000) 1620 Crystal size 0.10 x 0.06 x 0.05 mm³ Theta range for data 1.70 to 22.58° collection Index ranges -13<=h<=12, 0<=k<=16, 0<=l<=26 **Reflections collected** 5911 Independent reflections 5911 [R(int) = 0.0000] Completeness to theta 22.58 98.8 % Absorption correction None Max. and min. 0.9808 and 0.9622 transmission Full-matrix least-squares on F² Refinement method Data/restraints/parameter 5911/287/533 Goodness-of-fit on F² 0.832 Final R indices [I>2sigma(I)]

R indices (all data) Largest diff. peak and hole





Fig. 1 The structure of the Ru(II) pincer complex with thermal ellipsoids are drawn at the 30% probability level. All H-atoms are omitted for clarity. Selected bond lengths (Å) and angles (9: Ru(1)-N(1), 2.004(6); Ru(1)-N(2), 2.037(8), Ru(1)-N(4), 2.063(8); Ru(1)-N(6), 1.900(9); Ru(1)-O(1), 2.072(13), Ru(1)-O(3), 2.099(11). N(6)-Ru(1)-N(1), 172.4(4); N(2)-Ru(1)-N(4), 155.8(3); N(1)-Ru(1)-N(2), 78.7(3); N(1)-Ru(1)-N(4).

Spectroscopic/electrochemical analyses of Ru(II) complex

The UV-vis absorption spectra of the Ru(II) pincer complex in DMF solution are shown in Fig. 2. There are fairly strong and relatively broad absorption peaks with a maximum at 535 nm (ε = 1.44 × 10⁴ L mol⁻¹cm⁻¹), which can be assigned to the metal-to-ligand charge-transfer (MLCT) transition to a ¹MLCT state. The other high energy transitions in the region 300~390 nm are normally attributed to the overlapped π - π * intraligand transitions (ILCT) of the ligands. It is noted that this Ru(II) pincer complex displays a low-energy shoulder in the range of 600~800 nm in their absorption spectra, which also arise from MLCT transitions.32

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Fig. 2 UV-vis absorption spectra of the Ru(II) pincer complex in DMF solution.

The photoluminescence (PL) spectra of Ru(II) pincer complex in DMF solution at room temperature are displayed in Fig. 3. Upon excitation at their MLCT band, the Ru(II) pincer complex exhibits one broad luminescent band with a maximum emission at 590 nm. According to the previous reports,^{33,34} the optical energy gap (E_{0-0}) can be estimated by the intersection point ($\lambda_{intersect.}$) of the normalized absorption and emission spectra through the formula $E_{0-0} = 1240/\lambda_{intersect.}$. As shown in Fig. 3, the intersection points for the Ru(II) pincer complex are 578 nm, implying its E_{0-0} value can be calculated to be 2.15 eV.

The electrochemical characteristics of the Ru(II) pincer complex were examined by cyclic voltammetry (CV) in DMF solution. As shown in Fig. S3⁺, the first half-wave redox potential values (*vs.* SCE) were summarized in Table 2. The Ru(II) pincer complex exhibits a quasireversible oxidation at $E_{1/2} = 0.77$ V and a reduction at $E_{1/2} = -0.75$ V. According to Leeuw's experience formula,^{35,36} the HOMO level of the Ru(II) pincer complex could be estimated to be 0.98 V *vs.* NHE (the same as below), while the LUMO level of can be estimated to be -1.16 V according to the formula $E_{LUMO} = E_{HOMO} + E_{0-0}$.



Fig. 3 Normalized absorption and emission spectra of the Ru(II) pincer complex (λ_{ex} = 502 nm) in DMF solution.

Table 2	Electrochemical	data	of the	Ru(II)	pincer	complex
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Complex	E_{ox} / V	E_{ox} / V	E ₀₋₀	HOMO ^a /	LUMO ^b /	
	<i>vs</i> . SCE	vs. SCE	/ eV	V <i>vs</i> . NHE	V <i>vs</i> . NHE	
Ru(II)	0.77	-0.75	2 1/	0 08	-1 16	
complex	(Oxd1)	(Red ₁)	2.14	0.98	-1.10	

 a Calculated with $E_{\rm HOMO}$ = –($E_{\rm ox}$ + 4.71) eV. b Calculated with $E_{\rm LUMO}$ = ($E_{\rm HOMO}$ + $E_{\rm 0-0}$) eV.

