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A facile and selective synthesis of hydridotrirhenium cluster under solvothermal conditions

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Abstract

The selective synthesis of pure crystals of the hydridotrirhenium cluster $(\mu\text{-H})_3Re_3(CO)_{12}$ via direct hydrogenation of $Re_2(CO)_{10}$ by a solvothermal method in excellent yield is described. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The chemistry of metal clusters has drawn considerable interest due to their importance in synthesis and catalysis. In the field of rhenium hydridocarbonyl clusters, $(\mu\text{-H})_3Re_3(CO)_{12}$ (**1**) was the first complex reported by Kaesz and coworkers in 1964 [1], but its reaction chemistry did not appear extensively until the last decade [2–9]. Complex **1** has been utilized as a starting material for the hydridocarbonyl derivatives [2–6] and as a catalyst precursor for CO hydrogenation [10], water-gas shift reactions [11], alkane hydrogenolysis [12] and cyclooligomerization of thietane [13]. Several methods for the preparation of complex **1** have been described, but they are either time-consuming or less selective. Kaesz and coworkers first reported that the tetrahydroborate reduction of $Re_2(CO)_{10}$ followed by acidification can yield 50% of **1**, but in a rather tedious procedure [1]. Later, they found that direct hydrogenation (1 atm) of $Re_2(CO)_{10}$ affords **1** with $50-60\%$ yield, whereas it may not be possible to employ it to prepare large quantities of **1** (>0.5 g) due to the tendency to form rhenium metal [2]. Complex **1** has also been obtained by photolytic hydrogenation of $Re_2(CO)_{10}$ followed by thermolysis as reported by D'Alfonso and coworkers [14], but this process involves several stages.

Hydro(solvo)thermal synthesis, which aids the rapid transport ability of the solvent under superheated solvent at sub-, near- or supercritical conditions, often leads directly to crystal growth of the product similar to the formation of many mineral crystals in nature [15–17]. Considering the advantages, we extended this synthetic strategy to the preparation of $(\mu\text{-H})_3Re_3(CO)_{12}$ (**1**). In this paper, we report a simple and convenient synthesis of complex **1** in excellent yield by the solvothermal process. Complex **1** was obtained in an exclusively pure crystalline form and was easily separated from the solution.

2. Results and discussion

Hydrogenation of $Re_2(CO)_{10}$ by solvothermal method in *n*-octane in a stainless steel autoclave afforded $(\mu\text{-H})_3Re_3(CO)_{12}$ (**1**) in very high yield. Complex **1** was isolated as a beautiful colorless crystalline solid by decanting the supernatant solution; its structure and purity were confirmed by IR, ^{1}H-NMR, ^{13}C-NMR spectroscopy and elemental analysis. Its ^{1}H-NMR spectrum (in $CDCl_3$, 27°C) exhibited only one hydride peak at δ -17.24, ruling out the possibility of contamination with the tetranuclear $(\mu\text{-H})_4Re_4(CO)_{12}$ and dinu-

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clear $(\mu\text{-H})_2Re_2(CO)_8$ complexes. The purity of the crystals was very high and suitable for use as a starting material for most reactions. By carrying out the reactions at different pressures, temperatures and times, we arrived at the optimized condition of 350 psi of H_2 at 170°C in *n*-octane for 5 h for the maximum yield (86%) as shown in Table 1. The red colored byproduct $(\mu\text{-H})_4Re_4(CO)_{12}$ was not present in the optimized conditions and found to be negligible or absent at other conditions. When this reaction was carried out in toluene at 350 psi of hydrogen, the pressure dropped to 100 psi during the reaction and the yield of **1** was lower compared to the reaction in *n*-octane. This is due to the partial reduction of toluene to methylcyclohexane as confirmed by NMR studies. This suggests that *n*-octane can be employed as a good solvent for this synthesis.

The decanted solution from the reaction product was colorless and mainly contained the unreacted $Re_2(CO)_{10}$. Further hydrogenation of this solution again gave good yield of **1**, which proved the economic nature of this improved method. At low pressure without stirring, the yield was low, but with stirring the yield was dramatically increased.

