The Reaction Between the Tetrahydridodecacarbonyltetrarhenium Cluster and Methanol: a Fifth-order Reaction

Sen Ren Wang and Cheu Pyeng Cheng*

Department of Chemistry, National Tsing Hua University, Hsin Chu, Taiwan

The reaction between $H_4Re_4(CO)_{12}$ and methanol in chloroform, yielding $H_4Re_4(CO)_{12}(MeOH)_4$ at room temperature, is first order in $H_4Re_4(CO)_{12}$ and fourth order in methanol; no intermediate was detected by UV–VIS and ^1H NMR spectra.

The development of organotransition metal cluster chemistry remains largely in the domain of synthesis and characterization of new compounds,[1–3] as well as their catalytic application.[4] Few kinetic and mechanistic investigations have been made because of the complexity of reaction pathways; the majority have been related to ligand-substitution reactions.[5,6] The unsaturated tetrahedral cluster with face-bridging hydrides $H_4Re_4(CO)_{12}$[7,8] **1** is known to decompose in numerous organic solvents.[9–11] Here, we report that **1** reacts cleanly with methanol according to a fifth-order rate law to yield $H_4Re_4(CO)_{12}(MeOH)_4$ **A1** which is more reactive than **1**.† The reaction is also reversible.

The UV-VIS spectra (Fig. 1) of a chloroform solution containing **1** and MeOH exhibit two successive isosbestic points. The first at 407 nm indicates **1** (λ_{max} = 472 nm, $\varepsilon = 2.12 \times 10^4$ dm^3 mol^{-1} cm^{-1}) reacts with MeOH to form **A1** (λ_{max} = 372 nm). The second isosbestic point at 330 nm indicates the transformation of **A1** into the final product **A2**. Using spectral subtraction, the UV-VIS spectrum in the course of reaction can be accounted for solely by the presence of **1**, **A1** and **A2**. The ^1H NMR spectra of a $CDCl_3$ solution of **1** (18 mmol dm^{-3}) and MeOH (0.7 mol dm^{-3}) are in complete accord with the results of UV-VIS spectra. In the initial stage of the reaction,

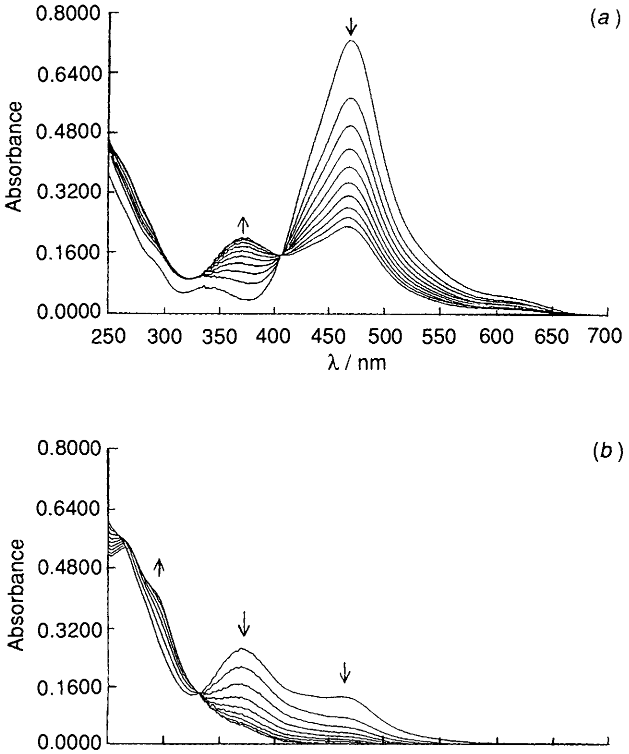

Fig. 1 UV-VIS spectra (measured on a Perkin-Elmer Lamda-5 spectrophotometer) for the reaction between $H_4Re_4(CO)_{12}$ (3.44×10^{-5} mol dm^{-3}) and MeOH (90 mmol dm^{-3}) in chloroform. (*a*) Spectra during the initial 63 min of the reaction, 7 min between successive spectra. (*b*) Spectra between 140 and 700 min, 70 min between successive spectra. Equilibrium between **1** and **A1** is obvious, though **A1** is predominant.

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† **A1** is more reactive than **1**; it also gives, a clean reaction. For example, when a chloroform solution of **1** (3.7 mmol dm^{-3}) is bubbled with CO for 1 h, only 34% was converted to $H_3Re_3(CO)_{12}$ with some $H_2Re_2(CO)_8$ (3%) and $HRe(CO)_5$ (1.6%) (monitored by ^1H NMR. Spectral data of these Re compounds: see N. Masciocchi, A. Sironi and G. D'Alfonso, *J. Am. Chem. Soc.*, 1990, **112**, 9395). In contrast, when the chloroform solution of **A1** is used, in 15 min 91.2% was converted to $H_3Re_3(CO)_{12}$ with $H_2Re_2(CO)_8$ (3.2%) and $HRe(CO)_5$ (0.8%). When $HC(PPh_2)_3$ (7.4 mmol dm^{-3}) is used as reagent, **A1** (3.7 mmol dm^{-3}) was converted to $H_3Re_3(CO)_9[\mu_3\text{-}HC(PPh_2)_3]$ (96%) in 15 min. In contrast, in refluxing CH_2Cl_2 for 8 h, besides three other compounds, only 42% of **1** is converted to $H_3Re_3(CO)_9[\mu_3\text{-}HC(PPh_2)_3]$.[11]