Photoreduction CO2 activity of the Ru(II) pincer, complex. loaded TiO2 nanoparticles DOI: 10.1039/C8CY00158H

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The Ru(II) pincer complex (denoted as Ru(N'NN')(ONO)) was loaded on TiO₂ nanoparticles (P25, Degussa) through an impregnation method. Typically, TiO₂ nanoparticles (30 mg) was mixed with a due amount of Ru(II) complex in DMF solution (20 mL) under stirring for 12 h, and then centrifugally separated and dried in vacuum at 60°C overnight to obtain the complex-loaded products, which is denoted as Ru(N'NN')(ONO)-TiO₂. The primary experimental results showed that both photocatalyst and irradiation are necessary for the CO₂ photoreduction system. Gaseous CO₂ were reduced to CO/CH₄ mixture using H₂O vapor as the hydrogen source, and no other products such as CH₃OH, HCHO or HCOOH was observed in the gas or liquid phase detected by using GC-FID method.¹⁶ The control experiment displayed neither CO nor other carbon containing organic matters can be detected using N2 instead of CO2, demonstrating CO/CH4 generation stemmed from the CO₂ photoreduction process.



Fig. 4 Effect of the Ru(N'NN')(ONO)-loading amount on the CO/CH_4 production activities of Ru(N'NN')(ONO)-TiO₂.

In the present gaseous photocatalytic CO₂ reduction system,¹⁶ the Ru(N'NN')(ONO)-loading amount has an obvious effect on the CO/CH₄ production activities of the Ru(N'NN')(ONO)-TiO2 under full spectrum irradiation of Xelamp as shown in Fig. 4. As can be seen, the pristine TiO₂ shows very low CO/CH₄ production rates of 1.82/0.82 μmol g⁻¹ h⁻¹ with an overall activity (TECN, total electron consumption number for CO/CH₄ production,^{2,16}) of 10.2 µmol g⁻¹ h⁻¹ (Table 3), whereas those Ru(N'NN')(ONO)-TiO₂ composites with different Ru(II) pincer complex-loading amount achieve much higher CO/CH₄ production activities. Among which, 0.25wt% Ru(N'NN')(ONO)-TiO₂ gives a maximum CO/CH₄ production activities of 26.6/17.2 µmol g⁻¹ h⁻¹ with an overall activity (TECN) up to 190.8 $\mu mol~g^{\text{-1}}~h^{\text{-1}}$ even though significant decreases in the CO/CH₄ production activities can be observed with further enhancing the Ru(II) complex-loading amount (Table S1). It indicates that loading the Ru(II) pincer complex bearing pyridyl-based N'NN' and quinolinyl-based ONO ligands on TiO₂ nanoparticles can effectively catalyse the CO₂ reduction reaction in the present heterogeneous photocatalytic system. Moreover, the 0.25wt% Ru(N'NN')(ONO) $-TiO_2$ shows gradually increasing trends of the CO/CH₄ production amounts with prolonging the irradiation time (Fig. S4⁺), indicating the Ru(II) pincer complex has a relatively good stability during the 3 h light irradiation of Xe-lamp.

For understanding the charge transfer behaviours in the present photocatalytic system, the photoluminescence (PL) spectra were carried out with both pristine TiO₂ and its complex-loaded product. As shown in Fig. 5, the single TiO₂ film exhibits obvious PL peaks with maximum at 475 nm upon excited by 330 nm wavelength, while those peaks of Ru(N'NN')(ONO)-TiO₂ are much weaker than that of TiO₂ in the same condition. It could be ascribed to the good charge transfer channel between the Ru(II) pincer complex and TiO₂ nanoparticles which made electron transfer from TiO₂ to Ru(II) complex easily, and then the fluorescence quenching of Ru(N'NN')(ONO)-TiO₂. The above calculated HOMO energy level (0.98 V, Table 2) for the Ru(II) pincer complex is more positive than the TiO₂'s conduction band (CB, -0.50 V³⁷). It is a benefit to the excited electrons of TiO₂ transferring to the HOMO of Ru(N'NN')(ONO), and then to its LUMO excited by visible light for the CO₂ reduction since the LUMO energy level (-1.16 V) is sufficient negative than the reduction potentials of CO₂/CO (-0.53 V) and CO₂/CH₄ (-0.24 V)² to drive to CO₂ reduction for the CO/CH₄ formation. Namely, Ru(N'NN')(ONO) in Ru(N'NN')(ONO)-TiO2 might serve as both light harvester and CO₂ reduction catalyst unit by accepting the photogenerated electrons of TiO₂'s CB, which is different from the traditional dye-sensitized semiconductor reported previously,16 where the excited dye molecules transfer the electrons to TiO₂'s CB for the CO₂ reduction under visible light irridiation. The detail photocatalytic mechanism for CO2 reduction in the present Ru(N'NN')(ONO)-TiO₂ is investigated underway.



