Spontaneous H—D Exchange in Hydrogenated 1-Methylallyldicyclopentadienyltitanium(III) - an Active Catalyst for the Isomerization and Hydrogenation of Unsaturated Hydrocarbons

By HENDRIK A. MARTIN and R. O. de JONGH*
(*Unilever Research Laboratory, Vlaardingen, The Netherlands*)

Summary Hydrogenation of $(C_5H_5)_2Ti(C_4H_7)$ yields an active homogeneous catalyst which can be used for the hydrogenation and isomerization of unsaturated hydrocarbons and which exchanges its cyclopentadienyl hydrogen atoms in a deuterium atmosphere yielding a deuteriated complex which can be converted with hydrogen chloride into pure $(C_5D_5)_2TiCl_2$.

DIMETHYLDICYCLOPENTADIENYLTITANIUM(IV), $(C_5H_5)_2TiMe_2$ (dimethyl-DCT), can be hydrogenated in solution to bis[dicyclopentadienyltitanium(II)], $[(C_5H_5)_2Ti]_2$, $[DCT]_2$:[1]

$$2(C_5H_5)_2TiMe_2 + 2H_2 \rightarrow [(C_5H_5)_2Ti]_2 + 4CH_4 \qquad (1)$$

In cyclohexane solution, π-allyldicyclopentadienyltitanium(III), $(C_5H_5)_2Ti(C_3H_5)$ (allyl-DCT), and some of its homologues also react with molecular hydrogen,[2] about 1·9 mole of H_2 (20°, 760 mm. Hg) being taken up per mole of allyl complex.† Treatment of the hydrogenated solutions of the allyl complex with hydrogen chloride gives dicyclopentadienyltitanium(III) monochloride; further oxidation yields the dichloride $(C_5H_5)_2TiCl_2$.[2] From this reaction and from evidence reported here, the complex [referred to as complex (A)] formed by hydrogenation of 1-methylallyl-DCT (1 mmole) in cyclohexane (100 ml.) is distinctly different from $[DCT]_2$[2](*cf.* ref. 3).

The absorption spectrum (400—1000 nm.) of solutions of (A)[2] is different from that of $[DCT]_2$;[2,3] we also found a shift of the absorption maxima of (A) (in an argon atmosphere) in the presence of cyclohexene which was not observed for $[DCT]_2$. If the solution of (A) is added to cyclo-octa-1,5-diene (in an argon atmosphere), complete isomerization to cyclo-octa-1,3-diene occurs at 20° in about 15 min. at a molar ratio substrate/catalyst = 150. In a hydrogen atmosphere (20°, 760 mm. Hg) a fast hydrogenation of unsaturated hydrocarbons is observed. 1-Methylallyl-DCT, therefore, is a convenient precursor for a homogeneous hydrogenation and isomerization catalyst.

Hydrogenation catalysts, derived from DCT dichloride with main-group organometallic compounds as co-catalyst, are well known.[4] Unlike complex (A), the main-group metal compounds may participate in the catalytic process, and other complexes may be formed.[1,5]

Isotopic exchange of hydrogen was observed when a cyclohexane solution of (A) was treated with molecular deuterium under mild conditions (20°, 760 mm. Hg).

---

† New measurement, *cf.* ref. 2.

After oxidation with hydrogen chloride in ether, the hitherto unknown perdeuterio-DCT dichloride, $(C_5D_5)TiCl_2$, could be isolated. Mass and i.r. spectra revealed only a very slight hydrogen contamination. The absorption spectra (230—700 nm.) of the H- and D-complexes were identical. A strong splitting of the C–D stretching frequency at 2307 and 2338 cm^{-1} was observed in the i.r. spectrum (KBr), which was not found with H-DCT dichloride, H- and D-ferrocene,[6] and H- and D-dibenzenechromium.[7] This may be ascribed to a change in the molecular symmetry caused by crowding of the cyclopentadienyl ligands in DCT dichloride.[8]

Deuteriation of cyclopentadienyl ligands in metallocenes has been effected by acid and base catalysis instead of by exchange with molecular deuterium.[9] Recently, exchange with molecular deuterium in triphenylphosphine complexes and triphenyl phosphite complexes of Group VIII metal hydrides has been reported,[10] only the hydrogen in the *ortho*-position of the phenyl group being involved.

