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Preliminary communication

Cationic titanium alkyls as alkene polymerisation catalysts: solvent and anion dependence

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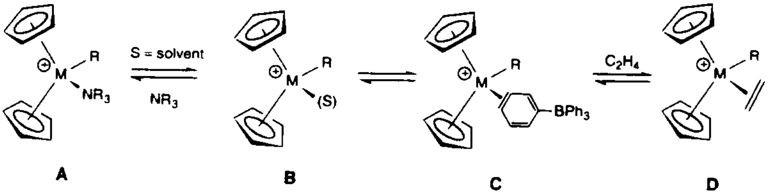
Abstract

The ethylene polymerisation activity of $[(Ind)_2TiMe]BPh_4$ decreases with decreasing solvent polarity but is enhanced if BPh_4^- is replaced by the less basic anion $[B\{C_6H_3(CF_3)_2\}_4]^-$. The reaction of $[PhNHMe_2]BPh_4$ with $Cp^*_2TiMe_2$ gives $[Cp^*_2TiMe]BPh_4$, the first isolable 14-electron titanium alkyl cation complex (Ind = indenyl, $Cp^* = C_5Me_5$)

Cationic 14-electron alkyl complexes of Group IV metals have been recognized as the catalytically active species in homogeneous Ziegler–Natta systems [1–3]. As we have previously shown, cationic alkyl complexes of the type $[Cp_2M{-}Me]BPh_4$ are readily generated in situ by protolysis of metal dialkyls with $[PhNHMe_2]BPh_4$; the insertion of ethylene into the titaniummethyl bond and chain growth can be directly monitored by NMR [4]. In such *in situ* systems, the establishment of an equilibrium is likely in which the highly electrophilic metal alkyl cation interacts with available electrophiles, such as the solvent, the free amine, the anion, and the alkene (**A**–**D**). The tendency of the tetraphenylborate anion to interact with d^0 metal centres has been demonstrated in the case of $(PhCH_2)_3Zr(\eta^6\text{-}C_6H_5BPh_3)$ [5] and recently for $C_2H_4(Ind)_2ZrMe(\eta\text{-}C_6H_5BPh_3)$ in toluene solution [6].



Since the alkene substrate has to compete for the vacant coordination site on the metal, the concentration of **D**, and therefore the catalytic activity of the system,

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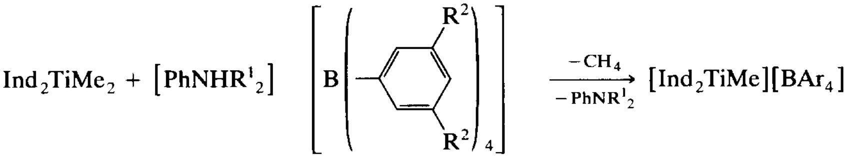
Table 1

Ethylene polymerisation activity of **3a**–**3c**

Run	Metal alkyl [a]	Anilinium salt	Solvent	Temperature (°C)	Productivity (kg PE [mol Ti]$^{-1}$ h^{-1})
1	**1**	**2a**	CH_2Cl_2	−20	7 4
2	**1**	**2b**	CH_2Cl_2	−20	7 0
3	**1**	**2a**	$C_2H_4Cl_2$	−20	2.0
4	**1**	**2a**	PhCl	0 [b]	0.8
5	**1**	**2a**	PhBr	−20 [c]	0 1
6	**1**	**2a**	$C_2H_2Cl_4$	−20	0 2
7	**1**	**2c**	CH_2Cl_2	−20	14 7
8	Cp_2TiMe_2	**2a**	CH_2Cl_2	−20	2 8
9	Cp'_2TiMe_2 [d]	**2a**	CH_2Cl_2	−20	4 2

[a] 0 65 mmol in 30 ml of solvent, 0 65 mmol **2a–c**, 1 bar ethylene [b] No formation of **3a** at −20 °C [c] Slow formation of **3a** [d] $Cp' = C_5H_4SiMe_3$

can be expected to depend on the reaction medium and the basicity of the anion. This has been verified by the reaction of bis(indenyl)titaniumdimethyl (**1**) with anilinium salts **2** in a variety of solvents (eq. 1). The results are collected in Table 1.



