New Synthesis of Chromium Trichloride Tetrahydrofuranate

JACOB SHAMIR

Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, 91904 Jerusalem, Israel

(Received August 29, 1988)

The complex of chromium trichloride with tetrahydrofuran is of great importance since it is used as an intermediate in the syntheses of various metal–organic complexes. However, the preparation of the THF complex with $CrCl_3$ poses some problems and a special technique has been described in the literature to this end [1]. Tetrahydrofuranates of metal chlorides which are appreciably soluble in the hot liquid ligand itself can be prepared, rather easily, by dissolving the anhydrous metal chloride in the parent ligand then allowing the crystallization to take place on cooling. Metal chlorides which have very limited solubility in the parent ligand can still be prepared by continuous extraction in a Soxhlet apparatus. The preparation of the chromium trichloride complex by the above-mentioned method is particularly difficult since $CrCl_3$ is practically insoluble in THF [2]. Anhydrous chromium trichloride, in general, is rather unreactive, as illustrated by its insolubility even in water. This inertness has been explained as resulting from the polymeric structure of chromium trichloride, being viewed as a series of interconnecting octahedral $Cr(III)Cl_6$ complexes, which are relatively inert to ligand substitution. The Cl^- ligands can, presumably, be labilized by the transfer of an electron from a catalytic amount of Cr(II) in the solid [3]. It has therefore been suggested that zinc dust be added to the reaction mixture to reduce the chromium to the divalent state [1]. In any case, anhydrous conditions have to be maintained and both reagents (the metal chloride as well as the THF) have to be dry. Thus THF itself has also to be predried in a separate set-up. This can be done by refluxing it over a sodium ribbon for about 5 h before the complexation reaction itself takes place. The latter is then performed by using an extraction process with a Soxhlet apparatus for about 10–15 h [1].

This paper describes a very easy synthesis of this complex, by performing the whole preparation in one simple apparatus and in a short time. The whole reaction takes place in a thionyl chloride environment which dehydrates both the chromium trichloride and the tetrahydrofuran.

Experimental

First, the hexa-hydrated chromium trichloride is dehydrated by refluxing the material with an excess of thionyl chloride. In this process, the very hygroscopic form of anhydrous chromium trichloride results [4]. A regular, simple reflux apparatus is used, consisting of a glass bulb fitted with a cooling condenser and protected from the humidity in the air by connecting a drying tube, filled with $CaCl_2$, onto its top. During the reaction, the green color of the hydrated salt changes to some kind of grayish color. An excess of commercial THF, without any special predrying, is then added to the reaction mixture through the top of the condenser and the drying tube is replaced on top of the condenser. A vigorous reaction takes place immediately with the formation of beautiful purple crystals, which are spread on the surface of the foaming mixture. The reaction is completed after about 15–30 min.

After cooling the mixture, the solid is filtered through sintered glass, with pumping. Since the anhydrous conditions are maintained by the presence of the thionyl chloride, even a water pump can be used. However, it is useful to place a wash bottle filled with a concentrated aqueous solution of sodium hydroxide in front of the pump to prevent the thionyl chloride from being released into the air. The solid can be washed with small amounts of CCl_4 or hexane. The whole reaction can be performed in the open air, since the chromium trichloride tetrahydrofuranate is quite stable in the open air for several hours without appreciable hydrolysis [1]. *Anal.* Calc. for $CrCl_3(C_4H_8O)_3$: Cr, 13.88. Found: Cr, 13.7%.

Samples in Nujol mulls on a sodium chloride window were used for recording the IR spectra.

Results and Discussion

The chromium trichloride tetrahydrofuranate can easily be synthesized in a short time and in a rather simple set-up. A pure product is obtained and no further purification is required.

Complexes with cobalt and copper chlorides can similarly be prepared, using their hydrates as starting materials. However, these complexes, particularly the cobalt one, hydrolyse more easily than the chromium complex and therefore it is best to filter them in a dry bag under a dry nitrogen atmosphere.

The purities of all these compounds have been checked by both quantitative analysis and their infrared spectra (Table 1), which were in good agreement with the literature data [2].

0020-1693/89/$3.50

TABLE 1. Infrared Frequencies of the COC Symmetric and Asymmetric Stretchings (cm^{-1})

	Asym. str. C–O–C	Sym. Str. C–O–C
THF, neat	1075	910
Cr complex	1010	850
Co complex	1025	870
Cu complex	1040	880

References

1 W. Herwig and H. H. Zeiss, *J. Org. Chem., 23* (1958) 1404.
2 R. J. Kern, *J. Inorg. Nucl. Chem., 24* (1962) 1105.
3 R. J. Angelici, *Synthesis and Techniques in Inorganic Chemistry*, W. B. Saunders, London, 1977, p. 34.
4 A. R. Gray, in T. Moeller (ed.), *Inorganic Synthesis*, Vol. 5, McGraw Hill, New York, 1957, p. 153.