With pure $[DCT]_2$[3] neither hydrogen–deuterium exchange nor catalytic activity was observed: it does not react with hydrogen and unsaturated hydrocarbons under mild conditions (20°, 760 mm. Hg), and hence cannot be an intermediate in the hydrogenation of 1-methylallyl-DCT.

The rate of hydrogenation of the precursors seems to determine whether complex (A) or $[DCT]_2$ is formed. Dimethyl-DCT reacts rapidly with hydrogen (20°, 760 mm. Hg) after an induction period.[1] Also, the rather unstable 1,1-dimethylallyl-DCT is hydrogenated very quickly.[2] In both cases, $[DCT]_2$ is formed in a way similar to equation (1).[1,2] The hydrogenation of 1-methylallyl-DCT, however, proceeds gradually[2] and leads to complex (A) (in dilute as well as in concentrated solutions). We have now observed that when dimethyl-DCT in a high dilution (1 mmole in 100 ml. cyclohexane) is hydrogenated with very efficient stirring (20°, 760 mm. Hg), complex (A) is formed (HCl reaction; absorption spectrum, in the 400—1000 nm. range; catalytic activity; H—D exchange). This suggests that in the hydrogenation of allyl-DCT and dimethyl-DCT, the complexes (A) and $[DCT]_2$ are formed *via* a similar intermediate. At a relatively high concentration of hydrogen with respect to the intermediate, complex (A) is formed. In the reverse case, no reaction with hydrogen occurs and the intermediate will lead to $[DCT]_2$.

We believe that complex (A) is a hydride. More details on the complex (A), the scope of the catalysis, and the synthesis of $(C_5D_5)_2TiCl_2$ will be reported elsewhere.

We thank Prof. Dr. D. A. van Dorp for his stimulating interest, Mr. J. de Bruyn for the interpretation of mass spectra, and Dr. J. Bus and Mr. A. A. Memelink for discussion of the i.r. spectra.

(*Received, September 26th,* 1969; *Com.* 1458.)

---

[1] K. Clauss and H. Bestian, *Annalen*, 1962, **654**, 8.

[2] H. A. Martin and F. Jellinek, *J. Organometallic Chem.*, 1967, **8**, 115.

[3] J.-J. Salzmann and P. Mosimann, *Helv. Chim. Acta*, 1967, **50**, 1831.

[4] M. F. Sloan, A. S. Matlack, and D. S. Breslow, *J. Amer. Chem. Soc.*, 1963, **85**, 4014; K. Shikata, K. Nishino, K. Azuma, and Y. Takegami, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1965, **68**, 358, 490; *Chem. Abs.*, 1966, **65**, 10452b; 1965, **63**, 7111a; Y. Tajima and E. Kunioka, *J. Org. Chem.*, 1968, **33**, 1689; I. V. Kalechits, V. G. Lipovich, and F. K. Shmidt, *Kinetics and Catalysis* (*U.S.S.R.*), 1968, **9**, 16; R. Stern, C. Hillion, and L. Sajus, *Tetrahedron Letters*, 1969, 1561.

[5] H. A. Martin and F. Jellinek, *J. Organometallic Chem.*, 1968, **12**, 149; H. H. Brintzinger, *J. Amer. Chem. Soc.*, 1967, **89**, 6871.

[6] E. R. Lippincott and R. D. Nelson, *Spectrochim. Acta*, 1958, **10**, 307.

[7] H. P. Fritz and J. Manchot, *Spectrochim. Acta*, 1962, **18**, 171.

[8] A. N. Nesmeyanov, E. I. Fedin, O. V. Nogina, N. S. Kochetkova, V. A. Dubovitskii, and P. V. Petrovskii, *Tetrahedron*, 1966, Suppl. **8**, part II, 389.

[9] V. N. Setkina and D. N. Kursanov, *Russ. Chem. Rev.*, 1968, **37**, 737.

[10] G. W. Parshall, *J. Amer. Chem. Soc.*, 1968, **90**, 1669; W. H. Knoth and R. A. Schunn, *ibid.*, 1969, **91**, 2403.