Mo₂(O₂CPh)₆(PEt₃)₂, the Second Example of Bridging η¹-O₂CR for Dimolybdenum (III) Compounds

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From the reaction of Mo₂Cl₄(THF)₃ with excess of NaO₂CPh and PEt₃ in THF three types of crystals have been obtained and recrystallized in CH₂Cl₂. They are brown compound Mo₂(O₂CPh)₆(PEt₃)₂·2CH₂Cl₂ (1), yellow β-Mo₂(O₂CPh)₄ (2), and black Mo₂O₆(O₂CPh)₆(PEt₃)₂·CH₂Cl₂ (3). When a strict ratio of Mo₂Cl₄(THF)₃:NaO₂CPh = 1:2 was applied, Mo₂(O₂CPh)₄(THF)₂ (4) was the only compound separated from the THF reaction mixture. Their structures have been determined by X-ray crystallography. There are three coordination modes of benzoate in 1: bridging η²-O₂CPh, bridging η¹-O₂CPh and terminal O₂CPh groups. Compound 2 is chemically well known, but was found to pack differently from the previously reported structure. Mo₂O₄(O₂CPh)₆(PEt₃)₂·CH₂Cl₂ (3) is a mixed-valence Mo (IV, V) tetranuclear compound in a butterfly arrangement. A molecule of 4 is actually a Mo₂(O₂CPh)₄ molecule with two THF molecules axially coordinating to the molybdenum atoms. The crystallographic data for these compounds are as follows: 1, triclinic P1 with a = 11.612(3) Å, b = 11.970(2) Å, c = 12.135(3) Å, α = 95.55(2)°, β = 117.51(2)°, γ = 98.84(2)°, V = 1450.8(7) Å³, Z = 1, R = 0.0673, and Rw = 0.0936; 2, monoclinic P2₁/n with a = 14.437(2) Å, b = 5.6168(7) Å, c = 15.979(3) Å, β = 93.93(1)°, V = 1292.7(4) Å³, Z = 2, R = 0.0217, and Rw = 0.0352; 3, trigonal (hexagonal setting) R₃ with a = 28.83(4) Å, c = 44.98(2) Å, V = 32370(10) Å³, Z = 18, R = 0.067, and Rw = 0.0451; 4, monoclinic P2₁/c with a = 9.456(4) Å, b = 17.757(8) Å, c = 10.887(3) Å, β = 109.63(2)°, V = 1722(2) Å³, Z = 2, R = 0.0330, and Rw = 0.0451.

KEY WORDS: Carboxylate; molybdenum; mixed valence.

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INTRODUCTION

The synthesis and characterization of edge-sharing dimolybdenum (III) compounds is being pursued in our laboratory in order to study the metal-metal bonding in different environments. \( \text{Mo}_2\text{Cl}_6(\text{THF})_3 \) has proved to be a useful starting material, allowing, for example, the successful synthesis of \( \text{Mo}_2\text{Cl}_4(\text{OAc})_2(\text{PET}_3)_2 \) [1]. From this compound, one could envision that a series of compounds might be synthesized. The reaction of \( \text{Mo}_2\text{Cl}_6(\text{THF})_3 \) with excess of KOAc and PET_3 to afford \( \text{Mo}_2\text{Cl}_4(\text{OAc})_2(\text{PET}_3)_2 \) seems quite straightforward, in which two chloride and the three labile THF groups are replaced by stronger ligands PET_3 and OAc⁻. One might have expected that, using other carboxylate salts, similar compounds with a general formula \( \text{Mo}_2\text{Cl}_4(\text{O}_2\text{CR})_2(\text{PET}_3)_2 \) could be obtained. On the contrary, the reactions of NaO_2CPh and Mo_2Cl_6(THF)_3 turned out to be very different. The reaction not only gave an unexpected compound \( \text{Mo}_2(\text{O}_2\text{CPh})_6(\text{PET}_3)_2 \cdot 2\text{CH}_2\text{Cl}_2 \) (1), it also gave a Mo(II) compound \( \beta\text{-Mo}_2(\text{O}_2\text{CPh})_4 \) (2) and a Mo(IV, V) compound \( \text{Mo}_4\text{O}_6(\text{O}_2\text{CPh})_6(\text{PET}_3)_2 \cdot \text{CH}_2\text{Cl}_2 \) (3). Compounds (2) and (3) can be regarded as the disproportionation products of Mo(III). Even when a strict ratio of \( \text{Mo}_2\text{Cl}_6(\text{THF})_3 : \text{NaO}_2\text{CPh} = 1:2 \) applied, only a Mo(II) compound \( \text{Mo}_2(\text{O}_2\text{CPh})_4(\text{THF})_2 \) (4) was separated from the reaction mixture, instead of the expected \( \text{Mo}_2\text{Cl}_4(\text{O}_2\text{CPh})_3(\text{PET}_3)_2 \). In this paper we report the syntheses and structures of four new compounds and present some discussion of the chemistry that leads to these diverse and unanticipated products.

EXPERIMENTAL SECTION

General Procedures. All manipulations were carried out under an atmosphere of nitrogen. Standard Schlenk and vacuum line techniques were used. Tetrahydrofuran, and hexanes were dried over and freshly distilled from potassium/sodium benzophenone ketyl, while dichloromethane was distilled from P_2O_5 prior to use. Triethylphosphine were purchased from Strem Chemicals and used as received. Anhydrous sodium benzoate was heated in vacuum before use. \( \text{Mo}_2\text{Cl}_6(\text{THF})_3 \) was prepared by literature methods [2] and dried in vacuum prior to use.

Preparation of \( \text{Mo}_2(\text{O}_2\text{CPh})_6(\text{PET}_3)_2 \cdot 2\text{CH}_2\text{Cl}_2 \) (1), \( \beta\text{-Mo}_2(\text{O}_2\text{CPh})_4 \) (2) and \( \text{Mo}_4\text{O}_6(\text{O}_2\text{CPh})_6(\text{PET}_3)_2 \cdot \text{CH}_2\text{Cl}_2 \) (3). A mixture of 0.50 g \( \text{Mo}_2\text{Cl}_6(\text{THF})_3 \) (0.81 mmol) and an excess of sodium benzoate (1.0 g, 6.9 mmol) was stirred in 20 mL of THF at 40°C for about 1 hr. When the color of the suspension changed from purple–red to yellow–brown, 0.36 mL (2.4 mmol) of PET_3 was added. The mixture was stirred for 24 hr at room