CHEMISTRY LETTERS, pp. 983-986, 1992.

Synthesis of Trinuclear Molybdenum Cluster Complex with Novel Skeleton, $[Mo_3(\mu_3\text{-}CCH_3)(\mu_3\text{-}O)(\mu\text{-}C_6H_5COO)_6(CH_3OH)_3]Cl$ through Bridging Carboxylate Ligand Substitution

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$[Mo_3(\mu_3\text{-}CCH_3)(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(H_2O)_3]^+$ undergoes bridging acetates substitution with benzoate ions in $CH_3OH\text{-}CH_3CN$ mixed solvent to give $[Mo_3(\mu_3\text{-}CCH_3)(\mu_3\text{-}O)(\mu\text{-}C_6H_5COO)_6(CH_3OH)_3]^+$, which can never be synthesized in principle by the conventional direct method.

Molybdenum in the oxidation state IV is known to form a variety of trinuclear complexes with metal-metal direct bond.[1,2] With carboxylate ions, they give complexes with a characteristic "$Mo_3(\mu_3\text{-}O)_2(\mu\text{-}RCOO)_6$" core. In addition to them, alkylidyne capped complexes, $[Mo_3(\mu_3\text{-}CCH_3)(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(H_2O)_3]^+$ [3a-c] and $[Mo_3(\mu_3\text{-}CCH_2CH_3)(\mu_3\text{-}O)(\mu\text{-}CH_3CH_2COO)_6(H_2O)_3]^+$,[3d] are also reported. They are interesting because they have unique μ_3-carbon donor (the carbyne ligand) and yet they are unusually stable in aqueous media. The μ_3-CR capped complexes were obtained by the reactin of $Mo(CO)_6$ with a mixture of $(RCO)_2O$ and RCOOH ($R=CH_3$, CH_3CH_2). The ^{13}C tracer study[3a] showed that the μ_3-CR ligand comes from alkyl group of carboxylic acid or its anhydride and is produced in the process of reduction. Therefore, the alkylidyne complexes so far reported, $[Mo_3(\mu_3\text{-}CR)(\mu_3\text{-}O)(\mu\text{-}RCOO)_6L_3]^+$, have the same R group in the μ_3-CR and μ-RCOO ligands. The objective of this paper is two-fold : firstly, we found for the first time that carboxylate bridged molybdenum trinuclear complexes do undergo bridging carboxylate substitution; secondly, by utilizing this substitution reaction, we successfully isolated the titled ethylidyne complex which has different R groups in the μ_3-capping and μ-bridging ligands.

Although many molybdenum trinuclear complexes with carboxylate bridges have been reported,[1,2] there has been no report on ligand substitution behavior except for our recent study concerning the terminal ligand substitutions.[4] While investigating the reactivity of molybdenum trinuclear complexes of this type, we found that the bridging acetates in $[Mo_3(\mu_3\text{-}X)(\mu_3\text{-}X')(\mu\text{-}CH_3COO)_6(H_2O)_3]^{n+}$ can fully or

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partly be substituted by other carboxylates ($RCOO^-$) including amino acid under certain conditions. The ease with which the substitution takes place appears to depend on the kind of the trinuclear core unit, "$Mo_3(\mu_3\text{-}X)(\mu_3\text{-}X')$",5) and the difference in pK_a values between incoming ($RCOO^-$) and leaving acetate.6) The titled compound $[Mo_3(\mu_3\text{-}CCH_3)(\mu_3\text{-}O)(\mu\text{-}C_6H_5COO)_6(CH_3OH)_3]^+$ was prepared as follows (Eq. 1).

$$[Mo_3(\mu_3\text{-}CCH_3)(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(H_2O)_3]^+$$

$$\xrightarrow[CH_3OH/CH_3CN]{C_6H_5CO_2H} [Mo_3(\mu_3\text{-}CCH_3)(\mu_3\text{-}O)(\mu\text{-}C_6H_5CO_2)_6(CH_3OH)_3]^+ \qquad (1)$$

$[Mo_3(\mu_3\text{-}CCH_3)(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(H_2O)_3]Cl\cdot 6H_2O$3a,4) (0.5 g) was dissolved in CH_3OH (20 cm^3) and diluted with CH_3CN (100 cm^3). To this solution, benzoic acid (1.0 g) and a few drops of Et_3N were added and the resulting orange solution was refluxed for 45 min. The solution was acidified with 0.5 M HCl (20 cm^3) and evaporated to dryness (M = mol dm^{-3}). Orange residue was washed throughly with Et_2O to remove unreacted benzoic acid. The resulting solid was again dissolved in CH_3OH (500 cm^3) and purified by a Dowex 50W-X2 cation exchange column (H^+ form). The orange band was eluted with 0.1 M HCl/CH_3OH solution. The eluate was concentrated to ca. 50 cm^3 and allowed to stand for a day at room temparature, to give orange solid (Yield 0.25 g). Recrystallization from methanol gave orange columnar crystals of $[Mo_3(\mu_3\text{-}CCH_3)(\mu_3\text{-}O)(\mu\text{-}C_6H_5COO)_6(CH_3OH)_3]Cl\cdot 3CH_3OH$.7)

