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Preliminary communication

Cyclopentadienyl ligands as a hydrogen source in the formation of titanium hydride complexes

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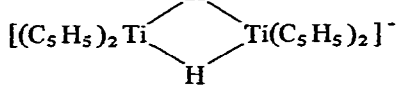
It has been previously shown that at room temperature, in the presence of some transition metal compounds ($TiCl_4$, Cp_2TiCl_2, $CrCl_3$, $MoCl_5$ etc.) molecular nitrogen may be reduced by means of metallic magnesium activated by its iodide[1,2]. The reaction was carried out in benzene–ether and gave ammonia after hydrolysis.

Whilst investigating one such nitrogen-fixating system, *i.e.*, $(C_5H_5)_2TiCl_2 + Mg + MgI_2$, we have found that in the absence of nitrogen titanium hydride complexes were formed as a result of hydrogen transfer from the cyclopentadienyl ligands.

Within 60–80 min after mixing $(C_5H_5)_2TiCl_2$ with Mg and MgI_2 (in a molar ratio of 1/8/3), the solution exhibited an ESR signal (*g* 1.994 ± 0.02)*, with triplet splitting (8–9 gauss) and a 1/2/1 intensity distribution, which did not change with time. Such a signal pattern is probably due to the interaction of an unpaired titanium electron with the two hydride ligands bound to the titanium center. In accord with such an assignment the decomposition of the reaction mixture with D_2O resulted in evolution of H_2. HD and D_2 produced in the ratio 1/2 – 4/0.5 – 2 respectively. The amount of H (g-atom) per mole of the initial titanium complex was found to be 1.4–1.8.

Similar ESR signals have been observed earlier during studies of the reduction of $(C_5H_5)_2TiCl_2$ with organolithium and magnesium derivatives[3], metallic magnesium (in the presence or absence of $i\text{-}C_3H_7Br$ activator)[3], sodium or lithium naphthalides[4] and other reducing agents[5]. On the basis of an analysis of the ESR spectra, the paramagnetic centers have been variously suggested as the anionic titanium dihydride complexes

$[(C_5H_5)_2TiH_2]^-$ and



$$[(C_5H_5)_2Ti\begin{smallmatrix}H\\ \\ H\end{smallmatrix}Ti(C_5H_5)_2]^-$$

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*The appearance of this signal was preceded by a number of intermediate signals which gradually disappeared (*cf.* ref.2).

respectively. The latter structure was assumed to arise through hydrogen abstraction from an alkyl group of the organometallic compound or from the solvent molecule[3,4].

In the reaction of $(C_5H_5)_2TiCl_2$ with Mg and MgI_2, carried out in deuterated solvent (a mixture of ether and benzene deuterated by 93 and 98% respectively), the *g*-factor and a pattern of the final triplet signal were found to be unchanged, and decomposition of this mixture with H_2O gave no D_2 and HD.

On the other hand when the deuterated analogue $(C_5D_5)_2TiCl_2$ (percentage of deuteration not less than 90%) was used instead of $(C_5H_5)_2TiCl_2$, the ESR spectrum exhibited an unresolved singlet instead of the triplet with the same *g*-factor. On dilution, a partly hyperfine pattern of this signal was observed (Fig.1).

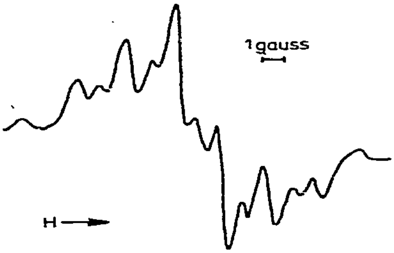

Fig.1. ESR spectrum of the diluted reaction solution of $(C_5D_5)_2TiCl_2$ + Mg + MgI_2 at room temperature in ether–benzene, and *in vacuo.*

In this case decomposition of the mixture with H_2O gave D_2, HD and H_2 in the ratio 1/2–3/0.4–1 respectively, the amount of D (g-atom) per mole of $(C_5D_5)_2TiCl_2$ being ca.2. Thus, the hydrogen source involved in the formation of titanium hydride complexes in the reaction of $(C_5H_5)_2TiCl_2$ with Mg and MgI_2 is not the solvent but the cyclopentadienyl ligands.

