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Note

Di- and tetraosmium carbonyl complexes with dicarboxylato ligands serving as intramolecular rings and intermolecular bridges

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ABSTRACT

The osmium(I) carbonyl complexes $Os_2(\mu\text{-sebacate})(CO)_4(dmso)_2$ (**1**) and $[Os_2(CO)_6]_2(\mu_4\text{-1,3-adamantanediacetate})_2$ (**2**) have been prepared by microwave heating and structurally characterized by X-ray crystallographic analysis. The reaction of $Os_3(CO)_{12}$ with sebacic acid in 1,2-dichlorobenzene at 205 °C produces $Os_2(\mu\text{-sebacate})(CO)_6$ in 45% yield. Subsequent treatment with dimethylsulfoxide at 70 °C results in conversion to the dmso adduct **1**. The reaction of $Os_3(CO)_{12}$ with 1,3-adamantanediacetic acid in 1,2-dichlorobenzene at 208 °C produces **2**. Clusters **1** and **2** contain $Os_2(CO)_4$ units with sawhorse geometries and Os–Os single bonds. In the diosmium complex **1**, a sebacato (decanedioato) ligand forms an intramolecular chelate ring within a single Os_2 sawhorse unit. In the tetraosmium complex **2**, two 1,3-adamantanediacetato ligands form intermolecular bridges that join two Os_2 sawhorse units into a molecular loop.

Introduction

Dicarboxylate anions (DCAs) are often used as the organic spacers that link metal-containing building blocks into hybrid inorganic–organic composites including metal-organic frameworks (MOFs) [1,2]. Many such MOFs have been prepared from building blocks that are small metal clusters such as bimetallic paddlewheel complexes, yet none of these contain osmium atoms [3]. There have been, however, several reports of macrocyclic ruthenium complexes in which DCAs form bridges across neighboring diruthenium tetracarbonyl units with sawhorse geometries [4]. These are prepared by reactions of $Ru_3(CO)_{12}$ with dicarboxylic acids followed by addition of axial ligands (L) to yield the three different structural motifs illustrated in Scheme 1. Malonic, succinic, glutaric, and adipic acids result in the formation of tetranuclear loops with two bridging DCAs; tartaric, terephthalic, and 4,4′-biphenyldicarboxylic acids lead to hexanuclear triangles with three bridging DCAs; and oxalic acid gives octanuclear squares with four bridging DCAs [5–11].

It was recently shown that microwave heating could be used to prepare diosmium(I) carbonyl sawhorse compounds of the type $Os_2(\mu\text{-carboxylate})_2(CO)_6$ in high yield by reacting $Os_3(CO)_{12}$ with carboxylic acids in a solvent with a high boiling point [12]. We are employing a similar method in our efforts to synthesize the first diosmium sawhorse clusters containing dicarboxylato ligands. By investigating the reactions of $Os_3(CO)_{12}$ with several dicarboxylic acids, we are attempting to produce complexes comprised of Os_2 sawhorse units coordinated to tetradentate DCAs that exhibit both intramolecular and intermolecular bonding modes. This note presents the results of our studies with sebacic (decanedioic) and 1,3-adamantanediacetic acids.

Experimental

Methods and materials

Microwave heating was carried out in a Discover-SP microwave reactor (2455 MHz, CEM Corp., Matthews, NC) using thick-walled, 35-mL glass vessels equipped with a magnetic stir bar and a PFTE-lined cap. In each case, the reactor was set to a maximum pressure of 300 psi, and the highest stir rate was used. Caution was exercised due to the toxic nature of CO and metal carbonyl compounds. All manipulations were carried out in a highly efficient fume hood. Extra precautions were taken when the reactions were under pressure; the microwave reactor was placed in a fume hood