This compound crystallizes in triclinic space group $P\bar{1}$ with $Z=2$.8) The X-ray structure of the complex cation is illustrated in Fig. 1. The bridging ligands are fully replaced by benzoate ions, and the "$Mo_3(\mu_3\text{-}CCH_3)(\mu_3\text{-}O)$" core unit remains unchanged. The complex ion has a pseudo C_3 axis passing through the μ_3-C and μ_3-O atoms. Three terminal positions are occupied by CH_3OH and overall trinuclear structure resembles those of structurally characterized analogues, $[Mo_3(\mu_3\text{-}CCH_3)(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(H_2O)_3]^+$ 3a,b) and $[Mo_3(\mu_3\text{-}CCH_2CH_3)(\mu_3\text{-}O)(\mu\text{-}CH_3CH_2COO)_6(H_2O)_3]^+$.3c) The Mo-Mo distances range from 2.756(2) to 2.808(2) Å, indicating the presence of the Mo-Mo direct bond as in the analogues.9)

The cyclic voltammogram of the benzoate complex $[Mo_3(\mu_3\text{-}CCH_3)(\mu_3\text{-}O)(\mu\text{-}C_6H_5COO)_6(CH_3OH)_3]^+$ in CH_3OH exhibits a reversible one electron redox wave corresponding to Mo_3(IV,IV,IV)/(IV,IV,V) at +0.28 V vs. Ag/Ag^+.10) The corresponding $E_{1/2}$ value of the acetate complex $[Mo_3(\mu_3\text{-}CCH_3)(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(CH_3OH)_3]^+$ is at +0.20 V vs. Ag/Ag^+. The $E_{1/2}$ value of the benzoate complex shifts far positively, reflecting a decrease in pK_a of the bridging ligands. A similar relation between $E_{1/2}$ and pK_a of bridging ligands is known for trinuclear Fe(III) complexes11) and dinuclear Ru(III) complexes.12)

Further related works are now in progress.

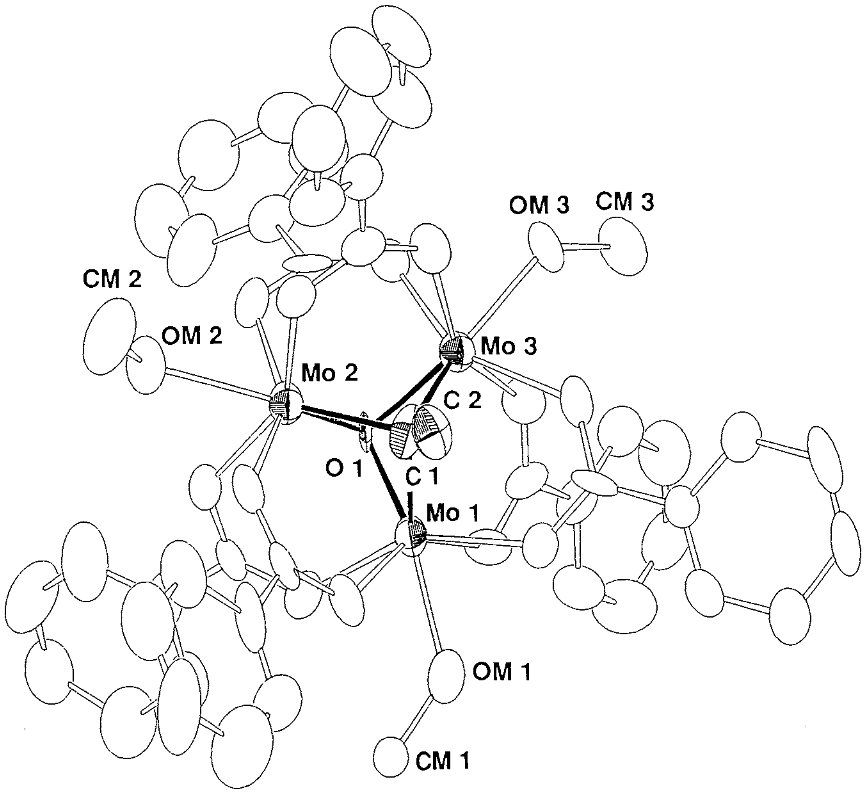

Fig. 1. The structure of $[Mo_3(\mu_3\text{-}CCH_3)(\mu_3\text{-}O)(\mu\text{-}C_6H_5COO)_6(CH_3OH)_3]^+$. Selected bond distances (Å) and angles (°) : Mo1-Mo2 2.756(2), Mo1-Mo3 2.808(2), Mo2-Mo3 2.784(2), Mo1-C1 2.06(2), Mo2-C1 2.07(2), Mo3-C1 2.10(2), Mo1-O1 1.96(1), Mo2-O1 1.95(1), Mo3-O1 2.00(1), Mo1-Mo2-Mo3 60.91(6), Mo1-Mo3-Mo2 59.05(6), Mo2-Mo1-Mo3 60.04(6).

