

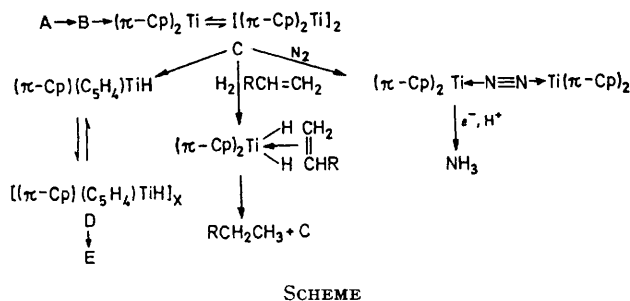
## The Involvement of Titanocene and Related Species in the Reduction of Dinitrogen and Olefins

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**Summary** Four sequential products have been spectrally detected in the reduction by sodium of dicyclopentadienyltitanium(IV) dichloride:  $[(\pi\text{-Cp})_2\text{TiCl}]_2$ ,  $[(\pi\text{-Cp})_2\text{Ti}]_{1-2}$ ,  $[(\pi\text{-Cp})(\text{C}_5\text{H}_4)\text{TiH}]_x$ , and  $(\pi\text{-Cp})(\text{C}_5\text{H}_4)\text{TiH}_2\text{Ti}(\text{C}_5\text{H}_4)(\pi\text{-Cp})$  ("stable titanocene"); the second of these reacts rapidly and reversibly with  $\text{N}_2$  to give a dark blue complex reducible to ammonia and appears to catalyse the cyclopentadienyltitanium-promoted rapid, room temperature-atmospheric pressure hydrogenation of olefins.

In one procedure for titanocene induced  $\text{N}_2$  fixation,<sup>1,2</sup>  $(\pi\text{-Cp})_2\text{TiCl}_2$  in toluene is stirred at room temperature with sodium sand under  $\text{N}_2$  at atmospheric pressure;<sup>3</sup> subsequent

the following sequence as a consequence of reaction of  $(\pi\text{-Cp})_2\text{TiCl}_2$  with sodium under argon (Figure 1): A,  $(\pi\text{-Cp})_2\text{TiCl}_2$ ; B,  $[(\pi\text{-Cp})_2\text{TiCl}]_2$ ; C,  $[(\pi\text{-Cp})_2\text{Ti}]_{1-2}$ ; D,  $[(\pi\text{-Cp})(\text{C}_5\text{H}_4)\text{TiH}]_x$ ; and E, "stable titanocene",  $[(\pi\text{-Cp})(\text{C}_5\text{H}_4)\text{TiH}]_2$ ,<sup>4</sup> the final product. Under nitrogen, only A, B, and C could be spectrally detected in turn, following which a black precipitate appeared; hydrolysis of the mixture yielded 0.6–0.7  $\text{NH}_3$ :Ti. Whereas A, B, D, and E in solution do not react with  $\text{N}_2$ , "active titanocene," C (prepared by use of 2 equiv. Na under argon for 6–10 days followed by filtration in drybox) in toluene reacts rapidly and reversibly with  $\text{N}_2$  below room temperature, forming a dark blue complex (Figure 2). In the i.r. spectrum, C



hydrolysis gives  $\text{NH}_3$ . Visible and i.r. spectroscopy have now been used to detect titanium species which appear in

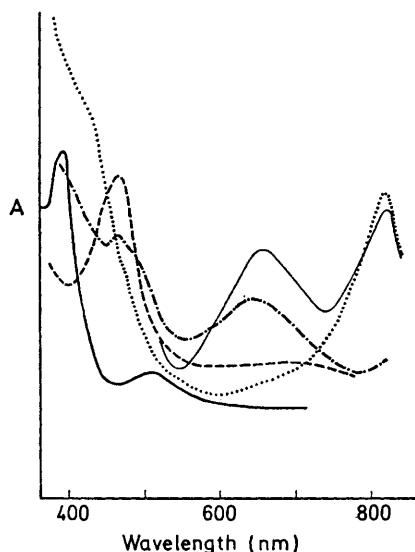


FIGURE 1. Visible spectra of A (—), B (---), C (-·-·-), D (— — —), and E (·····) in toluene at room temperature under argon.

† Although the basis for comparison is weak, compound C may very well be identical to the metastable titanocene dimer obtained by Marvich and Brintzinger<sup>2b</sup> by a much more indirect route and reported to have physical and chemical properties very similar to those of C.

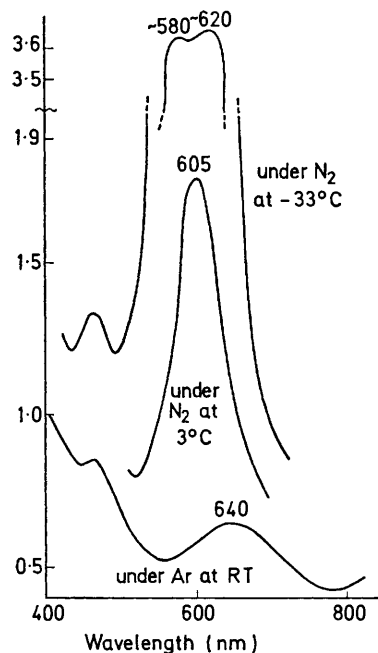


FIGURE 2. Visible spectra of  $[(\pi\text{-Cp})_2\text{Ti}]_2\text{N}_2$  in toluene as a function of temperature.