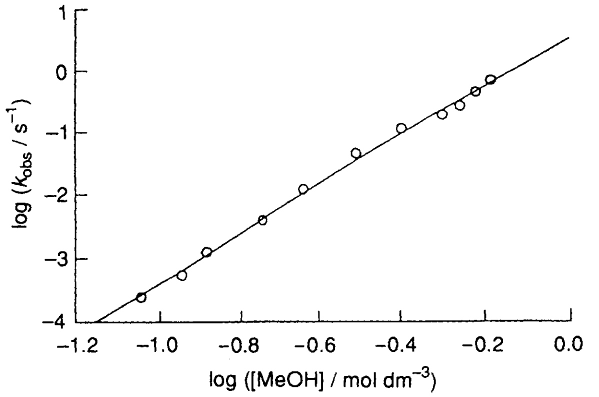

Fig. 2 Plot of log (k_{obs}) *vs.* log [MeOH] for the reaction between $H_4Re_4(CO)_{12}$ and MeOH; k_{obs} is the pseudo-first-order rate constant for the decay of $H_4Re_4(CO)_{12}$ as monitored at 472 nm

the signal at δ −5.05 **1** disappears with concomitant formation of signals at δ −5.85 (3H) and −8.52 (1H) (attributed to **A1**). In the later stage of the reaction, the signals of **A1** disappear with concomitant formation of a signal at δ −11.56 (attributed to **A2**). The concentration of MeOH must be carefully controlled to observe the first isosbestic point at 372 nm and the disappearance of δ −5.05.

Attempts to isoalte **A1** and **A2** failed because when the solutions containing them are subjected to drying either in a rotary evaporator or on a vacuum line, both **A1** and **A2** revert to **1**. Addition of $Et_4N{\cdot}BF_4$ to the solution containing **A2** and MeOH followed by addition of hexane, yielded quantitatively a yellow precipitate **A3**, assigned to be $[H_3Re_3(CO)_9(\mu_3\text{-}OMe)](Et_4N)$.[12]‡ Since the NMR spectrum of **A2**§ is virtually identical to that of **A3** except for the additional proton peak at δ 7.17, we assign **A2** to be $H_3Re_3(CO)_9(\mu_3\text{-}OMeH)$ with an acidic methanolic proton. The spectral data of **A1**¶ indicate that four methanol moieties coordinate to the Re cluster, which retains 12 carbonyls and four hydrides. Therefore, **A1** is assigned to be $H_4Re_4(CO)_{12}(MeOH)_4$. The reactions between **1** and MeOH are summarized in Scheme 1.

$$\underset{\mathbf{1}}{H_4Re_4(CO)_{12}} + MeOH \rightarrow \underset{\mathbf{A1}}{H_4Re_4(CO)_{12}(MeOH)_4} \rightarrow$$

$$\underset{\mathbf{A2}}{H_3Re_3(CO)_9(\mu_3\text{-}OMeH)}$$

$$\xrightarrow{Et_4N\cdot BF_4} \underset{\mathbf{A3}}{[H_3Re_3(CO)_9(\mu_3\text{-}OMe)](NEt_4)}$$

Scheme 1

In the pseudo-first-order condition of an excess of MeOH in $CHCl_3$, the decay of the absorbance of **1** is exponential. When [MeOH] exceeds 0.310 mol dm^{-3}, the technique of mixing in a flow UV cell was used to measure the reaction rate. When the methanol concentration was changed from 0.090 to 0.650 mol dm^{-3}, k_{obs} increased more than a thousandfold (Fig. 2). The slope of the log k_{obs} *vs.* log [MeOH] plot is 3.93 ± 0.8. Therefore, the rate law at 298 K can be expressed as eqn. (1).

$$\begin{aligned} \text{rate} &= d[\mathbf{1}]/dt \\ &= (3.62 \pm 0.16\ \text{mol}^4\ \text{dm}^{-12}\ \text{s}^{-1})\ [\mathbf{1}]\ [\text{MeOH}]^4 \end{aligned} \quad (1)$$

Here a clean fifth-order reaction was observed. This is the second example of such a high-order reaction in organometallic chemistry. The first example[13] is the reaction between $Re_2(CO)_9PPh_3$ and I_2, in which the fifth-order reaction pathway makes only a small contribution to the overall reaction rate. Besides the reversion of **A1** to **1**, a dilution experiment gives convincing evidence of the reversible formation of **A1**. Five min after a solution containing **1** (4 × 10^{-5} mol dm^{-3}) and MeOH (0.6 mol dm^{-3}) was prepared, all of **1** was converted to **A1**. When the solution was diluted with a dilute solution of chloroform to [MeOH] = 0.053 mol dm^{-3}, the UV–VIS spectra indicated the transformation of **A1** to **1** with an isosbestic point exactly the same as in the formation of **A1** [Fig. 1(*a*)].

