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Preparation, characterization and redox chemistry of oxo-centered triruthenium dimers linked by bis(diphenylphosphino)anthracene and -ferrocene

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Abstract

Diphosphine-bridged dimers of oxo-centered triruthenium–acetate cluster units, i.e., $[\{Ru_3O(OAc)_6(py)_2\}_2(dppan)](PF_6)_2$ (**2**) and $[\{Ru_3O(OAc)_6(py)_2\}_2(dppf)](PF_6)_2$ (**3**) were prepared by reaction of 2.3 equivalent $[Ru_3O(OAc)_6(py)_2(CH_3OH)](PF_6)$ with 9,10-bis(diphenylphosphino)anthracene (dppan) or 1,1′-bis(diphenylphosphino)ferrocene (dppf), respectively. Apparent redox wave splitting is observed in complex **2**, revealing the presence of electronic communication between two triruthenium units mediated through bridging dppan. The complexes were characterized by elemental analysis, IR, UV–Vis, ^{31}P NMR, and ES-MS spectroscopies, and cyclic and differential-pulse voltammetry. The crystal structure of complex **3** was determined by X-ray crystallography.

Keywords: Bis(diphenylphosphino)anthracene; Bis(diphenylphosphino)ferrocene; Electronic communication; P ligand; Redox properties; Ruthenium

1. Introduction

Design of multinuclear transition metal complexes that exhibit ligand-mediated electronic communication has attracted considerable attention in recent years [1,2], owing to the potential applications in the emerging fields of molecular-scale electronics and devices [3]. It is known that the oxo-centered triruthenium–carboxylate complexes with general formula $[Ru_3(\mu_3\text{-}O)(\mu\text{-}O_2CR)_6L_3]^n$ (R = alky or aryl, L = axial ligands) exhibit multiple redox behavior, rich mixed-valence chemistry and catalytic properties [4–12]. The substitution reactivity of axial ligands in the solvent-coordinated oxo-centered triruthenium–carboxylate complexes, $[Ru_3(\mu_3\text{-}O)(\mu\text{-}O_2CR)_6L_2(S)]^-$, $Ru_3(\mu_3\text{-}O)(\mu\text{-}O_2CR)_6(CO)L(S)$, and $Ru_3(\mu_3\text{-}O)(\mu\text{-}O_2CR)_6(CO)(S)_2$ (S = solvent molecules such as H_2O and CH_3OH), makes them excellent precursors to design ligand-linked oligomeric molecular materials based on $Ru_3(\mu_3\text{-}O)(\mu\text{-}O_2CR)_6$ cores with desired properties [11,12]. A series of ditopic *N*-heterocyclic-bridged dimers, trimers and hexamers of triruthenium clusters have been reported, which exhibit extensive electronic communications between the triruthenium redox centers [5c,5e,7–12]. Our interest has focused on the designed syntheses of diphosphine-linked dimeric oxo-centered triruthenium–acetate clusters as well as on modulating the diphosphine-mediating electronic

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communication between two triruthenium units by modifying both ancillary and bridging ligands [2a]. A series of dimeric triruthenium–acetate complexes $[\{Ru_3(O)(OAc)_6(L)_2\}_2(dppa)](PF_6)_2$ and $[\{Ru_3(O)(OAc)_6(L)_2\}_2(dppen)](PF_6)_2$ (dppa = bis(diphenylphosphino)acetylene, dppen = *trans*-1,2-bis(diphenylphosphino)ethylene; L = 4-di- methylaminopyridine, pyridine, abco(1-azabicyclo-[2,2,2] octane)), linked by dppa and dppen, respectively, have recently been described [2a]. As a part of our further studies on the chemistry of diphosphine-bridged oxo-centered trirutheniun cluster dimers, we report herein two new hexanuclear ruthenium complexes $[\{Ru_3O(OAc)_6(py)_2\}_2(dppan)](PF_6)_2$ (**2**) and $[\{Ru_3O(OAc)_6(py)_2\}_2(dppf)](PF_6)_2$ (**3**), where dppan and dppf are 9,10-bis(diphenylphosphino)anthracene and 1,1′-bis(diphenylphosphino)ferrocene, respectively.

2. Experimental

2.1. Materials

Dichloromethane and acetonitrile used in electrochemical and UV–Vis spectral measurements were distilled over CaH_2 under a nitrogen atmosphere before use. Other reagents were used as received. Hydrated ruthenium chloride and 1,1′-bis(diphenylphosphino)ferrocene (dppf) were purchased from Strem. 9,10-Bis(diphenylphosphino)anthracene (dppan) and the precursor compound $[Ru_3O(OAc)_6(py)_2(CH_3OH)](PF_6)$ (**1**) were prepared by the procedures described in the literatures [13,14].

