

New weakly coordinating counter anions for high activity polymerisation catalysts: $[(C_6F_5)_3B-CN-B(C_6F_5)_3]^-$ and $[Ni\{CNB(C_6F_5)_3\}_4]^{2-}$

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The new borate $[CPh_3]^+[CN\{B(C_6F_5)_3\}_2]^-$ and the anionic isocyanoborate complex $[Ni\{CNB(C_6F_5)_3\}_4]^{2-}$ are readily accessible in one-pot reactions and act as a highly efficient activators for metallocene polymerisation catalysts; turnover numbers of up to $53\,000\ s^{-1}$ appear to be the highest reported so far for ethene polymerisation catalysts.

The basicity of the counter anion X^- in cationic metal alkyl complexes $[L_nMR]^+X^-$ is known to be one of the most important factors that determine the ability of these complexes to act as catalysts for the polymerisation of alkenes.^{1,2} Research has been directed at reducing the nucleophilicity of such anions as far as possible, for example by increasing steric hindrance in borate and aluminate anions, such as $[B(C_6F_4SiR_3)_4]^-$, $[MeB(2-C_6F_4C_6F_5)_3]^-$, $[FA1(2-C_6F_4C_6F_5)_3]^{3-}$,³ or by using halogenated carboranes such as $[CB_{11}H_6Cl_6]^-$ and $[CB_{11}HF_{11}]^-$.^{4,5} Since the synthesis of such anions requires a very substantial preparative effort, for practical purposes $[B(C_6F_5)_4]^-$ and $[MeB(C_6F_5)_3]^-$ are most widely used.

An alternative strategy for reducing the nucleophilicity of borate anions is to distribute the negative charge over more than one boron atom. Such borate anions can be made by reacting $B(C_6F_5)_3$ with anions which can act as bridging groups. Thus the reaction of $B(C_6F_5)_3$ with KCN in Et_2O followed by treatment with Ph_3CCl in CH_2Cl_2 gives rise to $[CPh_3]^+[(C_6F_5)_3B-CN-B(C_6F_5)_3]^-$ **1** (Scheme 1). The synthesis is best conducted as a one-pot procedure.

As an activator for metallocene-based polymerisation catalysts, compound **1** has several practical advantages over the commonly employed $[CPh_3][B(C_6F_5)_4]$.⁶ The synthesis of $[B(C_6F_5)_4]^-$ requires the use of hazardous LiC_6F_5 which is prone to detonate on warming above $-20\ ^\circ C$;⁷ yields of $Li[B(C_6F_5)_4]$ tend to be variable, $[CPh_3][B(C_6F_5)_4]$ is frequently very difficult to crystallise and purify and is air sensitive. By contrast, $B(C_6F_5)_3$ is commercially available and can be made by safe alternative routes,⁸ it is readily converted into **1** in high yield, the product crystallises very easily, and we found that crystalline **1** can be exposed to air for weeks without any visible signs of deterioration.

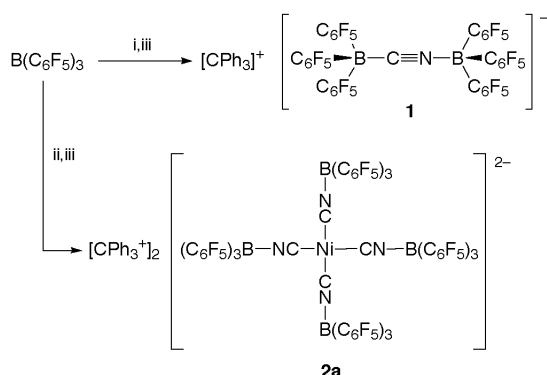
The crystal structure of **1** is shown in Fig. 1.[†] The anion is related to the borohydride $[H_3B-CN-BH_3]^-$ but gives a slightly

higher ν_{CN} stretching frequency (**1**: $2305\ cm^{-1}$; $[CN(BH_3)_2]^-$: $2260\ cm^{-1}$).⁹ The serendipitous formation of $[Ph_3B-CN-BPh_3]^-$ has also been reported ($\nu_{CN}\ 2255\ cm^{-1}$);¹⁰ this anion was however found to be prone to dissociation into BPh_3 and $[Ph_3BCN]^-$. The higher Lewis acidity of $B(C_6F_5)_3$ evidently makes such a dissociation less facile.

