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Preliminary communication

Complex catalysis

XXX *. Cationic alkyldicyclopentadienyltitanium complexes as catalysts for ethylene polymerization

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Abstract

The cationic methyldicyclopentadienyltitanium tetraphenylborate complexes $[Cp_2TiCH_3(L)]BPh_4$ (L = THF, Et_2O, MeOPh) were synthesized by partial protolysis of $Cp_2Ti(CH_3)_2$ by $[PhN(CH_3)_2H]BPh_4$ in a mixture of CH_2Cl_2 and the corresponding ether as solvent. They proved to be the catalysts for ethylene polymerization under normal pressure.

The formation of cationic Cp_2TiR^+ complexes as the catalytically active species for ethylene polymerization with the Ziegler–Natta catalyst, $Cp_2Ti(R)Cl/Al(R)Cl_2$, was suggested more than twenty years ago [1], but to now this hypothesis could not be confirmed unequivocally by preparation of a catalytically active cationic alkyldicyclopentadienyltitanium(IV) complex. Quite recently the $Cp_2TiCH_3{}^+$ cation has been trapped by insertion of the alkyne $PhC{\equiv}CSi(CH_3)_3$ into the titanium–methyl bond with formation of the corresponding cationic vinyltitanium complex as the tetrachloroaluminate in the $Cp_2TiCl_2/Al(CH_3)Cl_2$ catalytic system [2]. Moreover the synthesis of some methyl complexes, $[Cp_2TiCH_3(L)]BPh_4$ with L = RCN, PMe_3 pyridine, from $Cp_2Ti(CH_3)Cl$ and $NaBPh_4$ has been described [3].

None of these complexes, however, reacts with ethylene. We found that complexes of the same type can be prepared with ethers, which provide a less coordinating ligand L, by partial protolysis of $Cp_2Ti(CH_3)_2$ with *N,N*-dimethylanilinium tetraphenylborate in CH_2Cl_2 and/or the ethers as solvents according to equation 1:

$$Cp_2Ti(CH_3)_2 + [PhN(CH_3)_2H]BPh_4 \xrightarrow{L/CH_2Cl_2} [Cp_2TiCH_3(L)]BPh_4 + CH_4 + PhN(CH_3)_2 \quad (1)$$

(L = THF (I), L = Et_2O (II), L = $PhOCH_3$ (III))

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* For part XXIX see ref. 6.

The complexes I–III were obtained at room temperature as reddish orange (II) and reddish brown (I, III) crystalline substances, respectively; they are sensitive to air and were characterized by elemental analysis. For the tetrahydrofuran complex I, which is the most stable, the structure was established by ^{1}H and ^{13}C NMR spectroscopy. In the case of the other two complexes, up to now, instability in solution has prevented characterization by NMR. A diphenyl ether complex is also formed, however, it could not be isolated, because the compound decomposed slowly at temperatures as low as −78 °C and diphenyl ether is also lost by washing with CH_2Cl_2. Attempts to synthesize the *N,N*-dimethylaniline complex according to eq. 2 with $L' = PhN(CH_3)_2$ failed because decomposition took place as soon as protolysis began at about −20 °C. By contrast, the pyridine complex IV was prepared with $[pyH]BPh_4$:

$$Cp_2Ti(CH_3)_2 + [L'\text{-}H]BPh_4 \xrightarrow{CH_2Cl_2} [Cp_2TiCH_3(L')]BPh_4 + CH_4 \qquad (2)$$

(IV: L' = pyridine)

The pyridine complex IV gave no reaction with ethylene, but the ether complexes I–III catalyse ethylene polymerization in CH_2Cl_2 at room temperature under normal pressure. For the tetrahydrofuran complex I in a concentration of 0.9×10^{-3} mol l^{-1} a catalytic productivity of 50 mol of C_2H_4/mol Ti was found at 25 °C. The diethyl ether complex II catalyses ethylene polymerization at temperatures as low as −20 °C, with a solution of 1.3×10^{-3} mol l^{-1} at −15 °C, 700 mol C_2H_4/mol Ti were polymerized. The anisole complex III also polymerizes ethylene slowly in anisole as solvent. Further studies on modifying the structure and reaction conditions so that deactivation of the Cp_2TiR^+ catalyst is prevented, are in progress.

Experimental

[$Cp_2TiCH_3(THF)$]BPh_4 (I). 2.56 g (12.3 mmol) of $Cp_2Ti(CH_3)_2$ [4] were dissolved in 100 ml THF, under vigorous stirring, 5.43 g (12.3 mmol) of $[PhN(CH_3)_2H]BPh_4$ [5] were added during 15 min. After methane evolution had ceased, stirring was continued for another 30 min. The crystalline reddish brown precipitate was filtered off, washed twice with 15 ml THF and finally dried in vacuo. Yield: 4.9 g (68%). The complex dissolves well in nitromethane and is moderately soluble in THF and CH_2Cl_2. On contact with air, decomposition takes place within several minutes, to give a yellow substance/solution.

^{1}H NMR (in CD_2Cl_2 at 20 °C; 90 MHz) (ppm): 6.45 s (10H) Cp; 1.56 s (3H) CH_3; 3.22 m (4H), 1.87 m (4H) THF; 7.6–7.1 m (20H) BPh_4 ^{13}C NMR (in CD_2Cl_2 at 20 °C; 22.635 MHz) (ppm): 119.0 Cp; CH_3 covered by solvent signals; 76.2/25.6 THF; 136.5/126.4/122.5 BPh_4^-.

Catalysis of ethylene polymerization. Ethylene was bubbled through a clear solution of 0.263 g (4.5×10^{-4} mol) of I in 500 ml CH_2Cl_2 under normal pressure at 25 °C. After a few seconds the solution became turbid because of the polyethylene that formed. After 30 minutes methanol was added and the polyethylene was filtered off. The polymer was washed with hydrochloric acid, water and acetone, dried in vacuo, and identified from its IR spectrum. Yield 0.7 g.

[$Cp_2TiCH_3(Et_2O)$]BPh_4 (II), 2.06 g (9.90 mmol) $Cp_2Ti(CH_3)_2$ in 15 ml CH_2Cl_2 and 30 ml Et_2O with 4.43 g (10.03 mmol) $[PhN(CH_3)_2H]BPh_4$. Yield: 5.35 g (92%).

[$Cp_2TiCH_3(PhOCH_3)$]BPh_4 (III) was made from 0.71 g (3.41 mmol) $Cp_2Ti(CH_3)_2$

in 30 ml CH_2Cl_2 and 20 ml anisole with 1.5 g (3.4 mmol) $[PhN(CH_3)_2H]BPh_4$. Yield: 1.1 g (52 %).

$[Cp_2TiCH_3(py)]BPh_4$ (IV), was made from 1.32 g (6.34 mmol) $Cp_2Ti(CH_3)_2$ in 50 ml CH_2Cl_2 with 2.55 g (6.38 mmol) $[pyH]BPh_4$. Yield: 3.25 g (87%).

The complex forms red crystals, which are unstable in air and soluble in nitromethane, pyridine and acetonitrile, slightly soluble in CH_2Cl_2 and THF and insoluble in n-pentane, toluene, CCl_4, $CHCl_3$, Et_2O and 1,4-dioxane.

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