

Direct and high yield syntheses of $\text{Re}_2(\text{CO})_{10}$ and $\text{Re}(\text{CO})_5\text{Cl}$ by sodium reduction of K_2ReCl_6 under CO

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Received 10 March 1997; received in revised form 2 July 1997

Abstract

A convenient procedure for the synthesis of the rhenium carbonyls $\text{Re}_2(\text{CO})_{10}$ and $\text{Re}(\text{CO})_5\text{Cl}$ is reported. Sodium reduction of the easily available K_2ReCl_6 , under CO pressure (2400 psi, 280°C (external temperature), THF as solvent) affords $\text{Re}_2(\text{CO})_{10}$ and $\text{Re}(\text{CO})_5\text{Cl}$ in 81% and 86% isolated yield, respectively. Depending on the hexachlororhenate:Na ratio, either carbonyl derivative can be obtained almost exclusively. © 1997 Elsevier Science S.A.

Keywords: Rhenium carbonyls; Sodium reduction; Synthesis

1. Introduction

$\text{Re}_2(\text{CO})_{10}$ and $\text{Re}(\text{CO})_5\text{Cl}$ are the most common precursors used for the preparation of most of the organometallic rhenium compounds [1,2]. Several synthetic methods have been reported for these compounds. Most of them involve the reductive carbonylation of alkali metal or ammonium perrhenate or Re_2O_7 , under high pressure conditions, with or without the presence of a catalyst or auxiliary reducing agent [3–8]. Very recently, Top et al. reported a milligram scale synthesis of $\text{Re}_2(\text{CO})_{10}$ by reduction of $(\text{NH}_4)(\text{ReO}_4)$ at atmospheric CO pressure using diisobutylaluminium hydride as the reducing agent [9].

There are also a few reports involving rhenium halides as starting materials for the production of these rhenium carbonyls. In this regard, Hieber in 1939 reported the first synthetic method for the preparation of $\text{Re}(\text{CO})_5\text{Cl}$ in quantitative yield by heating ReCl_5 , ReCl_3 or K_2ReCl_6 in the presence of copper powder, for 30 h at 230°C and 200 atm of CO pressure [10]. Using the corresponding Re-halide and similar conditions, the bromo and iodo analogs were also obtained [10]. Later the same author published a 70% yield synthesis of $\text{Re}(\text{CO})_5\text{Cl}$ by using rhenium metal and an excess of CuCl_2 at 250°C under 210 atm of CO [11]. In none of

the cases was the presence of $\text{Re}_2(\text{CO})_{10}$ indicated. Two decades later, Davison et al. used ReCl_3 and ReCl_5 (but not K_2ReCl_6) to obtain $\text{Re}_2(\text{CO})_{10}$ in 70% yield, by treating the halides with a slight excess of sodium in THF, under 280 atm of CO and 130/250°C [12]. Recently, Alberto et al. prepared the anion $[\text{ReCl}_3(\text{CO})_3]^{-2}$, from a low pressure carbonylation of ReOCl_4^- in presence of $\text{BH}_3\text{-THF}$ [13]. To our knowledge, no other papers using rhenium halides for the preparation of carbonyl rhenium complexes have been published. We now report a convenient procedure based on the easily prepared K_2ReCl_6 , which employs relatively low CO pressures and, depending on the hexachlororhenate:Na ratio, allows the production of $\text{Re}_2(\text{CO})_{10}$ or $\text{Re}(\text{CO})_5\text{Cl}$ in yields as high as 81% and 86%, respectively.

2. Experimental

The high pressure reactions were carried out in a 200 ml stainless steel, general purpose reactor (Parr model 4753). Carbon monoxide (Matheson CP grade) was used as received. THF was distilled from Na-benzophenone ketyl before using. Sodium, as 50% paraffin dispersion (Aldrich), was treated three times with THF to wash out the paraffin. K_2ReCl_6 was prepared from KReO_4 in 82% yield, according to a literature procedure

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[14]. IR spectra were measured on a Perkin-Elmer FT 1605 spectrometer using KBr solution cells.