revealed intense peaks at 790 and 1010  $\text{cm}^{-1}$  but no absorption between 1800–2100  $\text{cm}^{-1}$  or 1200–1250  $\text{cm}^{-1}$ , consistent with the absence of either terminal or bridging Ti–H bonds and the presence of only  $\pi$ -bonded (Cp) ligands;<sup>5</sup> with CO, C in toluene is converted to  $\text{Cp}_2\text{Ti}(\text{CO})_2$ .<sup>†6</sup> Highly unstable at room temperature under argon, C generates D, which displays i.r. bands at 1815 and 1960  $\text{cm}^{-1}$ , representing Ti–H stretching vibrations,<sup>7</sup> and 660  $\text{cm}^{-1}$ , ascribed to multiple bond character in a carbene complex-like  $\text{TiC}_5\text{H}_4$  unit. The latter peak is not observed for C but is present in the spectrum of E.<sup>4</sup> In agreement with this interpretation, Ti–D frequencies in perdeuterated D

appear at 1305 and 1355  $\text{cm}^{-1}$ , while the 660  $\text{cm}^{-1}$  peak remains unchanged. If C in toluene is stirred for prolonged periods over sodium or heated at 100° for some hours, E is formed. Earlier observations and conclusions,<sup>1,2</sup> supplemented by these new findings, permit structural proposals and sequences comprising part of the Scheme.

In a new, titanocene-based method for rapid, room temperature-atmospheric pressure alkene hydrogenation,<sup>8</sup> a solution of sodium or lithium naphthalenide (Np) in THF was slowly added dropwise under an  $\text{H}_2$  atmosphere to a rapidly stirred solution of  $[(\pi\text{-Cp})_2\text{TiCl}]_2$ <sup>9</sup> or  $(\pi\text{-Cp})_2\text{TiCl}_2$  and dec-1-ene (Ti: olefin molar ratio of 1:4) in THF. Before one equiv. of Np (or two equiv. in the case of  $\text{Ti}^{\text{IV}}$  dichloride) had been added, a very rapid uptake of  $\text{H}_2$  commenced. Hydrogenation was complete within 1 h and before all the Np theoretically required to reduce all the titanium to  $\text{Ti}^{\text{II}}$  had been added. The product isolated was >95% pure decane, accompanied by small amounts of *cis*- and *trans*-dec-2-ene.

The short-lived but powerful hydrogenation catalyst is thought to be titanocene C. No room temperature hydrogenation-isomerization of dec-1-ene (in THF under  $\text{H}_2$ ) occurs with (i) Np in the absence of titanium compound, (ii)  $[(\pi\text{-Cp})_2\text{TiCl}]_2$  in the absence of Np, (iii) equivalent amounts of  $(\pi\text{-Cp})_2\text{TiCl}_2$  and LiH, which by themselves generate  $(\text{Cp}_2\text{TiCl})_2$  and  $\text{H}_2$ , (iv) titanocene E, prepared<sup>10</sup> by reaction of Np and  $(\pi\text{-Cp})_2\text{TiCl}_2$  or (v) Np and titanocene E. With sodium sand and naphthalene in place of Np, hydrogenation of dec-1-ene still occurs; but in the *absence* of the olefin, C is generated under these conditions. These observations exclude the possibility of catalysis by A, B, D, and E, and are consistent with the hydrogenation mechanism<sup>‡</sup> included in the Scheme.

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‡ The bridging hydrides  $[(\pi\text{-Cp})_2\text{TiH}_2\text{Ti}(\pi\text{-Cp})_2]$ <sup>10</sup> and  $[(\pi\text{-Cp})_2\text{TiH}]_2$ <sup>a,b</sup> also might be catalysts for the hydrogenation.

<sup>1</sup> For a review, see E. E. van Tamelen, *Accounts Chem. Res.*, 1970, **3**, 361.

<sup>2</sup> Brintzinger and his co-workers have provided further supporting evidence for the role of titanocene monomer in the co-ordination process: (a) J. E. Bercaw and H. H. Brintzinger, *J. Amer. Chem. Soc.*, 1971, **93**, 2045; (b) R. H. Marvich and H. H. Brintzinger, *ibid.*, 1971, **93**, 2046. However, see E. Bayer and V. Schurig, *Chem. Ber.*, 1969, **102**, 3378.

<sup>3</sup> This procedure has been employed in the preparation of "stable" titanocene dimer: J. J. Salzmann and P. Mosimann, *Helv. Chim. Acta.*, 1967, **50**, 1831.

<sup>4</sup> H. H. Brintzinger and J. E. Bercaw, *J. Amer. Chem. Soc.*, 1970, **92**, 6182.

<sup>5</sup> K. Nakamoto, "Infrared Spectra of Inorganic and Co-ordination Compounds," Wiley-Interscience, New York, 1970, p. 168.

<sup>6</sup> J. G. Murray, *J. Amer. Chem. Soc.*, 1959, **81**, 752.

<sup>7</sup> D. M. Adams, "Metal Ligands and Related Vibrations", St. Martin's Press, New York, 1968, p. 3.

<sup>8</sup> 1-Methallyldicyclopentadienyltitanium(III) has previously been used to effect the isomerization and hydrogenation of unsaturated hydrocarbons. H. A. Martin and R. O. de Jongh, *Chem. Comm.*, 1969, 1366.

<sup>9</sup> G. W. Watt and F. O. Drummond, jun., *J. Amer. Chem. Soc.*, 1970, **92**, 826.

<sup>10</sup> J. E. Bercaw and H. H. Brintzinger, *J. Amer. Chem. Soc.*, 1969, **91**, 7301.