

Preliminary communication

DINITROGEN CATALYTIC EFFECT ON REDUCTION OF Cp_2TiCl_2 BY Mn

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Summary

In the reduction of dichlorodicyclopentadienyltitanium(IV) with Mn powder in some 1,2-dialkoxyethanes at room temperature the reduction times are much shorter under N_2 than under Ar, although there is no significant gas absorption. A comparison with the same reduction under CO is also reported.

Since the discovery of dinitrogen complexes [1] an intensive research effort has been devoted to their chemistry, especially to that of the titanium [2], but to our knowledge there has been no report of a catalytic effect of dinitrogen. Such catalysis is the subject of the present communication.

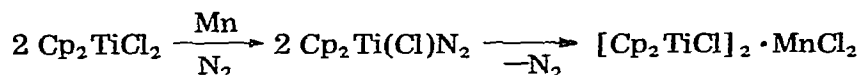
Dichlorodicyclopentadienyltitanium has been reported to be readily reduced by Zn or Mn in 1,2-dimethoxyethane at room temperature to give ZnCl_2 or MnCl_2 adducts of Cp_2TiCl [3]. Upon attempting this reduction in 1,2-diethoxyethane under Ar we observed only a very slow reaction which required six days to give the green titanium(III) complex previously described [3]. When the Ar was replaced by N_2 , however, the reduction was complete in about two days.

Similar results were obtained with 1,2-dibutoxyethane, but with 1,2-dimethoxyethane, tetrahydrofuran, 1,4-diethylene dioxide, or diethyleneglycol dimethyl ether the reduction was so fast that no differentiation could be made between the rates under N_2 and Ar. Probably these high rates are due to the higher solvating power of these solvents.

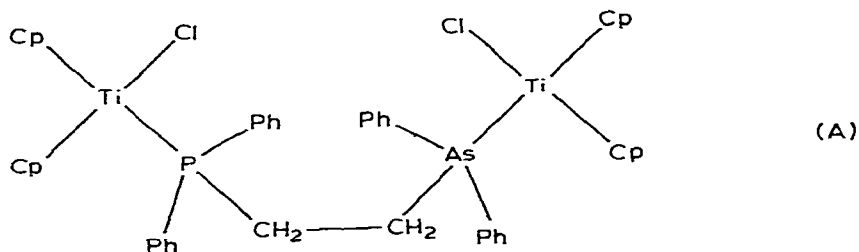
We initially assumed that a dinitrogen complex was formed under the N_2 at-

mosphere, but no significant gas absorption was noted even at low temperature (-78°C). Dinitrogen complexes were not obtained even upon replacing Mn (to prevent coordination of titanium(III) with MnCl_2) by 1% sodium amalgam; the latter reduced Cp_2TiCl_2 very rapidly under N_2 and Ar, no difference being evident.

Use of CpTiCl_3 in place of Cp_2TiCl_2 also resulted in a fast reduction, as evidenced by the sudden change of colour of the mixture from red to green on Mn addition. The rapid reduction of CpTiCl_3 was utilized to regulate the reduction of Cp_2TiCl_2 , simply by adding small amounts of CpTiCl_3 (5–10%) to Cp_2TiCl_2 . Under these conditions the reduction under a N_2 atmosphere was shortened to about $1\frac{1}{2}$ days and that with Ar to about $4\frac{1}{2}$ days. CpTiCl_2 , formed by reduction of CpTiCl_3 , probably reduces Cp_2TiCl_2 to Cp_2TiCl , thus reforming CpTiCl_3 . The latter acts as a catalyst by being reduced faster than Cp_2TiCl_2 . Thus, under various conditions, we have observed the same large difference in reduction times under Ar and under N_2 . If we assume that the effect does not arise from the difference in solubility between N_2 and Ar [4], or from the presence of impurities not revealed by the gas chromatographic analysis, we must conclude that N_2 does stabilize the reduced Cp_2TiCl species by occupying the fourth coordination site. Formation of the Cp_2TiCl adduct with MnCl_2 then occurs with ejection of N_2 :



The assumption that N_2 occupies a coordination site of the complex is supported by the fact that certain ligands analogous to dinitrogen can occupy such a position in a stable species [5] and that reduction of Cp_2TiCl_2 with Mn in presence of tertiary phosphines (L) leads to $\text{Cp}_2\text{Ti}(\text{Cl})\text{L}$. One of these ligands ($\text{Ph}_2\text{PCH}_2\text{CH}_2\text{AsPh}_2$) provided crystals suitable for an X-ray structural analysis which showed that the complex A was formed [6]:



That a ligand like N_2 can occupy a coordination site of the complex in a labile way has been proved by carrying out the reduction in presence of the isoelectronic CO ligand. It was found that the reduction, to give a green solution, took place within 6 h at room temperature and atmospheric pressure with absorption of one molecule of CO per atom of Ti. The solution showed two IR bands at 1960 and 1875 cm^{-1} , tentatively attributable to terminal and bridging CO, respectively. These two bands disappeared, with formation of the reduced titanium(III) species, simply upon removing CO under vacuum and replacing it with Ar.

No CO absorption was noted in the case of $[\text{Cp}_2\text{TiCl}]_2$ or from

$[\text{Cp}_2\text{TiCl}]_2 \cdot \text{MnCl}_2$, and so CO coordination appears to take place only during Cp_2TiCl_2 reduction. To our knowledge no carbonyl complexes of cyclopentadienyltitanium(III) species have been reported. Reduction under CO therefore provides further evidence for our view that N_2 behaves as a hidden ligand which enters the Ti coordination sphere to stabilize the first reduced intermediate, and is subsequently eliminated, thus, exerting a catalytic action. At present we have no idea how general is this behaviour, but other examples are likely to be discovered.

Experimental

All reagents were accurately dried and deoxygenated before use. Cp_2TiCl_2 was obtained commercially (Strem Chemicals). CpTiCl_3 and $[\text{Cp}_2\text{TiCl}]_2$ were prepared by published methods [7, 5]. The manganese powder had an average size under 0.01 mm. Purified gases were checked by passing them into a Cp_2TiCl slurry which immediately turns to yellow and red in the presence of traces of oxygen.

Reductions were carried out as follows: Mn powder (0.15 g) was added, at room temperature under N_2 , to Cp_2TiCl_2 (0.5 g), partially dissolved in 50 cm³ of 1,2-diethoxyethane. After about two days the red suspension became green and a thin layer of green solid deposited on the unreacted Mn powder. Under Ar the same process required about six days. The green product is excessively sensitive to air, in which it immediately turns yellow, giving rise to polymeric oxochloro derivatives of titanium(IV) [8]. If the solution of the green product is allowed to stay in presence of Mn powder, under N_2 or Ar, a deep blue colour is observed after some days (with no N_2 absorption, as verified by using a suitable constant pressure gas buret). Reduction with 1% sodium amalgam was carried out at room temperature and also at -30°C .

$[(\text{Cp}_2\text{TiCl})_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{AsPh}_2)]$ was prepared by reducing Cp_2TiCl_2 in diethyleneglycol dimethyl ether with Mn, then filtering and adding an excess of the ligand. After some days light-green crystals were formed.

Reduction with Mn under CO was carried out similarly.

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Note added in proof: Some cyclopentadienyltitanium carbonyls have been described recently, but carbonylation of Cp_2TiCl was unsuccessful (E.J.M. de Boer, L.C. ten Cate, A.G.J. Staring and J.H. Teuben, *J. Organometal. Chem.*, 181 (1979) 61).