Tetrahedron Letters No.28, pp. 2497-2499, 1970. Pergamon Press. Printed in Great Britain.

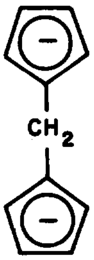
1,1'-METHYLENETITANOCENE DICHLORIDE

Thomas J. Katz and Nancy Acton

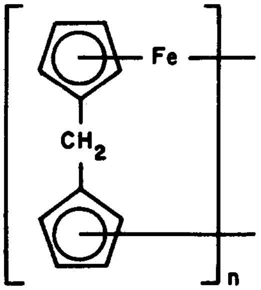
Department of Chemistry, Columbia University
New York, New York 10027

(Received in USA 13 April 1970; received in UK for publication 19 May 1970)

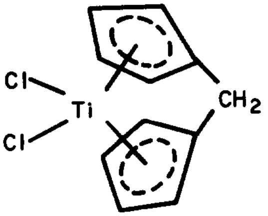
A hydrocarbon dianion such as biscyclopentadienylmethane dianion, I, made up of two linked cyclopentadienyl anions might be expected to react with transition metal halides to give either polymeric or bridged metallocenes, which would probably be difficult to prepare in other ways. However this method has been used only infrequently.[1] The anion I was recently shown to react with ferrous chloride to give the $[1^n]$ferrocenophanes, II, where n = 2, 3, 4 and 5.[1d] We are reporting here that the same dianion reacts with titanium tetrachloride to give the monomeric bridged titanocene dichloride, III, and that this material with lithium naphthalenide in tetrahydrofuran (THF) fixes nitrogen and with diethylaluminum chloride polymerizes ethylene.



I



II



III

A slurry of the anion I, prepared by reacting its conjugate acid[2] in THF with two moles of n-butyllithium in n-hexane at -78° and subsequently left to warm to room temperature, was poured onto a mixture of a slight excess of titanium tetrachloride with n-pentane. After stirring at 0° for four hours, the solvent was removed and the residue extracted with chloroform. Removal of solvent, sublimation (230-240° at 10^{-6} mm.), and recrystallization from chloroform continuously saturated with HCl gave compound III (ca. 30% yield), maroon crystals that do not melt below 360°.[3] Analytical, mass spectrometric,[4] and spectroscopic[5] data agree with the structure.

1,1'-Methylenetitanocene dichloride can replace biscyclopentadienyltitanium dichloride (Cp_2TiCl_2) in a known procedure for fixing nitrogen.[6,7] Thus in THF with six equivalents of lithium naphthalenide[6a] and with nitrogen blown through at room temperature and atmospheric pressure, one mole of ammonia is formed per gram atom of titanium after hydrolysis of the reaction mixture. In an experiment in which nitrogen was reacted simultaneously with III and lithium naphthalenide in THF and with Cp_2TiCl_2 and lithium naphthalenide under the same conditions (1×10^{-2}M. titanium compound, 6.2×10^{-2}M. lithium naphthalenide, room temperature, atmospheric pressure) both yielded 1 mole of NH_3 per Ti atom in less than 1 hr.

The titanium compound III can also replace Cp_2TiCl_2 as a component of a Ziegler catalyst.[8] When 1.8 mmoles of diethylaluminum chloride (in 2 ml. toluene) was added to 0.83 mmole of III in 200 ml. toluene while ethylene was being blown through at room temperature and atmospheric pressure, 4.0 g. polyethylene, mp 127-129°, was produced within 45 minutes while under identical conditions Cp_2TiCl_2 gave 4.3 g. polyethylene, mp 126-134° (lit.[8a] 137°).

The observation that III is an effective component of these catalyst mixtures shows that in the active catalyst, formed by reducing biscyclopentadienyltitanium dichloride, the two cyclopentadienyl rings do not occupy *trans*-octahedral coordination positions about the titanium atom. This means that in the Ziegler polymerization the growing chain and the ethylene to which it adds can not occupy equivalent octahedral positions if the remaining two positions are bridged.[9]

Acknowledgement--This research was supported by the U. S. Army Research Office-Durham. We are grateful for this support.

FOOTNOTES

(1) (a) A. Luttringhaus and W. Küllick, *Makromol. Chem.*, **44-46**, 669 (1961);

(b) T.J. Katz, V. Balogh, and J. Schulman, *J. Amer. Chem. Soc.*, **90**, 734 (1968);

(c) T.J. Katz, and J. Schulman, *ibid.*, **86**, 3169 (1964);

(d) T.J. Katz, N. Acton, and G. Martin, *ibid.*, **91**, 2804 (1969);

(e) H.L. Lentzer and W.E. Watts, *Chem. Commun.*, **26** (1970).

(2) H. Schaltegger, M. Neuenschwander, and D. Meuche, *Helv. Chim. Acta*, **48**, 955 (1965).

(3) *Cf*. Cp_2TiCl_2: G. Wilkinson and J.M. Birmingham, *J. Amer. Chem. Soc.*, **76**, 428 (1954); L. Summers, R.H. Uloth, and A. Holms, *ibid*., **77**, 3604 (1955).

(4) The most intense parent peak is at m/e 260, the base peak at m/e 224 (M-HCl).

(5) NMR τ3.16 (triplet, J = 2.7 Hz), 4.08 (triplet, J = 2.7 Hz), 5.84 (singlet), in intensity ratios of 4.02:4.06:1.91.

(6) (a) G. Henrici-Olivé and S. Olivé, *Angew. Chem. Intern. Ed. Engl.*, **7**, 386 (1968);
  (b) E.E. van Tamelen, G. Boche, S.W. Ela, and R.B. Fechter, *J. Amer. Chem. Soc.*, **89**, 5707 (1967);
  (c) M.E. Vol'pin and V.B. Shur, *Nature*, **209**, 1236 (1966);
  (d) M.E. Vol'pin, V.B. Shur, and M.A. Ilatovskaya, *Bull. Acad. Sci. USSR*, **9**, 1644 (1964).

(7) The experimental techniques were modeled after those of M.E. Vol'pin and V.B. Shur, *Doklady Chemistry*, **156**, 1102 (1964).

(8) (a) D.S. Breslow and N.R. Newburg, *J. Amer. Chem. Soc.*, **81**, 81 (1959);
  (b) G. Natta, P. Pino, G. Mazzanti, and V. Giannini, *ibid*., **79**, 2975 (1957).

(9) G. Henrici-Olivé and S. Olivé, *Angew. Chem. Intern. Ed. Engl.*, **6**, 790 (1967), *cf*. nitrogen fixation: *idem*., *ibid*., **8**, 650 (1969).