2.2. Physical measurements

Elemental analyses (C, H, N) were performed on a Perkin–Elmer model 240C automatic instrument. The electrospray mass spectra (ES-MS) were recorded on a Finnigan LCQ mass spectrometer using dichloromethane–methanol as mobile phase. The UV–Vis spectra in acetonitrile solutions were measured on a Perkin–Elmer Lambda 25 UV–Vis spectrometer. The IR spectra were recorded on a Magna750 FT-IR spectrophotometer using KBr pellets. The ^{31}P NMR measurement was made on a Varian UNITY-500 spectrometer with 85% H_3PO_4 as an external standard. The cyclic voltammogram (CV) and differential pulse voltammogram (DPV) were measured with a Potentiostat/Galvanostat Model 263A in dichloromethane solutions containing 0.1 M $(Bu_4N)PF_6$ as supporting electrolyte. CV was performed at a scan rate of 100 mV s^{-1}. DPV was measured at a rate of 20 mV s^{-1} with a pulse height of 10 mV. Platinum and glassy graphite were used as counter and working electrodes, respectively, and the potentials were measured against an Ag/AgCl reference electrode. The potential measured was always referenced to the half-wave potentials of the ferrocenium/ferrocene couple ($E_{1/2} = 0.585$ V) as the internal reference.

2.3. Synthesis

2.3.1. $[\{Ru_3O(OAc)_6(py)_2\}_2(dppan)](PF_6)_2$ (**2**)

To a dichloromethane (35 mL) solution of **1** (232.0 mg, 0.230 mmol) was added 9,10-bis(diphenylphosphino)anthracene (54.5 mg, 0.100 mmol) with stirring for two days. The green residue obtained by removing the solvent in vacuo was purified via column chromatography (Al_2O_3, CH_2Cl_2/CH_3OH 100:1) to give 167 mg of the product. Yield: 67%. *Anal.* Calc. for $C_{82}H_{84}F_{12}N_4O_{26}P_4Ru_6$: C, 39.40; H, 3.39; N, 2.24. Found: C, 40.25; H, 3.29; N, 2.22%. ES-MS (*m*/*z*): 1104 $[M - 2PF_6]^{2+}$, 1411 $[Ru_3O(OAc)_6(py)_2(dppan)(CH_3OH)]^+$, 1397 $[Ru_3O(OAc)_6(py)_2(dppan)(H_2O)]^+$, 1379 $[Ru_3O(OAc)_6(py)_2(dppan)]^+$, 864 $[Ru_3O(OAc)_6(py)_2(CH_3OH)]^+$. IR spectrum (KBr, cm^{-1}): 1608m (COO), 1554m (COO), 1421s (COO), 843s (PF_6). UV–Vis spectrum (MeCN): λ_{max}/nm (ε, $dm^3\ mol^{-1}\ cm^{-1}$) = 269 (68 290), 315 (18 030), 444 (19 555), 662 (9420). ^{31}P NMR spectrum (202.3 MHz, CD_3CN, ppm): δ −18.5 (s, Ru-*P*-An-*P*-Ru), −143.3 (h, $J_{^{31}P\text{–}^{19}F} = 708$ Hz, *P*F$_6$).

2.3.2. $[\{Ru_3O(OAc)_6(py)_2\}_2(dppf)](PF_6)_2$ (**3**)

It was synthesized by the same procedure as **2** using 1,1′-bis(diphenylphosphino)ferrocene (dppf) in place of 9,10-bis(diphenylphosphino)anthracene. Yield: 56%. *Anal.* Calc. for $C_{78}H_{84}F_{12}FeN_4O_{26}P_4Ru_6$: C, 37.36; H, 3.38; N, 2.23. Found: C, 37.48; H, 2.99; N, 2.12%. ES-MS (*m*/*z*): 1109 $[M - 2PF_6]^{2+}$, 1404 $[Ru_3O(OAc)_6(py)_2(dppf)(H_2O)]^+$, 1386 $[Ru_3O(OAc)_6(py)_2(dppf)]^+$, 865 $[Ru_3O(OAc)_6(py)_2(CH_3OH)]^+$, 818 $[Ru_3O(OAc)_6(py)(CH_3OH)_2]^+$. IR spectrum (KBr, cm^{-1}): 1606m (COO), 1556m (COO), 1419s (COO), 843s (PF_6). UV–Vis (MeCN): λ_{max} ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) = 240 (68 290), 316 (18 350), 398 (10 470), 658 (8910). ^{31}P NMR spectrum (202.3 MHz, CD_3CN, ppm): δ 28.2 (s, Ru-*P*-Cp$_2$Fe-*P*-Ru), −143.1 (h, $J_{^{31}P\text{–}^{19}F} = 708$ Hz, *P*F$_6$).

2.4. Crystallographic measurements and structure determinations

The crystal of $\mathbf{3} \cdot 4H_2O$ suitable for X-ray diffraction was obtained by layering petroleum onto the solution of 1,2-dichloroethane–dichloromethane (v/v, 1:2). Crystal coated with epoxy resin was measured on a SIEMENS SMART CCD diffractometer and the reflection data were collected at 293 K by ω scan technique using graphite-monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation. An absorption correction by SADABS was applied