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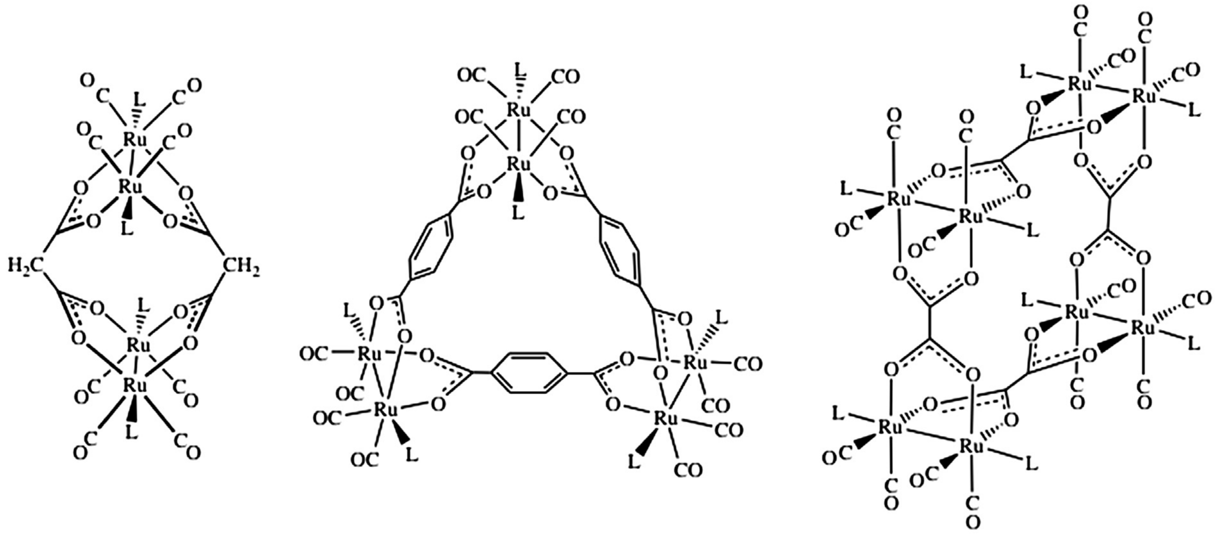

Scheme 1.

and the hood sash was left down until a few minutes after the pressure had been released. The $Os_3(CO)_{12}$ was purchased from Strem; all other reagents and solvents were obtained from Aldrich. All chemicals were used as received. Infrared spectra were obtained using a Nicolet Avatar 320 FTIR with a CaF_2 solution cell. ^1H NMR spectra were recorded on an EM360 NMR spectrometer. Preparative thin-layer chromatography (TLC) was carried out on Analtech silica gel 60 (0.50 mm) plates. Elemental analyses were conducted by ALS Environmental.

*Synthesis of $Os_2(\mu\text{-decanedioate})(CO)_4(dmso)_2$ (**1**)*

A 70.6 mg (0.0779 mmol) sample of $Os_3(CO)_{12}$ and a 25.2 mg (0.125 mmol) sample of sebacic acid were added to 7 mL 1,2-dichlorobenzene in a 35-mL reaction vessel equipped with a magnetic stir bar. This mixture was stirred and irradiated in the microwave reactor at 205 °C for 15 min. The resulting pale yellow solution was left to evaporate until approximately 0.5 mL remained. It was subsequently diluted with dichloromethane and subjected to TLC with an eluent of 1.6:1 hexanes/dichloromethane. Three colorless bands were collected under UV light. The top band consisted of 2.6 mg (4.0% yield) of $Os_4(\mu\text{-}H)_4(CO)_{12}$. Band 2 consisted of 39.8 mg (45.5% yield) of $Os_2(\mu\text{-decanedioate})(CO)_6$. IR ($\nu_{CO}$, $CHCl_3$): 2099 (m), 2065 (vs), 2014 (s), 1997 (vs) cm^{-1}. ^1H NMR ($CDCl_3$): ∂ 1.23 (m, 12H, C_6H_{12}), 2.34 (m, 4H, CH_2) ppm. Band 3 consisted of 1.9 mg of an unknown compound with an IR spectrum very similar to that of band 2. The major product, $Os_2(\mu\text{-decanedioate})(CO)_6$, was dissolved in a mixture of 5 mL $CHCl_3$ and 1.5 mL dmso, then stirred at 70 °C for 40 min. Slow evaporation of the majority of the solvent resulted in the formation of numerous single crystals of cluster **1**. A total of 31.5 mg (31.8% yield based on $Os_3(CO)_{12}$) was collected by filtration. IR ($CHCl_3$, cm^{-1}): 2039 (vs), 1995 (w), and 1962 (vs) for ν_{CO}; 1115 for ν_{SO}. ^1H NMR ($CDCl_3$): ∂ 1.26 (m, 12H, C_6H_{12}), 2.34 (m, 4H, CH_2), 3.16 (s, 6H, CH_3) ppm. Anal. Calc. for $C_{18}H_{28}O_{10}S_2Os_2$: C, 25.46; H, 3.32%. Found: C, 25.64; H, 3.31%.