The significant aspect of this solvothermal method is the selective and high yield synthesis of **1** without contaminating it with the tetranuclear byproduct $(\mu\text{-H})_4Re_4(CO)_{12}$. Kaesz have reported that $Re_2(CO)_{10}$ undergoes hydrogenation reaction to form **1**, $(\mu\text{-H})_4Re_4(CO)_{12}$ and CO gas [2]. The complex $(\mu\text{-H})_4Re_4(CO)_{12}$ would transform to **1** and $ReH(CO)_5$ in the presence of CO [18]. Since $ReH(CO)_5$ is unstable upon thermolysis, it decomposes to form $Re_2(CO)_{10}$ and H_2 as observed by both Kaesz and Shapley [18,19]. Our solvothermal hydrogenation of $Re_2(CO)_{10}$ was carried out in a closed system. Along with the formation of **1**, the intermediate $(\mu\text{-H})_4Re_4(CO)_{12}$ continued to react with the eliminated CO to form **1** and $ReH(CO)_5$, while the latter was then converted to $Re_2(CO)_{10}$ and H_2 at high temperature. As a consequence, fine-tuning of the solvothermal conditions would convert $Re_2(CO)_{10}$ to **1** in high yield. This is likely the reason why we obtained **1** in excellent yield under the optimized conditions (350 psi of H_2, 170°C) and avoided the formation of the tetranuclear byproduct $(\mu\text{-H})_4Re_4(CO)_{12}$. Indeed, in an open system hydrogenation of $Re_2(CO)_{10}$ at 1 atm for 2 days results in the formation of the tetranuclear complex $(\mu\text{-H})_4Re_4(CO)_{12}$ in high yield as reported by Cheng and coworker [20].

Our method of synthesis of $(\mu\text{-H})_3Re_3(CO)_{12}$ is simple and more efficient than those previously reported. This synthetic strategy enjoys considerable advantages such as high yield, high selectivity, high purity, easy handling, easy separation, and large-scale production.

3. Experimental

3.1. General data

Hydrogen gas (99.9999%, Air Liquide) and $Re_2(CO)_{10}$ were purchased from commercial sources and were used as received. *n*-Octane and toluene were dried by stirring over CaH_2 and were freshly distilled prior to use. IR spectra were recorded on a Perkin–Elmer 882 infrared spectrophotometer and NMR spectra were obtained on a Bruker ACP-300 spectrometer. Elemental analyses were performed using a Perkin–Elmer 2400 CHN elemental analyzer. The high pressure reaction was carried out in a 600 ml stirred reactor (Parr reactor no. 4563).

3.2. Synthesis of $(\mu\text{-H})_3Re_3(CO)_{12}$

Complex $(\mu\text{-H})_3Re_3(CO)_{12}$ (**1**) was prepared by a solvothermal method by using $Re_2(CO)_{10}$ as the starting material at the required H_2 pressure at a given temperature for a specified period (Table 1). A typical procedure for the synthesis is listed here. A suspension of $Re_2(CO)_{10}$ (1.000 g, 1.532 mmol) in *n*-octane (150 ml) was placed in an autoclave under nitrogen atmosphere. After the autoclave was sealed, the system was evacuated, hydrogen was introduced and kept at 350 psi. The autoclave was then heated with stirring at a given temperature for 5 h. The gas was slowly vented out after cooling. Beautiful colorless crystals of **1** separated out and they were collected by decanting the superna-

Table 1
Reaction conditions and yields for $(\mu\text{-H})_3Re_3(CO)_{12}$

$Re_2(CO)_{10}$ (g)	Pressure of H_2 (psi)	Time (h)	Temperature (°C)	$(\mu\text{-H})_3Re_3(CO)_{12}$ (%)	$(\mu\text{-H})_4Re_4(CO)_{12}$ (%)
1.000	190	8	150	20	Trace
0.500	200	4	150	22	Trace
1.000	200	5	170	54	Nil
1.000	350	5	170	86	Nil
2.000	350	5	170	81	Nil
1.000	400	5	170	65	Nil
1.000	500	5	170	68	Nil

tant solution, washed with *n*-octane, and dried in vacuo. Pure crystals of **1** were obtained in a yield of 86% (0.789 g, 0.879 mmol). IR (cyclohexane): ν(CO) 2094m, 2030vs, 2008s, 1982m cm^{-1} [Lit. [1] (cyclohexane): ν(CO) 2093m, 2030vs, 2008s, 1983m cm^{-1}]. ^{1}H-NMR: δ (CDCl$_3$, 27°C) -17.24 (s, Re–H). ^{13}C-NMR: δ (CDCl$_3$, 27°C): 181.4 (s, CO$_{\text{axial}}$), 179.5 (s, CO$_{\text{equatorial}}$). Anal. Calc. for $C_{12}H_3O_{12}Re_3$: C, 16.05; H, 0.34. Found: C, 16.00; H, 0.36.

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