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Improved synthesis of carbonylrhenium

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Abstract

An improved procedure for the preparation of $Re_2(CO)_{10}$ is reported. Carbonylation of methanol solutions of $NaReO_4$ (3200 psi, 230 °C, 48 h) in the presence of a metallic copper catalyst affords $Re_2(CO)_{10}$ in 90% yield.

Carbonylrhenium is a versatile precursor for a wide range of organometallic compounds. Synthetic methods currently available are based on the pioneering studies of Hieber [1]. Carbonylation of Re_2O_7 at 5250 psi and 250 °C in an autoclave lined with copper/silver alloy was reported to afford $Re_2(CO)_{10}$ in quantitative yield. A more recent investigation of this reaction by Muetterties and Stolzenberg employed comparable conditions and reported yields of 80–85% for a small scale reaction [2]. These investigators also reported that the presence of a metallic copper surface seemed to be beneficial. Re_2O_7 is an inconvenient starting material since it is very hygroscopic and must be placed in the autoclave in sealed ampoules, which are then crushed under pressure. An alternative preparation based on potassium perrhenate was also reported by Hieber to afford $Re_2(CO)_{10}$ in unspecified yield. This procedure requires carbonylation of "finely powdered" $KReO_4$ at 7500 psi and 270 °C. In our hands, this reaction affords only traces of $Re_2(CO)_{10}$. We now report a convenient procedure based on sodium perrhenate which employs much lower pressures and gives a nearly quantitative yield of $Re_2(CO)_{10}$.

Experimental

Rhenium metal powder was obtained from Rhenium Alloys Inc., Elyria, Ohio. Carbon monoxide (Mattheson CP grade) was used as received. All other reagents and solvents were reagent grade and used as received. Infrared spectra were recorded on a Perkin–Elmer 337 instrument.

Preparation of sodium perrhenate

Rhenium metal powder (5.30 g, 28.5 mmol) was placed in a 125 ml Erlenmeyer flask immersed in an ice bath. Dropwise addition of 35 ml of 30% hydrogen

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peroxide over 10 minutes followed by heating to ca. 60 °C for 1 h caused almost complete dissolution of the metal [3]. The solution was filtered while hot. Both flask and filter paper were rinsed with 75 ml hot water. The combined solution and rinsings were titrated with 1 *M* NaOH to pH 8. Water was removed on the rotary evaporator. The resulting white solid was further dried in vacuo (10^{-3} mmHg) for 10 h.

Preparation of carbonylrhenium

The $NaReO_4$ was dissolved in 100 ml absolute methanol and the resulting solution was added to a 500 ml stainless steel autoclave along with ca. 0.5 g of fresh copper filings [4*]. The reactor was pressurized with carbon monoxide to 1000 psi and vented. (*Caution*: Carbon monoxide is very toxic.) This flushing procedure was repeated three times. After pressurization to 1700 psi (29 °C), the reactor was heated to 230 °C (Working pressure 3200 psi). Heating was continued for 48 h. After cooling 12 h and venting of the gases the reactor was opened. A large amount of a white precipitate was noted. The methanol solution was decanted off and evaporated on a rotary evaporator leaving a yellow residue. The precipitate was removed from the reactor and combined with the residue from the methanol solution. Sublimation (60–70 °C, 10^{-3} mmHg) onto a water-cooled probe over a 4 h period affords 8.35 g of $Re_2(CO)_{10}$ as colorless crystals. (12.8 mmol, 90% based on Re metal). Infrared spectrum: (CCl_4, ν(CO), cm^{-1}) 2070m, 2012s 1974m. These values are identical to the reported spectrum [5].

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4 While the precise role of the copper metal in this reaction remains unclear, it does affect the yield of $Re_2(CO)_{10}$. When the same conditions of temperature and pressure were employed in the absence of copper, only a 75% yield of $Re_2(CO)_{10}$ was obtained.

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* A reference number with an asterisk indicates a note in the list of references.