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Crystallographic report

A synthetic precursor for hetero-binuclear metal complexes, $[Ru(bpy)(dppy)_2(CO)_2](PF_6)_2$ (bpy = 2,2′-bipyridine, dppy = 2-(diphenylphosphino)pyridine)

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In the title complex, $[Ru(bpy)(dppy)_2(CO)_2](PF_6)_2$ (bpy = 2,2′-bipyridine, dppy = 2-(diphenylphosphino)pyridine), the ruthenium atom exhibits a slightly distorted octahedral coordination with the carbonyl ligands in cis positions. In addition, two dppy ligands coordinate to the ruthenium center through the phosphorus atoms in mutually trans positions and two pyridyl nitrogen atoms of the dppy direct toward two carbonyl ligands. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: crystal structure; ruthenium; carbonyl complex

INTRODUCTION

Ruthenium mono-bipyridine compounds containing carbonyl groups have been widely studied owing to their high activity in the water-gas shift reaction and in the reduction of CO_2.[1,2] Ziessel and co-workers[3] proposed a mechanism for electrocatalytic reduction of CO_2 that includes a highly air-sensitive, blue polymeric $\{Ru(bpy)(CO)_2\}_n$ (bpy = 2,2′-bipyridine).[3] This indicates that multinuclear compounds are active species in the CO_2 reduction, and it is important to explore new homo- or hetero-binuclear complexes as model species. In particular, construction of hetero-nuclear systems containing the above mono-bpy carbonyl fragment would provide important and new insights into the mechanisms of CO_2 reduction, because the compounds formed may function as active species in catalytic cycles. Herein, we report the synthesis and structure of a new synthetic precursor for hetero-binuclear metal complexes possessing the $\{Ru(bpy)(CO)_2\}$ fragment and two uncoordinated nitrogen donor atoms.

EXPERIMENTAL

Ruthenium trichloride was purchased from Furuya Metals. Silver nitrate (Wako Pure Chemicals), 2,2′-bipyridine (Nacalai Tesque), 2-(diphenylphosphino)pyridine (Aldrich), and potassium hexafluorophosphate (Tokyo Kasei) were used without purification. Solvents (acetonitrile, acetone, and ethanol) were HPLC grade and used without further purification. $[Ru(CO)_2Cl_2]_n$, *cis*(CO),*trans*(Cl)-$[Ru(bpy)(CO)_2Cl_2]$, and $[Ru(bpy)(dppy)(CO)_2Cl]PF_6$ (dppy = 2-(diphenylphosphino)pyridine) were prepared by the reported methods.[4,5]

Synthesis

$[Ru(bpy)(dppy)(CO)_2Cl]PF_6$ (80 mg, 0.11 mmol) and dppy (70 mg, 0.27 mmol) were added to CH_3CN (20 cm^3), and then the mixture was refluxed with stirring for 6 h in the presence of one equivalent of aqueous $AgNO_3$ (16 mg/10 cm^3). After the resulting AgCl was removed by filtration, the filtrate was evaporated to *ca* 10 cm^3 under reduced pressure. The addition of a saturated aqueous solution of KPF_6 to the solution resulted in a colorless precipitate. The crude product was purified from acetone–ethanol to give $[Ru(bpy)(dppy)_2(CO)_2](PF_6)_2$ as colorless crystals (100 mg, 75%). Anal. Found: C, 48.77; H, 3.26; N, 4.88. Calcd for $C_{46}H_{36}F_{12}N_3O_2P_4Ru$: C, 48.90; H, 3.22; N, 4.96%. ^1H NMR (δ, CD_3CN): 6.83–8.68 (36H, bpy and dppy). ^{13}C NMR (δ, CD_3CN): 125.60, 125.93, 126.29, 127.45, 129.32, 130.37, 130.51, 130.60, 130.67, 133.10, 133.20, 133.28, 133.37, 139.01, 139.06, 141.74, 150.71, 150.87, 151.01, 153.83, 154.43, 155.81 (bpy and dppy), 195.38 (CO). IR (cm^{-1}, KBr): 2043, 2083 (νCO). ESI-MS (m/z, CH_3CN): 420 ($[M - (PF_6)_2]^{2+}$). Cyclic voltammetry (vs. $Ag|AgNO_3$, CH_3CN): $E_{pc} = -1.06, -1.29$ V.

