Notes

Synthesis and Characterization of Molybdenum-Triosmium Alkyne Complexes

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Synthesis of alkyne ($RC{\equiv}CR$) substituted clusters and the scission of alkyne $C{\equiv}C$ bonds on a cluster have been of current interest due to their potential as models for the $C{\equiv}C$ bond activation on metal surfaces.[1] We recently described the synthesis and structures of tungsten-triosmium alkyne complexes $CpWOs_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}C_2R_2)(\mu\text{-}H)$ ($Cp{=}\eta^5\text{-}C_5H_5$) together with their conversion to the dialkylidyne complexes $CpWOs_3(CO)_9(\mu_3\text{-}CR)_2H$ upon decarbonylation.[2] In examining the generality of this alkyne scission reaction in group 6 metals-triosmium mixed metal cluster complexes, we have prepared analogous molybdenum-triosmium alkyne complexes. The reaction of $Os_3(CO)_{10}(NCMe)_2$ with $CpMo(CO)_3H$ produces two molybdenum-triosmium cluster complexes, $CpMoOs_3(CO)_{12}(\mu\text{-}H)$ (1) and $CpMoOs_3(CO)_{11}(\mu\text{-}H)_3$ (2). The cluster compound 1 reacts with various alkynes to form two isomeric alkyne derivatives (symmetrical and/or unsymmetrical), $CpMoOs_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}C_2R_2)(\mu\text{-}H)$. Both isomers show identical structures as were shown in tungsten-triosmium alkyne complexes.[2] The symmetrical isomer of an electron-withdrawing alkyne ($R{=}CO_2Et$) undergoes isomerization to the unsymmetrical isomer upon heating. In contrast with the tungsten-triosmium alkyne complexes, the present molybdenum alkyne complexes have failed to undergo alkyne scission reactions.

Experimental Section

General Comments. Solvents were dried prior to use. Anhydrous Me_3NO (mp. 225-230°C) was obtained from Me_3-$NO{\cdot}2H_2O$ (98% Aldrich Chemical Ltd.) by sublimation (three times) at 90-100°C under vacuum. $Os_3(CO)_{11}(NCMe)$[3] and $CpMo(CO)_3H$[4] were prepared as described in the literature. All reactions were carried out under an atmosphere of nitrogen in oven-dried glassware. The progress of the reactions was monitored by analytical thin-layer chromatography (precoated TLC plates, Silica Gel 60 F-254, E. Merck). Preparative TLC was carried out using glass-backed silica gel plates ($20{\times}20$ cm) prepared from silica gel G (Type 60, E. Merck).

Infrared spectra were obtained on a Nicolet 5-MX FT-IR spectrophotometer. ^{1}H-NMR (300 MHz) spectra were recored on a Bruker AM-300 spectrometer.

Reaction of $Os_3(CO)_{10}(NCMe)_2$ with $CpMo(CO)_3H$. A dichloromethane (100 m*l*)-acetonitrile (40 m*l*) solution of $Os_3(CO)_{11}(NCMe)$ (137.7 mg, 0.150 mmol) was treated with an acetonitrile solution (100 m*l*) of anhydrous trimethylamine oxide (11.2 mg, 0.150 mmol) to produce $Os_3(CO)_{10}(NCMe)_2$. After evaporation of the solvent *in vacuo*, the $Os_3(CO)_{10}(NCMe)_2$ was redissolved in toluene (100 m*l*). To this solution was slowly added solid $CpMo(CO)_3H$ (110.3 mg, 0.448 mmol). The reaction mixture was heated to reflux for 0.5 h. Evaporation of the solvent under vacuum and purification by preparative TLC (petroleum ether : dichloromethane=3 : 2) provided brown $CpMoOs_3(CO)_{12}(\mu\text{-}H)$ (1, 74.1 mg, 0.0693 mmol, 46%, $R_f{=}0.33$) and orange-red $CpMoOs_3(CO)_{11}(\mu\text{-}H)_3$ (2, 8.3 mg, 0.0083 mmol, 5.3%, $R_f{=}0.39$) as crystalline solids.

Compound 1: ^{1}H-NMR ($CDCl_3$, 25°C) δ 5.28 (s, 5H), −17.5 (s, 1H); IR (CCl_4) ν (CO) 2090 (m), 2068 (m), 2058 (vs), 2042 (s), 1996 (s), 1946 (vw), 1914 (w) cm^{-1}.

Compound 2: ^{1}H-NMR ($CDCl_3$, 25°C) δ 5.3 (s, 5H), −19.5 (br, 3H); IR (CCl_4) ν (CO) 2094 (m), 2063 (vs), 2055 (vs), 2014 (vs), 2006 (s), 1991 (s), 1958 (s) cm^{-1}.