Fig. 5 Photoluminescence (PL) spectra of the pristine TiO_2 and its complex-loaded product.

Conclusions

A new Ru(II) complex bearing both conjugated N'NN' and ONO pincer ligands were synthesized and fully characterized. The crystal structure of Ru(II) pincer complex exhibits that the Ru(II) centre adopts a slightly distorted octahedral geometry, in which two pincer ligands are located perpendicularly to each other. And the

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two benzyl moieties of N'NN' ligand lie in the same side of the coordination plane defined by three N atoms of N'NN' and the Ru(II)– centre with the dihedral angels of the benzyl group and the Ru(II)– N'NN' plane being 89.1° and 74.9°, respectively. The resultant Ru(II) pincer complex displays high efficiency for gaseous CO_2 photoreduction to produce CO/CH_4 upon loaded to TiO_2 nanoparticles in a gaseous photocatalytic system containing CO_2 and H_2O vapour. It demonstrates the feasibility of developing more efficient artificial photosynthesis based on Ru(II) pincer complexloaded semiconductor.

Experimental section

General information

All manipulations were carried out under purified Ar atmosphere using standard Schlenk techniques. Ligand 4,8dihydroxyquinoline-2-carboxylic acid (ONO) was prepared according to the literature with slightly modification.^{21,22} Complex [RuCl(N'NN')(CH₃CN)₂]Cl was prepared from [RuCl₂(pcymene)]₂ with 2,6-bis(N-benzyl-benzimidazol-2-yl)pyridine (N'NN') according to the procedure reported elsewhere.²³ All solvents were distilled under an Ar atmosphere over appropriate agents, and stored in gas-tight solvent bulbs. DMSO-d₆ was dried with CaH₂ and vacuum-transferred by appropriate methods and vacuum-distilled prior to use.

¹H and ¹³C NMR spectra were recorded at 300 MHz, 75 MHz Varian Gemini 300 spectrometer. The ¹H NMR chemical shifts were referenced to the residual hydrogen signals of the deuterated solvents or TMS, and the ¹³C NMR chemical shifts are referenced to the ¹³C signals of the deuterated solvents. MALDI-TOF-MS spectra were taken on a Bruker BIFLEX III ultrahigh resolution Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer with alpha-cyano-4-hydroxycinnamic acid as a matrix. UV-Vis absorption spectra were recorded on a TU-1810 spectrophotometer with scanning from 250 to 900 nm. Fluorescence spectra were recorded on a K2 ISIS spectrometer. Fourier transform infrared (FTIR) spectrum was recorded by using a Nicolet iS10 spectrometer (Thermo Electron).

Preparation of 4,8-dihydroxyquinoline-2-carboxylic acid (ONO)

To a solution of *o*-ansidine (2.46 g, 0.02 mol) in methanol (40 mL) was added dimethyl acetylenedicarboxylate (2.84 g, 0.02 mol) dropwisely and then heated to reflux for 3 h. Upon cooling to room temperature, the solvent was removed by evaporation and the residue (3.37 g, 63.6%) was added to stirred diphenyl ether (50 mL, which were preheated to $250 \,^{\circ}\text{C}$) for ten minutes. After cooling to room temperature, petroleum ether (150 mL) was added to the mixture and the brown precipitate formed, which was collected and dried under vacuum to form a brown solid of methyl 4-hydroxy-8-methoxyquinoline-2-carboxylate. Yield: 1.93 g (65.1%); ¹H NMR (CDCl₃, 300 MHz): δ = 9.42 (s, 1H), 7.89 (d, 1H), 7.31 (d, 1H), 7.08 (s, 1H), 6.97 (d, 1H), 4.04 (d, 6H).

Methyl 4-hydroxy-8-methoxyquinoline-2-carboxylate (1.17 g, 0.005 mol) was dissolved in 48% hydrobromic acid (30 mL) and the solution was heated in a sealed tube at 120 \degree for 72h.

