

CARBON MONOOXIDE-INDUCED DISPROPORTIONATION OF DICYCLOPENTADIENYL TITANIUM CHLORIDE DIMER TO DICYCLOPENTADIENYL TITANIUM DICARBONYL AND DICYCLOPENTADIENYL TITANIUM DICHLORIDE

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Summary

Dicyclopentadienyltitanium chloride dimer under CO atmosphere undergoes disproportionation leading to dicyclopentadienyltitanium dicarbonyl and dicyclopentadienyltitanium dichloride.

We recently described [1] the reduction of Cp_2TiCl_2 by manganese powder under CO to give $(\text{Cp}_2\text{TiCl})_2$ and to a carbonyl derivative showing the same infrared absorptions as $\text{Cp}_2\text{Ti}(\text{CO})_2$. After CO absorption was complete the solution still was green, however, whereas $\text{Cp}_2\text{Ti}(\text{CO})_2$ is red. For some reason the reduction process was limited mainly to $(\text{Cp}_2\text{TiCl})_2$. The latter was shown not to be reduced further even in the presence of CO [1,2].

We observed, however, that on standing for a long time under CO, pure $(\text{Cp}_2\text{TiCl})_2$ in tetrahydrofuran gave a red deposit of $\text{Cp}_2\text{Ti}(\text{CO})_2$. The CO absorption was determined quantitatively at 20°C and found to be 1/4 of the theoretical value for the formation of $\text{Cp}_2\text{Ti}(\text{CO})_2$. The remaining product corresponded to a stoichiometric mixture of $(\text{Cp}_2\text{TiCl})_2$ and Cp_2TiCl_2 (green solution). Both compounds could be isolated separately when the solvent was completely removed.

The 1/1 stoichiometry of this mixture and its behaviour correspond to the formula of adducts in which a coordination site of one molecule of $(\text{Cp}_2\text{TiCl})_2$ or of two molecules of Cp_2TiCl is occupied by Cl. This is in agreement with the fact that upon adding Cp_2TiCl_2 to $(\text{Cp}_2\text{TiCl})_2$ in 1/1 ratio or upon adding to $(\text{Cp}_2\text{TiCl})_2$ more than 2 moles of tetraethylammonium chloride per mole of Ti, CO absorption was completely blocked. Reduction by CO possibly implies attack on a fifth position

of the Cp_2TiCl dimer. Recent results obtained in the electrochemical reduction of Cp_2TiCl_2 indicate that reduction begins by electron transfer to Cp_2TiCl_2 without Cl dissociation [3]. Insertion of Cp_2TiCl_2 between two Cp_2TiCl units cannot be excluded, however, even though it is not easy to explain why reduction does not occur.

The reduction of $(\text{Cp}_2\text{TiCl})_2$ must involve the following steps: (a) attack by CO on $(\text{Cp}_2\text{TiCl})_2$ possibly on a fifth coordination site, (b) disproportionation, and (c) adduct formation between Cp_2TiCl_2 and $(\text{Cp}_2\text{TiCl})_2$.

Molecular weight determination carried out either on the solution of the product obtained by reduction with CO and filtration of $\text{Cp}_2\text{Ti}(\text{CO})_2$ or on a mixture of Cp_2TiCl_2 and $(\text{Cp}_2\text{TiCl})_2$ gives a value of 690 amu; this value is in agreement with the presence in solution of a product of formula $[\text{Cp}_2\text{TiCl}_2(\text{Cp}_2\text{TiCl})_2]$ (676 amu). In conclusion, the compound $\text{Cp}_2\text{Ti}(\text{CO})_2$ can be prepared directly by $(\text{Cp}_2\text{TiCl})_2$ and CO via disproportionation. The process is blocked by the formation of an adduct between $(\text{Cp}_2\text{TiCl})_2$ and Cp_2TiCl_2 .

Experimental

General procedures

All reactions were carried out under an inert atmosphere. Organic solvents were deoxygenated and dried by distillation from suitable drying agents [4]. Cp_2TiCl_2 was obtained commercially (Strem Chemicals). $(\text{Cp}_2\text{TiCl})_2$ was prepared as previously described [5].

Infrared spectra were recorded on a Perkin-Elmer 283 B spectrophotometer. Molecular weights measurements were made with a Knauer osmometer by the vapour pressure method, under N_2 atmosphere in tetrahydrofuran solutions, with dibenzoyl and Cp_2TiCl_2 as standards.

Reactions

(a) $(\text{Cp}_2\text{TiCl})_2$ (0.2 g) was dissolved in 30 cm^3 of an anhydrous tetrahydrofuran and stirred under CO, the volume of the latter being measured in a buret at 20°C; after about three days the colour of the solution changed from green to brown-red and an absorption of CO was observed which corresponded to 1/4 mol of titanium. The solution showed two vibrational bands in the IR spectrum at 1960 and 1875 cm^{-1} . After partial evaporation of the solvent and addition of n-hexane a brown-red, air-sensitive powder ($\text{Cp}_2\text{Ti}(\text{CO})_2$) was obtained.

(b) Equimolar amounts of Cp_2TiCl_2 and $(\text{Cp}_2\text{TiCl})_2$ were dissolved in tetrahydrofuran and the solution was stirred under CO at 20°C as above; after several days no absorption of CO was observed.

(c) A large excess of Et_4NCl was added under CO to a tetrahydrofuran solution of $(\text{Cp}_2\text{TiCl})_2$; after stirring for several days at 20°C no absorption of CO was observed.

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