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Preliminary communication

ACTIVATED METALS

VIII*. PREPARATION OF CHROMIUM HEXACARBONYL FROM CHROMIUM METAL

REUBEN D. RIEKE**, KARL ÖFELE and E.O. FISCHER

Anorganisch-chemisches Laboratorium der Technischen Universität München (Deutschland)

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The formation of metal carbonyls by the direct reaction of the metal with CO at elevated temperatures and pressures is a well-established procedure for a wide variety of metals. However, for certain metals this procedure fails due to the low reactivity of the metal. Chromium is such a metal and all attempts to react the metal with CO have failed to yield any $Cr(CO)_6$***. We have recently reported a general procedure for the generation of activated metals [3]. In this communication we would like to report the preparation of chromium powder by this process and the direct reaction of the metal with CO to yield $Cr(CO)_6$.

The standard procedures for the preparation of $Cr(CO)_6$ involve the chemical reduction of chromium(II) or chromium(III) compounds in an autoclave under CO pressure [4]. It also has been reported recently that the electrochemical reduction of chromium compounds under CO pressure yields $Cr(CO)_6$ [5]. We have found that chromium metal prepared by the reduction of $CrCl_3$ or better $CrCl_3 \cdot 3THF$ with potassium in either THF or benzene is highly active and will react with CO (280 atm) at elevated temperatures to yield $Cr(CO)_6$. It had been observed that the generation of active magnesium by the reduction of $MgCl_2$ in the presence of KI leads to a much more reactive magnesium [3c, e]. We found in this work that reduction of the chromium salts in the presence of KI produces higher yields of $Cr(CO)_6$ (35%). The optimum ratio of KI to $CrCl_3 \cdot 3\,THF$ was 1/1. Reduction in the presence of KBr gave similar yields; however, reduction in the presence of KCl gave yields of only 30%.

Much improved yields were obtained if the reduction of $CrCl_3 \cdot 3\,THF$ was carried out in benzene rather than THF. In these cases, the benzene was stripped off after the reduction was complete and then THF was added to the black

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[*] For part VII see ref. 1.

[**] On leave from the University of North Carolina, Chapel Hill, North Carolina. Alfred P. Sloan Research Fellow 1973—1975. NATO Fellow 1973—1974.

[***] It has been reported that Cr—Fe alloy will react with CO to yield $Cr(CO)_6$ [2].

powder. The resulting slurry was then added to the autoclave and reaction with CO gave yields of $Cr(CO)_6$ of 50% or better. Reduction of $CrCl_3 \cdot 3\,THF$ in benzene in the absence of KI resulted in yields of $Cr(CO)_6$ of only 30%. Also use of KBr or KCl in the benzene reductions resulted in lower yields of $Cr(CO)_6$.

In order to determine if the black material added to the autoclave was in fact chromium metal or a mixture of Cr^{II} salts and potassium the following reduction of $CrCl_3 \cdot 3\,THF$ with potassium in benzene was repeatedly extracted with THF to remove and to determine soluble chromium(II) salts. Also the amount of unreacted potassium was determined by repeated extraction of the black material with alcohol and water and subsequent acidic titration of the extracts. From these two determinations, it was established that a minimum of 58% of the $Cr(CO)_6$ formed in the autoclave reaction originated from chromium(0 In a separate experiment, the black material was extracted repeatedly with THF to remove all the soluble chromium salts and was then treated with CO under the same conditions as in the previous reactions. The yield of $Cr(CO)_6$ was 30% based on the material placed in the autoclave. Thus, it is clear that Cr^0 is produced in the reduction and this Cr^0 will react with CO to yield $Cr(CO)_6$. It is difficult to determine the exact amount of $Cr(CO)_6$ which originates from Cr^0 in the black powder due to its instability. Thus, excessive manipulations of the black powder even under argon or very long reduction times in the generation of the black powders seem to deactivate the Cr^0.

We had recently reported on the preparation of highly reactive magnesium. We found that the reduction of chromium salts with the highly reactive magnesium in an autoclave leads to high yields of $Cr(CO)_6$. The use of magnesium generated in the presence of KI to reduce $CrCl_3 \cdot 3\,THF$ in THF in the autoclave resulted in yields in excess of 80% of $Cr(CO)_6$.

Experimental

Preparation of $Cr(CO)_6$ from chromium powder

The following is the general procedure used in the preparation of chromium powder. A dry three-necked 100 ml round-bottomed flask equipped with a reflux condenser and a glass magnetic stirrer was filled with argon. To this flask were added K (1.60 g, 0.041 moles) freshly cut under hexane, KI (2.28 g, 0.0137 moles), $CrCl_3 \cdot 3\,THF$ (5.14 g, 0.0137 moles) and purified benzene (50 ml) which had been stored under argon. The mixture was heated to 80°C for a total of 2 h. Initially, the $CrCl_3 \cdot 3\,THF$ dissolved in the benzene giving a deep purple solution. However, before the potassium melted a heavy pink-purple precipitate came out of solution. Within a few minutes after the potassium melted, the solution began to turn brown-black and became less viscous. After heating for a total of 2 h, the benzene was stripped off at room temperature. THF (25 ml) was then added to the brown-black powder and the resulting slurry was placed in an autoclave filled with argon. The autoclave was filled with high purity CO (280 atm) and heated at 220°C for a total of 16—20 h. The resulting black slurry was filtered and the black solid was washed with THF (5 × 5 ml). The combined filtrates were diluted with water causing the $Cr(CO)_6$ to precipitate out. The product was collected by centrifugation and filtration yielding 1.384 g $Cr(CO)_6$, 51% yield (based on material placed in the autoclave). The $Cr(CO)_6$ obtained had the same melting point and IR spectrum as an authentic sample. Appreciable longer reaction times, higher reaction temperatures and the use of low purity CO led to decreased yields of $Cr(CO)_6$.

Preparation of $Cr(CO)_6$ by reduction with activated magnesium

Preparation of activated magnesium by reduction of $MgCl_2$ (2.04 g, 0.0214 moles) with potassium (2.50 g, 0.0384 moles) in the presence of KI (3.55 g, 0.0214 moles) in THF (50 ml) was carried out as previously described [3c, e]. The black slurry was placed in an autoclave filled with argon. $CrCl_3 \cdot 3\,THF$ (3.37 g, 0.009 moles) was then added and finally the autoclave was filled with high purity CO (280 atm). The autoclave was heated for 16—20 h at 220°C. The work-up was the same as described above yielding 1.56 g of $Cr(CO)_6$, 83% yield.

Preparation of $Cr(CO)_6$ by extraction of chromium powder

Potassium (1.51 g, 0.0386 moles), $CrCl_3 \cdot 3\,THF$ (4.83 g, 0.0129 moles) and KI (2.14 g, 0.0129 moles) were heated in benzene (50 ml) at 90°C for 2 h. The black material was filtered from the brown benzene solution and the brown-black residue washed with benzene (3 × 10 ml) and then with THF (6 × 10 ml) until the THF was colorless. The combined benzene and THF extracts were evaporated and the remaining brown crystals were dissolved in water and the chromium content determined as Cr_2O_3 yielding 256 mg of Cr. Thus 38.1% of Cr remained only partially reduced in the form of chromium(II) salts. The black material was then extracted with n-butanol (5 ml), methanol (5 ml) and finally water (200 ml); The water wash was carried out until the water was neutral. Titration of the alkaline solution required 87.4 ml of 0.1 *N* HCl. This corresponds to 341 mg of K or 22.7% of the original amount.

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