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After the solution was cooled, the precipitate was collected and put in the deionic water (15 mL), the mixture was adjusted to pH~2.5 with 6M NaOH to give a yellow powder, which was collected and dried under vacuum to give a yellow solid of ligand ONO. Yield: 0.87 g (85%). ¹H NMR (DMSO-d₆, 300 MHz): δ = 7.55 (d, 1H), 7.32 (s, 1H), 7.14 (d, 1H), 6.90(s, 1H). Which is consistent to the reported literature.²²

Preparation of Ru(N'NN')(ONO)

To a yellow solution of lithium 4,8-dihydroxyquinoline-2carboxylate prepared in situ from 4,8-dihydroxyquinoline-2carboxylic acid (40 mg, 0.195 mmol) and LiOH H₂O (16.4 mg, 0.390 mmol) in CH₃OH (10 mL), complex [RuCl(N'NN') (CH₃CN)₂] Cl (138.5 mg, 0.195 mmol) was added at room temperature under Ar atmosphere. The mixture was then refluxed for 12 h under Ar atmosphere, in which a violet solid was precipitated. After cooling, the solvent was removed by filtration and the residues were washed sequentially with methanol (10 mL) and diethyl ether (2 × 10 mL). The solid was dried under vacuum to give a violet powder of Ru(N'NN')(ONO). Yield: 0.1220 g (78.6%). A single crystal suitable for X-ray diffraction analysis was obtained by slow diffusion of diethyl ether into the saturated NMP (N-methyl-2pyrrolidinone) solution of Ru(N'NN')(ONO). ¹H NMR (DMSO-d₆, 300 MHz): δ = 8.08 (s, 2H), 7.79 (s, 1H), 7.66 (s, 2H), 7.22 - 7.45 (m, 20H), 6.10 (s, 4H) (H in - OH has not been found); IR(KBr pellets, cm⁻¹): 3433 (s, br), 3061 (m), 1650 (s, br); MALDI TOF-MS (m/z) calcd. for C₄₃H₂₉N₆O₄Ru [M+H]⁺ 796.81, found 796.30; Elemental analysis: calcd. for C₄₃H₂₉N₆O₄Ru: C, 64.90, H 3.80, N 10.56. Found: C 65.22, H 4.00, N 10.43.

Photocatalytic performance measurement

Photocatalytic CO₂ reduction was carried out in a home-made gas-closed circulation system irradiated by a 300 W Xe-lamp (PLS-SXE300/300UV, Perfectlight, China) with spectral range of 200-2500 nm and output light power of 6.6 W (UV) and 17.6 W (Vis).¹⁶ Typically, catalyst (60 mg) was uniformly dispersed onto the watch-glass with an area of ~28 cm², which was then put in the reaction cell (Pyrex glass) with a total volume of 500 mL. Prior to the light irradiation, the above system was thoroughly vacuum-treated to completely remove air. CO₂ and H₂O vapor were produced from the reaction of NaHCO₃ (1.00 g, introduced into the reactor before being sealed) and H_2SO_4 solution (5.0 mL, 4.0 M, introduced into the reactor via a syringe after the vacuum treatment). During irradiation, 2 mL gas was taken from the reactor at regular intervals (1 h) for the gas concentration analysis using a gas chromatograph (SP-7820, TDX-01 column, Rainbow chemical instrument Co. Ltd., China) equipped with a flame ionized detector (FID) and methanizer. The produced gases were calibrated with a standard gas mixture and their identity determined using the retention time.

X-ray crystallography

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A Bruker SMART APEX II diffractometer with graphitemonochromated Mo-K α (λ = 0.71073 ÅPiwas^{0.2}Mpfoved⁵%d collect the intensity data for the single crystal of Ru(N'NN')(ONO). The data was collected at about 100 K using ω -scan techniques. The structure was solved by direct methods using SHELXL-97.³⁸ Multi-scan empirical absorption corrections were applied to the data set using the program SADABS.³⁹ The structure was refined with SHELXL-97.³⁷ Hydrogen atoms bound to carbon were placed at calculated positions and refined using a riding mode. All non-hydrogen atoms were refined by full-matrix least squares on F² using the SHELXTL grogram package.⁴⁰ Cell refinement, data collection, and reduction were done by Bruker SAINT.⁴¹ The crystallographic data is available in the SI as CIF file and deposited in CCDC number 1536357.

Conflicts of interest

There are no conflicts to declare.

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A rare example of Ru(II) pincer complex for efficient photoreduction of CO_2 to CO/CH_4 in gaseous system is developed.