(1)

(**1**) (**2a**, $R^1 = Me$, $R^2 = H$,
2b, $R^1 = Et$, $R^2 = H$;
2c, $R^1 = Et$, $R^2 = CF_3$) (**3a–c**)

Of the solvents investigated, dichloromethane produced the most active catalysts. In bromobenzene, formation of **3a** was slow at −20°C and was not observed at all in chlorobenzene at that temperature. The productivity quoted is for runs of 1 h duration, although in all cases the initial activity is high and decays noticeably after ca. 10 min, particularly in 1,1,2,2-tetrachloroethane (run 6). Due to its insolubility, **2a** does not react with **1** in toluene, nor was ethylene polymerisation observed with catalysts pre-formed in dichloromethane, followed by replacement of the halocarbon by toluene. Formation of **3a** is not observed with $[NHMe(SiMe_3)_2]BPh_4$ or $[NH_2(SiMe_3)_2]BPh_4$ in CH_2Cl_2.

Replacement of BPh_4^- by the less basic anion $[B\{C_6H_3(CF_3)_2\}_4]^-$ leads to a significant increase in catalytic activity (run 7). This anion imparts excellent solubility properties and is remarkably stable under acidic conditions [7]. The results can be understood by the low tendency of **2c** to give complexes of type **C** or to deactivate the catalyst via phenyl group transfer. **2c** resembles in this respect $[B(C_6F_5)_4]^-$ [8].

Runs 1, 8 and 9 illustrate the dependence of catalytic activity on the Cp ligand· Indenyl > $C_5H_4SiMe_3$ > C_5H_5. Analogous zirconium complexes are significantly less active than titanium under these low-temperature conditions.

Efforts to isolate "base-free" cationic 14-electron alkyl complexes have generally been unsuccessful. Although formation of complexes of type $[Cp_2MR]BPh_4$ is facile and essentially quantitative (NMR), precipitation from dichloromethane solutions by the addition of hexane gave products which could not be freed adequately from $PhNMe_2$ and hexane residues. The catalytic activity of such "purified" complexes is almost identical to catalysts prepared *in situ*. However, the reaction of $Cp^*_2TiMe_2$ with **2a** in CH_2Cl_2 leads to the precipitation of $[Cp^*_2TiMe]BPh_4$ (**4**) as an orange-brown microcrystalline solid. Complex **4** is only very sparingly soluble in CH_2Cl_2 and could not recrystallised. The composition was verified by NMR in pyridine-d_5; only traces of dimethylaniline or solvents were found to be present. The 14-electron complex is the first example of an isolable alkyl cation of titanium free of stabilising donor ligands. The structure of the THF adduct of **4** is known [9]. Like $[Cp^*_2TiMe(THF)]BPh_4$, **4** is sterically too hindered to act as an ethylene polymerisation catalyst. The formation of **4** is in contrast to the analogous reaction of Cp^*ZrMe_2 with **2a** which leads to Cp^*_2Zr-*m*-$C_6H_4BPh_3$ via metallation of the anion [3].

Experimental section

All reactions were carried out under argon. Solvents were dried over $LiAlH_4$ or $LiAlH_4$/methylalumoxane mixtures and trap-to-trap distilled. Polymerisations were carried out as described previously [4] and quenched after 1 h by injecting 10 ml of methanol.

$[Cp^*_2TiMe]BPh_4$ (**4**). To a solution of 0.8 g (2.3 mmol) $Cp^*_2TiMe_2$ in 10 ml dichloromethane at -20°C was added 0.8 g (1.8 mmol) **2a**. The mixture was stirred for 2 h at -20°C, filtered, and the orange-brown residue washed with cold dichloromethane (3 × 10 ml) and dried *in vacuo* for 3 h at -10°C, yield 0.95 g (1.45 mmol, 81%). The compound is thermally sensitive and decomposes slowly above $+10$°C. Analysis. Found: C, 82.1; H, 8.0; N, 0.3. $C_{45}H_{53}BTi$ calc.: C, 82.8: H, 8.2; N, 0%. ^1H NMR (90 MHz, pyridine-d_5): δ 0.60 (s, 3 H, Ti-Me), 1.65 (s, 30 H, Cp*), 7.09–7.45 (m, 12 H, aryl), 8.05 (m, 8 H, aryl).

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