Crystallography

Intensity data for $[Ru(bpy)(dppy)_2(CO)_2](PF_6)_2$ were collected at 173 K on a Rigaku/MSC Mercury CCD diffractometer for a colorless crystal $0.10 \times 0.15 \times 0.25$ mm^3. $C_{46}H_{36}F_{12}N_3O_2P_4Ru$, $M = 1129.76$, monoclinic, $C2/c$, $a = 15.386(2)$, $b = 14.868(2)$, $c = 22.432(3)$ Å, $\beta = 112.618(5)°$, $V = 4736(1)$ Å^3, $Z = 4$, $\mu(Mo\ K\alpha) = 0.557\ mm^{-1}$, 5415 unique data ($\theta_{max} = 27.5°$), 3848 data with $I > 2\sigma(I)$, $R_1 = 0.073$, $R_w = 0.161$ (all data), $\rho_{max} = 2.58\ e^-$ Å^{-3}. Programs used: teXsan,

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DIRDIF94, PATTY, CRYSTALCLEAR, and ORTEP. CCDC deposition number: 224362.

RESULTS AND DISCUSSION

The title compound, $[Ru(bpy)(dppy)_2(CO)_2](PF_6)_2$ (**I**), is synthesized in the stepwise reactions from $[Ru(bpy)(CO)_2Cl_2]$ and dppy which has been used extensively in constructing many binuclear complexes.[6] The ^{13}C NMR spectrum of **I** consists of a single resonance in the carbonyl region, indicating that the compound is obtained as a single isomer and two carbonyl moieties coordinate to the ruthenium center under the same environment. Further definition of the geometry of **I** comes from the IR spectrum, which shows two carbonyl stretching bands. Consequently, the carbonyl groups must occupy mutually cis positions. The structure of **I** has been further determined by X-ray crystal structure analysis.

We crystallized the colorless compound **I** from an acetone–ethanol mixture. The pure and colorless crystals were used in a single-crystal X-ray diffraction study, which confirmed the assumption of the *cis*-CO type (Fig. 1). Although two coordination modes for dppy, i.e. the *P*-mono and *P*,*N*-bidentate, have been established by X-ray crystallography in mononuclear systems,[7] the dppy ligands coordinate to the ruthenium center through only the phosphorus atom. The geometry about the ruthenium is slightly distorted octahedral. The bond angles between cis ligands, except for the N–Ru–N angle (the five-membered chelate ring), are all close to the ideal value of 90°. The bond distances from ruthenium to its neighboring atoms all appear normal. Ruthenium(II)–phosphorus distances span the range 2.21–2.44 Å, depending on the trans ligand.[8,9] The Ru–P distance of 2.407(1) Å is longer than that of the 2.327(6) Å Ru–P distance with trans chloride in $[Ru(bpy)(dppy)(CO)_2Cl]^+$.[5] The Ru–C–O angle (176.8(4)°) is approximately linear, and the Ru–C and C–O distances (1.901(5) Å and 1.142(5) Å respectively) are normal. Thus, there are no significant differences in the RuCO moiety compared with other ruthenium(II) carbonyl complexes containing polypyridyl ligands.[10] A prominent feature of the structure is that the two pyridyl nitrogen atoms of the dppy ligands direct toward two carbonyls. The existence of carbonyl ligands may influence the orientation of aromatic rings of the dppy ligand. Complexation of the second metal atom, therefore, would be possible by utilizing these uncoordinated pyridyl nitrogen atoms.

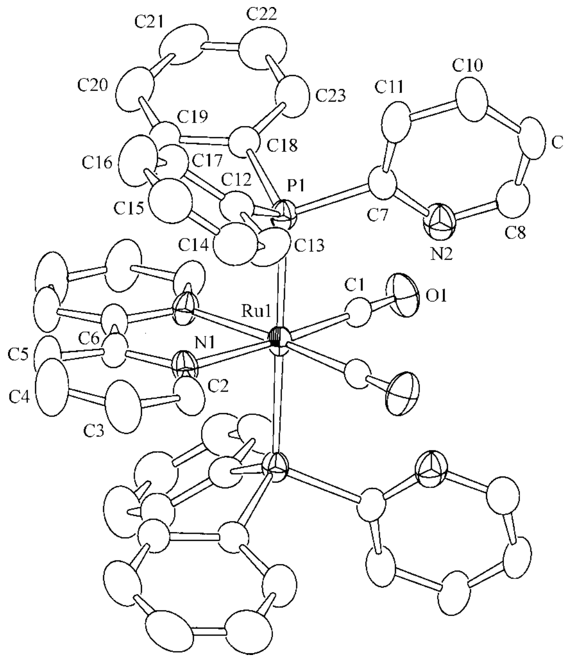

Figure 1. Molecular structure of **I**. Hydrogen atoms are omitted for clarity. Key geometric parameters: Ru1–C1 1.901(5), Ru1–P1 2.407(1), Ru1–N1 2.101(4), C1–O1 1.142(5) Å; Ru1–C1–O1 176.8(4)°.

CONCLUSIONS

We have found a new route to construct a binuclear system with a highly catalytically active $\{Ru(bpy)(CO)_2\}$ fragment. The synthetic and structural studies described here are the basis for further synthetic studies, which are already in progress, and will be reported later.

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