Similar behaviour was observed with sodium naphthalide (NpNa) in THF as a reducing agent (molar ratio of $(C_5H_5)_2TiCl_2$/NpNa 1/3.5). Again in this case, use of $(C_5D_5)_2TiCl_2$ instead of $(C_5H_5)_2TiCl_2$ resulted in a change of the ESR spectrum; instead of the signal (*g* 1.994 shown in Fig.2, and observed earlier by Henrici-Olivé and

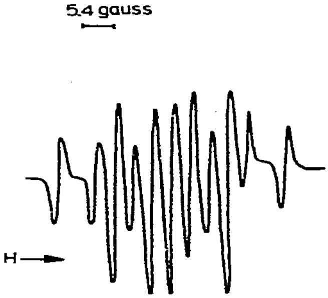

Fig.2. ESR spectrum of the reaction solution of $(C_5H_5)_2TiCl_2$ + NpNa at room temperature in tetrahydrofuran, and *in vacuo.*

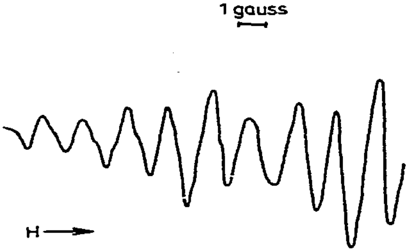

Fig.3. ESR spectrum of the diluted reaction solution of $(C_5D_5)_2TiCl_2$ + NpNa at room temperature in tetrahydrofuran and *in vacuo* (only the high field part of the spectrum is shown).

Olivé[4], a singlet with the same *g*-factor was obtained. The hyperfine pattern of this singlet, as obtained on dilution, is given in Fig.3. Decomposition of the mixture obtained from $(C_5D_5)_2TiCl_2$ and NpNa (molar ratio of $(C_5D_5)_2TiCl_2$/NpNa 1/3.5) with H_2O gave D_2, HD and H_2 (1/10/17). The amount of D (g-atom) per mole of $(C_5D_5)_2TiCl_2$ was about 0.3★ in this case. Thus with sodium naphthalide, the formation of hydride complexes also seems to be, at least partially, due to a hydrogen transfer from the cyclopentadienyl rings to the titanium atom★★.

Unlike sodium naphthalide and magnesium, the reduction of both $(C_5H_5)_2TiCl_2$ and $(C_5D_5)_2TiCl_2$ with ethylmagnesium bromide in ether produces a triplet ESR signal pattern. This is in agreement with the data of Brintzinger[3], who showed that in this case a hydride ion transfers to the titanium atom generally from the alkyl group of Grignard reagent. However, again, when the reduction products of $(C_5D_5)_2TiCl_2$ were treated with H_2O, small quantities of HD and D_2 (in a molar ratio of D_2/HD/H_2 1/51/380) were evolved.

It is interesting to note that the reduction of $C_5H_5TiCl_3$ with the mixture of Mg and MgI_2 proceeds analogously to that described for $(C_5H_5)_2TiCl_2$, producing a final ESR signal of triplet form with *g* 1.994 (*cf.* also ref.5). No such signal pattern was observed for $(CH_3)_5C_5TiCl_3$ where the cyclopentadienyl ring hydrogens are substituted by methyl groups. This indicates that in the reduction of $C_5H_5TiCl_3$ with magnesium the C–H bonds of the cyclopentadienyl ligands are also probably the source of hydride hydrogen.

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★The reaction mixture obtained by reduction of $(C_5H_5)_2TiCl_2$ with NpNa (molar ratio of $(C_5H_5)_2TiCl_2$/NpNa 1/3.5) after treatment with D_2O gave H_2, HD and D_2 in the ratio 1/4.7/5.7. The amount of H (g-atom) per mole of $(C_5H_5)_2TiCl_2$ was about 0.5.

★★In the recent communication of Van Tamelen *et al.*[6], similar conclusions were reached regarding the hydrogen source in the formation of titanium hydride complexes from $(C_6H_5)_2TiCl_2$ + NpNa reaction mixtures.

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