Reaction of 1 with Di-p-tolylacetylene. A dichloromethane (30 m*l*)-acetonitrile (10 m*l*) solution of 1 (20.0 mg, 0.0187 mmol) was treated with an acetonitrile solution (10 m*l*) of anhydrous Me_3NO (1.47 mg, 0.0196 mmol). After evaporation of the solvent *in vacuo*, to the toluene solution (30 m*l*) of the residue was added an excess of di-p-tolylacetylene (7.7 mg, 0.0374 mmol) at room temperature. The resulting solution was heated at 95°C for 1 h. After evaporation of the solvent, purification by preparative TLC afforded orange $CpMoOs_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}C_2Tol_2)(\mu\text{-}H)$ (3a, 14.5 mg, 0.0119 mmol, 64%, $R_f{=}0.31$): ^{1}H-NMR ($CDCl_3$, 25°C) δ 6.92-6.79 (AB pattern, 8H), 5.46 (s, 5H), 2.28 (s, 6H), −20.8 (s, 1H); IR(C_6H_{12}) ν(CO) 2080 (m), 2063 (s), 2020 (vs), 2006 (w), 1985 (m), 1966 (w) cm^{-1}.

Reaction of 1 with Ethyne. A dichloromethane (40 m*l*)-acetonitrile (20 m*l*) solution of 1 (20 mg, 0.0188 mmol) was treated with anhydrous Me_3NO (1.48 mg, 0.0198 mmol) in a 500 m*l* glass pressure bottle. After evaporation of the solvent *in vacuo*, the residue was dissolved in toluene (50 m*l*), a partial vacuum was drawn over the solution, and the bottle was charged with C_2H_2 to a pressure of 35 psig. The resulting solution was heated at 85°C for 0.5 h. Evaporation of the solvent and purification by preparative TLC (petroleum ether : dichloromethane=3 : 2) gave orange $CpMoOs_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}C_2H_2)(\mu\text{-}H)$ (4a, 2.8 mg, 0.0028 mmol, 15%, $R_f{=}0.5$); ^{1}H-NMR ($CDCl_3$, 25°C) δ 9.35 (s, 2H), 5.42 (s, 5H), −21.16 (s, 1H); IR (CCl_4) ν (CO) 2083 (w), 2065 (s), 2022 (vs), 2006 (m), 1994 (m), 1962 (w) cm^{-1}.

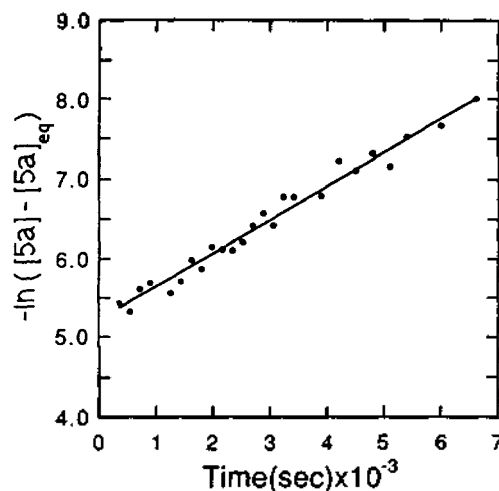**Reaction of 1 with Diethyl Acetylenedicarboxylate.** The same procedure was used as for the preparation of
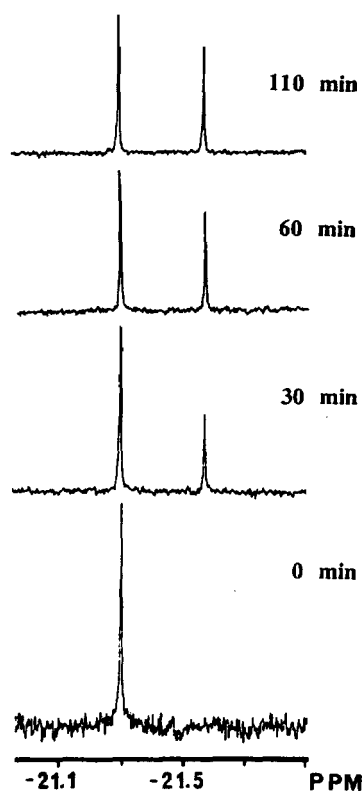
Figure 1. ¹H-NMR spectra (hydride region) for the isomerization of **5a** to **5b** as a function of time (300 MHz, toluene-d_8, 80℃).

Figure 2. First-order rate plot for the isomerization of **5a** to **5b** at 80℃ : $[5a]_{eq}$=equilibrium concentration of **5a**.

first-order kinetics and showed good fits to a common plot of $-\ln\{[5a]-[5a]_{eq}\}$ vs. time (see Figure 2).