*Synthesis of $[Os_2(CO)_6]_2(\mu_4\text{-1,3-adamantanediacetate})_2$ (**2**)*

A 63.9 mg (0.0705 mmol) sample of $Os_3(CO)_{12}$ and a 28.4 mg (0.113 mmol) sample of 1,3-adamantanediacetic acid were added to 7 mL 1,2-dichlorobenzene in a 35-mL reaction vessel equipped with a magnetic stir bar. This mixture was stirred and irradiated in the microwave reactor at 208 °C for 15 min. The resulting yellow solution was left to evaporate in the hood. The crude product was dissolved in dichloromethane and subjected to TLC in an eluent of 1:1 hexanes/dichloromethane. Four mostly colorless bands were collected under UV light. The top band consisted of 1.7 mg (2.9% yield) of $Os_4(\mu\text{-}H)_4(CO)_{12}$. Band 2 consisted of 12.4 mg (14.7%) of cluster **2**. IR (ν_{CO}, $CHCl_3$): 2099 (m), 2066 (vs), 2013 (s), and 1997 (vs) cm^{-1}. ^1H NMR ($CDCl_3$): ∂ 1.34 (m, 14H, $C_{10}H_{14}$), 2.00 (s, 2H, CH_2) ppm. Anal. Calc. for $C_{40}H_{36}O_{20}Os_4$: C, 30.07; H, 2.27%. Found: C, 31.44; H, 2.44%. The IR spectra of bands 3 and 4 were very similar to that of band 2, but the identities of these products have not yet been determined because they were produced in much lower quantities. Samples of cluster **2** slowly decompose upon exposure to the air. Crystals of this compound were grown by slow evaporation of a hexanes/CH_2Cl_2 solution under a stream of nitrogen gas.

X-ray crystallography

The crystal structure determinations of compounds **1** and **2** were carried out using a Bruker APEX II CCD-based diffractometer equipped with a low-temperature device and a Mo-target X-ray tube. The diffraction data were collected at 100(2) K for cluster **2** and at 200(2) K for cluster **1** because it was unstable (crystal was broken) at lower temperatures. Data collection, indexing, and initial cell refinements were carried out using APEX2 [13], with the frame integrations and final cell refinements carried out using SAINT [14]. An absorption correction was applied using the program SADABS [15], and all non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in idealized positions and were refined using a riding model. The structures were solved and refined using SHELXTL [16]. The structures were examined using the Addsym subroutine of PLATON to ensure that no additional symmetry could be applied to the models [17]. Refinement details and structural parameters for both compounds are summarized in Table 1.

Results and discussion

Syntheses of new osmium clusters

Reaction of $Os_3(CO)_{12}$ with sebacic acid at 205 °C leads to the formation of $Os_2(\mu\text{-decanedioate})(CO)_6$ in 46% yield, and further