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# **REDUCTION OF AMMONIUM PERRHENATE BY CO: A CONVENIENT METHOD FOR PREPARING $\text{Re}_2(\text{CO})_{10}$ (\*)**

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*Summary* — Decacarbonyldirhenium(0),  $\text{Re}_2(\text{CO})_{10}$ , was obtained in yields as high as 69% by carbonylation of ammonium perrhenate(VII) at 250-290 °C with CO at about 150 atm pressure in toluene as medium.

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The known methods of preparation of  $\text{Re}_2(\text{CO})_{10}$  are: a) reductive carbonylation of  $\text{Re}_2\text{O}_7$  at high temperature and pressure,<sup>1</sup> b) reductive carbonylation<sup>2</sup> of anhydrous rhenium chlorides with sodium in tetrahydrofuran at superatmospheric pressure of CO at 130 °C, and c) reduction of  $\text{KReO}_4$  by copper<sup>3</sup> in the presence of CO (320 atm) at 300 °C. Decacarbonyldirhenium was also obtained by reducing  $\text{Re}_2\text{S}_7$  with copper in the presence of CO at 85 atm at 200 °C.<sup>4</sup>

We have now found that the readily available ammonium perrhenate(VII)<sup>a</sup> is converted in good yields to  $\text{Re}_2(\text{CO})_{10}$ , carbon monoxide being the reducing agent. Yields as high as about 70% were obtained by operating at 250-300 °C with CO at about 150 atm (maximum high-temperature pressure) in toluene as reaction medium. No carbonylation of rhenium was observed, even under more drastic conditions, with  $\text{KReO}_4$ , thus showing that the ammonium counter-cation is essential for the rhenium reduction by CO. Commercially available CO (containing up to 3%  $\text{H}_2$ ) could be used without being largely detrimental for the yields. On the other hand, the use of the CO: $\text{H}_2$  1.1 mixture reduced the yields drastically.

In attempts to get some insight into the mechanism of this reaction, the carbonylation was also carried out with carbon monoxide of the purest available grade: under these conditions,  $\text{H}_2$  was found to be produced, presumably *via* a route different from the water gas shift (WGS) reaction, in view of the fact that  $\text{Re}_2(\text{CO})_{10}$  is a poor<sup>6</sup> WGS promoter. It is to be noted that while reduction of covalent metal oxides such as  $\text{Re}_2\text{O}_7$ <sup>1</sup> and  $\text{OsO}_4$ <sup>7</sup> by CO to give the corresponding metal carbonyls has been used in the past, this appears to be the first case of a  $\text{MO}_4^-$  species as the ammonium derivative undergoing reduction and complexation by CO.

Work is in progress aimed at clarifying the reaction mechanism and the identity of the by-products and at exploring the generality of this new synthetic method.

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<sup>a</sup> Ammonium perrhenate,  $\text{NH}_4\text{ReO}_4$ , obtained from aqueous solution (a saturated solution is 0.23 M<sup>5</sup> at 20 °C), after drying *in vacuo* at room temperature, does not retain lattice water.

## EXPERIMENTAL

In a typical experiment,  $\text{NH}_4\text{ReO}_4$  (9.92 g, 37.0 mmol) was introduced in a 700  $\text{cm}^3$  stainless steel autoclave equipped with a magnetic stirrer. After evacuation, dry toluene (200  $\text{cm}^3$ ) was introduced by suction and commercially available CO (containing about 3% of  $\text{H}_2$ ) was compressed up to about 90 atm at room temperature. The autoclave was stirred and heated at 290° C for 40 h. The gas was vented and the content of the autoclave, consisting of a yellow solution and some gray solid, was discharged, no special precaution being used for avoiding the admission of air. The solution was evaporated to small volume at atmospheric pressure and then cooled to about 430° C. The solid  $\text{Re}_2(\text{CO})_{10}$  which crystallized out was filtered and dried *in vacuo* (7.4 g, 61.3% yield). The carbonyl was found to be spectroscopically pure in comparison with an authentic sample ( $\nu_{\text{CO}}$ , toluene: 2069m, 2008s and 1971m-s  $\text{cm}^{-1}$ ). In another experiment, carried out with 10.4 g (38.8 mmol) of  $\text{NH}_4\text{ReO}_4$  under similar pressure and temperature conditions, but using CO of the purest available grade (no detectable  $\text{H}_2$  present), the gas after the carbonylation was analysed and found to contain about 5 mmol of  $\text{H}_2$ . The reaction mixture was filtered and a 69% yield of  $\text{Re}_2(\text{CO})_{10}$  was obtained by sublimation of the solid residue after evaporation of the solvent under reduced pressure.

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