Results and Discussion

The reaction of $Os_3(CO)_{10}(NCMe)_2$ with excess $CpMo(CO)_3H$ in refluxing toluene produces both a monohydrido complex, $CpMoOs_3(CO)_{12}(\mu\text{-}H)$ (**1**, 46%), and a trishydrido complex, $CpMoOs_3(CO)_{11}(\mu\text{-}H)_3$ (**2**, 5%). The structure of compound **1** is isomorphous with that of the known tungsten analogue, $CpWOs_3(CO)_{12}(\mu\text{-}H)$,[5] based on the spectroscopic data. The trishydrido compound **2** was previously isolated by Shore and co-workers[6] from the reaction of $(\mu\text{-}H)_2Os_3(CO)_{10}$ with $[CpMo(CO)_2]_2$ and was structurally characterized as shown below.

3a, except that a toluene solution of the reaction mixture was heated at 80℃ for 1.5 h using compound **1** (50 mg, 0.047 mmol) with diethyl acetylenedicarboxylate (16.4 mg, 15.5 µl, 0.0964 mmol). The solvent was evaporated, and the crude product was purified by preparative TLC (dichloromethane : petroleum ether=5 : 1) to provide a mixture of two isomers $CpMoOs_3(CO)_{10}[\mu_3\text{-}\eta^2\text{-}C_2(CO_2Et)_2]$ (µ-H) (**5a** and **5b**, 19.6 mg, 0.0146 mmol, 31%, R_f=0.38) as an orange solid. Recrystallization from petroleum ether-dichloromethane at room temperature gave orange crystals of isomer **5a** (11.2 mg, 18%, 0.0083 mmol). The solvent of the red supernatant was evaporated and red crystals of isomer **5b** (8.4 mg, 13%, 0.0063 mmol) were isolated after recrystallization from methanol-dichloromethane at −10℃ .

Compound **5a**: ¹H-NMR (CDCl₃, 25℃) δ 5.47 (s, 5H), 4.22 (q, 4H, J=7.1 Hz), 1.27 (t, 6H, J=7.1 Hz), −21.29 (s, 1H); IR (C_6H_{12}) ν (CO) 2155 (w), 2126 (s), 2091 (m), 2971 (s), 2056 (m), 2032 (vs), 2014 (m), 1996 (w) cm⁻¹.

Compound **5b**: ¹H-NMR (CDCl₃, 25℃) δ 5.39 (s, 5H), 4.18 (q, 4H, J=7.1 Hz), 1.28 (t, 6H, J=7.1 Hz), −21.57 (s, 1H); IR (C_6H_{12}) ν (CO) 2155 (w), 2126 (s), 2091 (m), 2971 (s), 2056 (m), 2032 (vs), 2014 (m), 1996 (w) cm⁻¹.

Isomerization of 5a to 5b. Orange crsytals of compound **5a** (ca, 5 mg) were transferred to an NMR tube, and toluene-d_8 (0.6 ml) was added to an NMR tube. The tube was heated at 80℃ , while the hydride signals, at −21.29 for **5a** and at −21.57 for **5b**, were monitored periodically by ¹H-NMR (see Figure 1). The data followed reversible
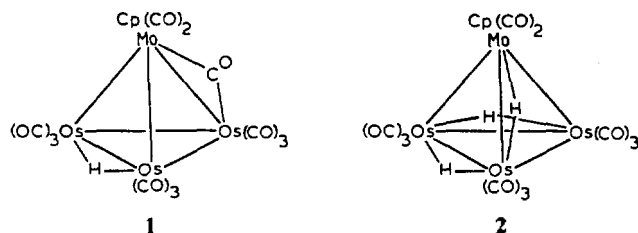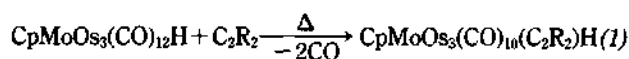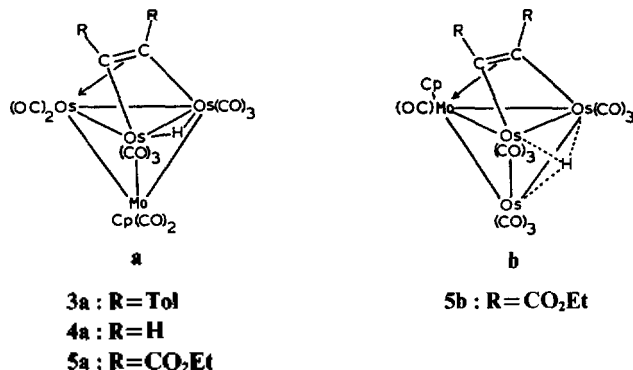