This work was supported by Grant-in-Aids for Scientific Research No.02303006 and No. 01430009 (Priority Area of "Molecular Approaches to Non-equilibrium Process in Solution") from the Ministry of Education, Science, and Culture, Japan.

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4) K. Nakata, A. Nagasawa, N. Soyama, Y. Sasaki, and T. Ito, *Inorg. Chem.*, **30**, 1575 (1991). In this paper, we found that the CCH_3-cap shows remarkable labilizing effect for the substitution of the terminal unidentate ligand.

5) We have investigated the bridging acetate substitution of $[Mo_3(\mu_3\text{-}X)(\mu_3\text{-}X')(\mu\text{-}CH_3COO)_6(H_2O)_3]^{n+}$ (X=X'=O; X=CCH_3, X'=O) by other carboxylates such as benzoate, monochloroacetate, and alanine, and found that the complex having the "$Mo_3(\mu_3\text{-}CCH_3)(\mu_3\text{-}O)$" core unit undergoes much faster substitution. This is the case with the rate of the terminal ligand substitution.4) (K. Nakata, Ph. D. Thesis, Tohoku University, Sendai, 1992). Details will be reported elsewhere.

6) As pK_a of the incoming carboxylate becomes lower, the bridging ligand substitution is difficult to occur or only partial substitution takes place. (K. Nakata, Ph. D. Thesis, Tohoku University, Sendai, 1992). Details will be reported elsewhere.

7) Elemental analysis. Found: C , 45.74 ; H , 4.46 ; Cl , 2.88%. Calcd for $C_{50}H_{57}O_{19}ClMo_3$: C , 46.73 ; H , 4.47 ; Cl , 2.76%. ^1H NMR (CD_3OD) δ=2.40(s, 3H μ_3-CCH_3), 7.0-9.0(m, 30H μ-C_6H_5COO). $^{13}C\{^1H\}$ NMR (CD_3OD) δ=32.5(μ_3-$C\mathit{C}H_3$), 129.3, 129.5, 131.0, 131.1, 132.3, 132.5, 133.8, 134.0(μ-C_6H_5COO), 178.3, 178.6(μ-$C_6H_5\mathit{C}OO$), 296.4(μ_3-$\mathit{C}CH_3$). Absorption maxima in CH_3OH: λ_{max}=338 nm (ε/M^{-1} cm^{-1} per Mo_3 = 14400).

8) The crystal ($0.20\times0.25\times0.10$ mm^3) sealed in a glass capillary was used for data collection. Crystal data: $[Mo_3(\mu_3\text{-}CCH_3)(\mu_3\text{-}O)(\mu\text{-}C_6H_5COO)_6(CH_3OH)_3]Cl\cdot3CH_3OH$, $C_{50}H_{57}O_{19}ClMo_3$, fw= 1285.26, triclinic, space group $P\bar{1}$, a=11.960(3) Å, b=22.317(7) Å, c=10.235(6) Å, α=96.44(4) °, β=91.43(4) °, γ=89.86(3) °, V=2714(2) $Å^3$, Z=2, d_{calcd}=1.573 g cm^{-3}, d_{obsd}=1.54 g cm^{-3} (floatation method). Data were collected on a Rigaku AFC-5R diffractometer at 13°C with graphite-monochromated Cu Kα radiation. A total of 8215 reflections were obtained and independent 4924 reflections with $|F_o|>3\sigma|F_o|$ were used in the structure determination. Though counter anion, Cl^-, was disordered and its positon could not be determined, the presence of Cl^- has been confirmed by the elemental analysis and the specific gravity measurement. The current R factor is 0.09.

9) The Mo-Mo distances reported for $[Mo^{IV}{}_3(\mu_3\text{-}X)(\mu_3\text{-}X')(\mu\text{-}RCOO)_6(H_2O)_3]^{n+}$ range from 2.742 to 2.767 Å.2)

10) Cyclic voltammograms were measured in CH_3OH containing n-Bu_4NPF_6(0.1 M) with glassy carbon working-, Pt counter- and Ag/Ag^+ (0.1 M $AgClO_4$ in CH_3OH) reference electrodes.

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(Received March 27, 1992)