The fifth-order reaction is definitely not elementary. However, no intermediate was detected either by UV–VIS or ^{1}H NMR spectra. A possible mechanism is indicated in Scheme 2.

$$\mathbf{1} + MeOH \rightleftharpoons H_4Re_4(CO)_{12}(MeOH) \qquad K_1 = k_1/k_{-1} \quad (2)$$

$$H_4Re_4(CO)_{12}(MeOH) + MeOH \rightleftharpoons H_4Re_4(CO)_{12}(MeOH)_2 \qquad K_2 = k_2/k_{-2} \quad (3)$$

$$H_4Re_4(CO)_{12}(MeOH)_2 + MeOH \rightleftharpoons H_4Re_4(CO)_{12}(MeOH)_3 \qquad K_3 = k_3/k_{-3} \quad (4)$$

$$H_4Re_4(CO)_{12}(MeOH)_3 + MeOH \rightleftharpoons H_4Re_4(CO)_{12}(MeOH)_4 \qquad K_4 = k_4/k_{-4} \quad (5)$$

Scheme 2

To be consistent with the methanol four-order kinetics, eqns. (2–4) of Scheme 2 must be in equilibrium, and eqn. (5) is the rate-determining reaction. The rate expression is given below as eqn. (6).

$$\text{rate} = k_4K_1K_2K_3[\text{MeOH}]^4[\mathbf{1}]/(1 + K_1[\text{MeOH}] + K_1K_2[\text{MeOH}]^2 + K_1K_2K_3[\text{MeOH}]^3) \quad (6)$$

The law indicates that all terms containing [MeOH] in the denominator are ≪1. K_1[MeOH] must definitely be much less than unity; $k_1[\text{MeOH}] \ll k_{-1}$. The restrictions on K_2 and K_3 are very loose; they must satisfy the condition that the third and fourth terms are less than 1. Further information on the relative magnitude of the reaction is that $k_4[\text{MeOH}] > k_{-4}$ when [MeOH] is between 0.09 and 0.65 mol dm^{-3}. Furthermore, k_1, k_2, $k_3 \gg k_4$.

When butane-1,2-diol was used in place of methanol in the reaction with **1**, a virtually identical reaction sequence occurred as indicated by the UV–VIS and ^{1}H NMR spectra. **1** is transformed into **B1** [isosbestic point λ: 409 nm, δ −5.76 (3H), −7.09 (1H)] which was subsequently transformed into **B2** (isosbestic point λ 330 nm, δ −11.52). Again with careful examination of the UV–VIS and ^{1}H NMR spectra during the reaction course, no intermediate was detected.

Many other alcohols and diols can also react with **1**; the structure–reactivity relation is under investigation. The chemistry of **A1*** is also under investigation.

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‡ *Selected spectroscopic* data for **A3**: δ_H (400 MHz, [$^2H_6$]acetone): 4.74 (s, 3H), 3.29 (q, 8H, 7.1 Hz), 1.40 (t, 12H, 7.1 Hz), −11.50 (s, 3H); δ_C (100 MHz, [$^2H_6$]acetone): 195.7, 186.1, 85.6, 29.7, 7.5; ν_{CO}/cm^{-1} (acetone): 2008.7s, 1924.3s, 1908.1s; M$^+$(^{187}Re): 977; elemental analysis were satisfactory. Following the same preparation procedure with EtOH instead of MeOH, we obtained the known compound: $[H_3Re_3(CO)_9(\mu_3\text{-}OEt)](Et_4N)$[12] in quantitative yield. The ^{1}H NMR spectrum of this ethanol product was virtually the same as **A3** except for the difference in OEt and OMe.

§ *Selected spectroscopic* data for **A2**: δ_H (400 MHz, CD_2Cl_2): 7.15 (s, 1H), 3.55 (s, 3H), −11.56 (s, 3H); δ_C (100 MHz, CD_2Cl_2, quantitative): 195.7(3C), 186.7(6C), 86.2(1C); ν_{CO}/cm^{-1} (CH_2Cl_2): 2025s, 2013s, 1920s.

¶ *Selected spectroscopic* data for **A1**: δ_H (400 MHz, CD_2Cl_2): 8.58 (s, 2H), 8.31 (s, 1H), 7.58 (s, 1H), 3.75 (s, 9H), 3.73 (s, 3H), −5.85 (s, 3H), −8.02 (s, 1H); δ_C (100 MHz, CD_2Cl_2, quantitative, 250 K): 197.0 (3C), 193.8 (9C), 58.4 (3C), 58.3 (1C); ν_{CO}/cm^{-1} ($CHCl_3$): 2012s, 1930s.

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