2.1. Preparation of $\text{Re}_2(\text{CO})_{10}$

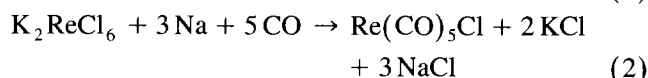
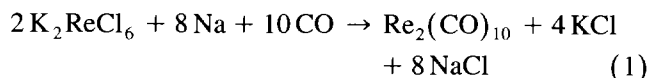
K_2ReCl_6 , (3.0 g, 6.29 mmol), Na powder (0.651 g, 28.3 mmol, 12.5% excess) and 70 ml of THF were introduced into the reactor vessel equipped with a magnetic stirring bar. The reactor was pressurized with carbon monoxide to 1000 psi and vented (*Caution*: carbon monoxide is very toxic; the experimental procedure must be carried out in an efficient fumehood). This flushing procedure was repeated three times. After pressurizing to 1100 psi at 25°C, the reactor was externally heated with a high-temperature bath of fused salts ($\text{NaNO}_2:\text{KNO}_3:\text{NaNO}_3$, 40:53:7), to 280°C (working pressure 2400 psi). The heating was continued for 40 h under magnetic stirring. After cooling to room temperature and venting of the gases, the reactor was opened. The reaction mixture, consisting of a yellow solution and dark brown solid, was filtered through celite. The solid was washed twice with 20 ml of THF. At this point, the IR spectrum in the CO region showed only $\text{Re}_2(\text{CO})_{10}$ and a small amount of $\text{Re}(\text{CO})_5\text{Cl}$ (about 5%). The solution was rotary evaporated and the yellow-brown residue extracted twice with 75 ml of hexane and filtered through a short neutral alumina column. After hexane evaporation to dryness 1.660 g (81% yield) of white crystalline solid of $\text{Re}_2(\text{CO})_{10}$ was obtained. From the solid insoluble in hexane about 0.100 g of $\text{Re}(\text{CO})_5\text{Cl}$ were recovered, after crystallization from acetone-methanol. IR spectrum of $\text{Re}_2(\text{CO})_{10}$ in hexane was identical to that of an authentic sample ($\nu(\text{CO})$, cm^{-1} : 2070 (m), 2013 (s), 1976 (m)).

2.2. Preparation of $\text{Re}(\text{CO})_5\text{Cl}$

The reactor was charged with 3.0 g (6.29 mmol) of K_2ReCl_6 , 0.488 g (21.2 mmol, 12.3% excess) of Na powder and 70 ml of THF. Then, under similar reaction conditions (pressure, temperature and time) to those mentioned above, the reactor was heated, then cooled, vented and opened (*Caution*: carbon monoxide is very toxic; the experimental procedure must be carried out in an efficient fumehood). A large amount of brown solid was noted. The reaction mixture was poured into a celite filter and the solid collected, was washed through with warm acetone. Solvent was rotary evaporated and the residue dissolved in a minimum amount of warm acetone. Methanol was added dropwise under magnetic stirring until no more precipitation was noted, the mixture was maintained at -15°C overnight. The white crystalline solid $\text{Re}(\text{CO})_5\text{Cl}$ was removed by filtration. Yield 1.85 g (86%), IR $\nu(\text{CO})$ values are identical to those found in an authentic sample ($\nu(\text{CO})$, CH_2Cl_2 , cm^{-1} : 2040 (s), 1980 (m)).

3. Conclusion

The reductive carbonylation of K_2ReCl_6 with sodium provides new direct syntheses of the rhenium carbonyl complexes $\text{Re}_2(\text{CO})_{10}$ and $\text{Re}(\text{CO})_5\text{Cl}$, as shown in Eqs. (1) and (2), respectively.



Under the same experimental conditions, the ratio $\text{K}_2\text{ReCl}_6:\text{Na}$ is crucial for the production of the carbonyl derivatives: a 1:4.50 ratio gives $\text{Re}_2(\text{CO})_{10}$ in 81% yield, while a 1:3.37 ratio gives $\text{Re}(\text{CO})_5\text{Cl}$ in 86% yield.

The relatively low working CO pressure used in this procedure allows the preparation of these important precursors by using a general purpose bomb reactor.

Acknowledgements

This research was generously supported by The Third World Academy of Science under Research Grant Contract No. 94-115 RG/CHE/LA. We also wish to thank MOLYMET CHILE for the loan of potassium perrhenate, FONDECYT (Grants 708/92 and 1960383), DGIP Universidad Católica de Valparaíso (Proy. 125.753-95) and Fundación Andes for a doctoral fellowship to B.O.

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