Synthesis and Copolymerization Reaction of a Triosmium Alkylidyne Carbonyl Cluster

\[ \text{[Os}_3(\mu-\text{H})_2(\text{CO})_9(\mu_3-\text{CNC}_5\text{H}_4-\text{CH}=\text{CH}_2)] \]

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A neutral triosmium alkylidyne carbonyl cluster containing the 4-vinylpyridine (4vpy) moiety \( [\text{Os}_3(\mu-\text{H})_2(\text{CO})_9(\mu_3-\text{CNC}_5\text{H}_4-\text{CH}=\text{CH}_2)] \) (1) has been prepared as red crystalline solids in good yield. Monomer (1) was copolymerized with styrene in the presence of \( \alpha,\alpha'-\text{azobis(isobutyronitrile)} \) (AIBN) in chloroform at 60°C and a polymer-immobilized alkylidyne cluster of osmium was obtained. To compare the spectroscopic properties with the copolymers, a structurally similar repeating unit of the copolymers, \( [\text{Os}_3(\mu-\text{H})_2(\text{CO})_9(\mu_3-\text{CNC}_5\text{H}_4-\text{CH}_2\text{CH}_3)] \) (2), has also been synthesized and characterized.

KEY WORDS: Triosmium alkylidyne carbonyl clusters; polyvinylpyridine; MLCT transition.

INTRODUCTION

In recent years, there has been growing interest in the synthesis of polymer-immobilized clusters of the noble metals (PCNM) due to their potential applications in the production of different polymeric materials with unusual properties [1]. The wide and selective applications of PCNM as catalysts in organic syntheses have also attracted much attention [2–6]. Approaches based on the (co)polymerization of cluster-containing monomers have not been studied extensively [7]. In view of this, we have prepared a series

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of soluble PCNM with complete spectroscopic characterization and molecular weight determination.

In this work, cluster (1) was first prepared as a new vinyl type monomer of Os₃-derivative and its copolymerization reaction with styrene was studied.

**EXPERIMENTAL**

All reactions unless otherwise stated were carried out under an atmosphere of dry dinitrogen using standard Schlenk and vacuum line techniques. Dichloromethane was dried over CaH₂ and n-hexane was distilled from sodium benzophenone ketyl. The compound [Os₃(μ-H)₃(CO)₉(μ₃-CCI)] was prepared as described previously [8]. AIBN was recrystallized from methanol. Styrene and 4-vinylpyridine were freshly distilled under vacuum immediately before use. All other reagents were used as received. Infrared spectra were recorded on a BIO-RAD FTS-7 IR spectrometer using 0.5 mm solution cells. The ¹H NMR spectra were recorded on a JEOL GSX270FT-NMR spectrometer using deuteriated solvents as lock and reference [SiMe₄ (δ = 0)]. Mass spectra were recorded on a Finnigan MAT 95 instrument with fast atom bombardment technique. Electronic absorption spectra were obtained in a microprocessor-controlled Perkin Elmer UV/VIS spectrophotometer Lambda 3B, thermostatted by a Lauda circulating bath. Routine separation of products were performed in the air by thin-layer chromatography with plates coated with Merck Kieselgel 60 GF₂₅₄.

**Synthesis of Monomer (1)**

[Os₃(μ-H)₃(CO)₉(μ₃-CCI)] (87.3 mg, 0.1 mmole) was dissolved in CH₂Cl₂ (7 ml). An excess of 4-vinylpyridine (0.11 ml, 1.0 mmole) was added and DBU (15.2 mg, 0.1 mmole) was added dropwise while the reaction mixture was stirred at 0°C. Immediate color change from pale yellow to deep red was observed. After stirring for 30 minutes, the solution was concentrated to 3 ml under vacuo. Purification was accomplished by column chromatography, eluting with n-hexane: CH₂Cl₂ (60:40 v/v). Complex (1) was isolated and obtained as red crystalline solids in 69% yield (65 mg) after recrystallization from a n-hexane/CH₂Cl₂ solution.

IR (CHCl₃) vₓ/cm⁻¹: 2089 m, 2055 vs, 2024 vs, 1984 s, 1949 m, 1934 m. ¹H NMR (CD₂Cl₂): δ 9.52 (d, 2.6-pyH, J = 7.0 Hz), δ 7.41 (d, 3.5-pyH, J = 7.0 Hz), δ 6.75 (dd, CH = CH₂, J = 17.6 Hz, 10.7 Hz), δ 6.33 (d, CH = CH₂, J = 17.6 Hz), δ 5.97 (d, CH = CH₂, J = 10.7 Hz), δ -18.96