1   **2**

The complex $CpMoOs_3(CO)_{12}H$ reacts with various alkynes to give isomeric $CpMoOs_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}C_2R_2)H$ clusters according to Eq. (1). Better yields have been obtained by initial decarbonylation with $Me_3NO/MeCN$ followed by heating in toluene (80-95℃). Two isomers of $CpMoOs_3(CO)_{10}(C_2R_2)H$, symmetrical (isomer **a**) and/or

$$CpMoOs_3(CO)_{12}H + C_2R_2 \xrightarrow[-2CO]{\Delta} CpMoOs_3(CO)_{10}(C_2R_2)H \quad (1)$$

unsymmetrical (isomer **b**), are formed depending on the substituents R of an alkyne. The structures of the two isomers are also isomorphous with those of the known tungsten analogues, symmetrical $CpWOs_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}C_2R_2)(\mu\text{-}H)$ and unsymmetrical $CpWOs_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}C_2R_2)(\mu_3\text{-}H)$, respectively.[2]

Notes

Bull. Korean Chem. Soc., Vol. 14, No. 2, 1993 297

3a : R=Tol
4a : R=H
5a : R=CO₂Et

5b : R=CO₂Et

With the two alkynes [R=H or Tol (=p-C$_6$H$_4$Me)] only symmetrical isomers (3a and 4a) are formed, while both symmetrical (5a) and unsymmetrical (5b) isomers are obtained with an electron-withdrawing alkyne (R=CO₂Et). The ¹H-NMR spectra of symmetrical isomers 3a, 4a and 5a reveal that both substituents R₂ in an alkyne are equivalent. With the tungsten analogue of 5b, two distinct ethyl groups of resonances were observed in the ¹H-NMR spectrum, indicating its unsymmetrical structure.[2] The unsymmetrical nature of this tungsten analogue is due to an unsymmetrical ligand arrangement with respect to the tungsten atom. The ¹H-NMR spectrum of 5b at room temperature, however, exhibits a single resonance for the two ethyl groups. This may indicate that two ligands, a carbonyl and a cyclopentadienyl ligands, on the molybdenum atom undergo a fast two-fold exchange at room temperature. The close similarities of the carbonyl regions of the IR spectra between the tungsten[2] and molybdenum complexes indicate the structural correspondence in the various alkyne clusters.

The diaryl alkyne WOs₃ clusters were reported to undergo scission of the alkyne ligand to provide dialkylidyne compounds.[2] However, attempted alkyne scission reaction with compounds 3a, 4a and 5a did not produce any alkyne scission products and only resulted in extensive decomposition of the starting materials. The symmetrical isomer 5a isomerizes to the unsymmetrical isomer 5b upon heating. Kinetic measurements for the isomerization 5a→5b were carried out at 80℃ by ¹H-NMR spectroscopy. Crystals of 5a were dissolved in toluene-d₈ in an NMR tube, and signals due to 5b were observed to grow in as a function of time. Relative concentrations of the two isomers were measured by integration of the peaks at δ −21.29 due to μ-H of 5a and at δ −21.57 due to μ₃-H of 5b in the ¹H-NMR spectrum as is shown in Figure 1. The two isomers are in equilibrium, and analysis according to reversible first order kinetics gives good fits of experimental data: K_{eq}=[5a]/[5b]=0.749± 0.004, k_{obs}=(4.22± 0.23)×10⁻⁴ s⁻¹, k_1=(1.81± 10)×10⁻⁴ s⁻¹, and k_{-1} =(2.41± 0.13)×10⁻⁴ s⁻¹ (see Figure 2). These data compare with k=(4.1± 0.2)×10⁻⁵ s⁻¹ at 100℃ reported in the irreversible isomerization of CpWOs₃ (CO)₁₀[μ₃-η²-C₂(CO₂Et)₂](μ-H).[2]

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The Surface Composition of Cu-Mn Alloys in Ultrahigh Vacuum and in the Presence of Oxygen

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In relation to the materials design, plenty of chemical and physical properties of alloys depend makedly on natures of surfaces and interfaces. Nowadays it is necessary to understand the relationship between externally controllable factors such as the bulk composition, temperature and ambient condition, and surface properties such as the surface compositon, surface structure and chemical activity. In particular, the information about the surface composition of alloys is of great importance. Generally surface composition of the alloys greatly differ from bulk, so called surface segregation. Reactions involved in the catalysis, oxidation, corrosion, *etc.* are known to be sensitive to surface composition.[1-3] Therefore characterization of alloy surfaces with respect to composition and reactivity is essential for understanding surface chemistry and for controlling materials performance.

In this note, first, surface composition is predicted based on unified model. Second, surface composition of four Cu-Mn alloys has been followed by means of X-ray photoelectron spectroscopy (XPS), one of the well established surface characterization techniques, as a function of annealing in ultra high vacuum and oxygen chemisorption.

Model Prediction of Surface Compositon of Cu-Mn Alloys

If there is no phase separation and no ordered phase in