Another type of anion with even more extensively delocalised charges is represented by metal complexes of the isocyanoborate anion, accessible from $B(C_6F_5)_3$ and metal cyanides. For example, the reaction with $K_2[Ni(CN)_4]$ gives off-white microcrystalline $K_2[Ni\{CNB(C_6F_5)_3\}_4]$ which on treatment with Ph_3CCl in dichloromethane affords orange **2a** ($\nu_{CN}\ 2234\ cm^{-1}$) (Scheme 1), while metathesis with $[HNMe_2Ph]Cl$ leads to colourless crystals of $[HNMe_2Ph]_2[Ni\{CNB(C_6F_5)_3\}_4]\cdot Me_2CO$ **2b** ($\nu_{CN}\ 2239\ cm^{-1}$). The crystal structure confirms the square geometry of the anion in **2a** (Fig. 2).[†]

The suitability of **1** and **2a** as activators for metallocene polymerisation catalysts was tested at 1 bar and under pressure at temperatures up to *ca.* $100\ ^\circ C$ using *rac*- $Me_2Si(indenyl)_2ZrMe_2$ **3** and Cp_2ZrMe_2 **4** as standard test metallocenes. The results are collected in Table 1; for comparison the literature data for other high-activity catalysts have also been included.

Activity tests at 1 bar are frequently used to assess catalyst performance, and short reaction times are thought to prevent mass-transport limitations.³ However, exposing mixtures of **1** and **3** to ethene at 1 bar resulted in the instantaneous formation of polymer films on the surface of the rapidly stirred liquid which impeded feed gas diffusion. Higher pressure was therefore employed to reduce mass transport problems. At 7 bar ethene pressure and $5\ \mu mol$ **1** at a starting temperature of $20\ ^\circ C$ in toluene, a significant reaction exotherm raised the temperature to $> 60\ ^\circ C$, and ethene polymerisation was found to be so rapid that after about 2 min gas take-up stopped because the



Scheme 1 Reagents and conditions: i, KCN, Et_2O , room temp.; ii, $K_2[Ni(CN)_4]$, Et_2O ; iii, Ph_3CCl , CH_2Cl_2 .

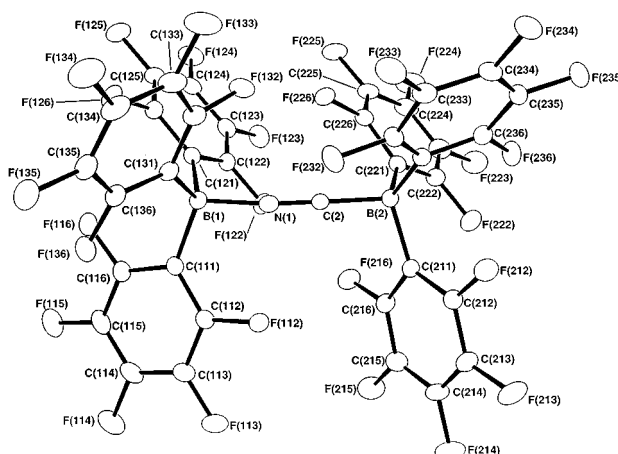


Fig. 1 Structure of the anion in **1**. Selected bond lengths (Å) and angles (°): N(1)–C(2) 1.144(2), N(1)–B(1) 1.593(2), C(2)–B(2) 1.583(2); C(2)–N(1)–B(1) 173.55(14), N(1)–C(2)–B(2) 174.50(14), N(1)–B(1)–C(111) 108.41(11), N(1)–B(1)–C(121) 103.76(11), N(1)–B(1)–C(131) 104.75(11).

Table 1 Ethene polymerisation results

Run	Metallocene (μmol)	Activator (μmol)	AlBu ₃ / μmol	Ethene/ bar	T/ $^{\circ}\text{C}$	t/min	Polymer yield/g	Product- ivity ^a	10 ³ M _w	M _w /M _n	Ref.
1	3 (2.5)	1 (2.5)	—	1 ^b	60	0.5	0.423	20.4	n.d.	—	^c
2	3 (2.5)	1 (2.5)	500	1 ^b	25	0.5	0.375	18.1	206	4.5	^c
3	4 (5)	1 (5)	—	1 ^b	25	1.0	0.523	6.3	310	3.6	^c
4	4 (10)	2a (5)	—	1 ^b	25	2.0	0.433	1.3	n.d.	—	^c
5	3 (1)	1 (0.2)	1000	7 ^d	60	4	71.1	760	94.7	2.1	^c
6	3 (5)	MAO (Al:Zr 1000:1)	—	7 ^d	60	6	74.0	21	n.d.	—	^c
7	4	MAO (67 000:1)	—	8	90	360	—	283	—	—	13
8	(C ₂ H ₄)(fluorenyl) ₂ ZrCl ₂	MAO (500:1)	—	14	100	60	—	352	401	2.1	14

^a In 10⁶ g PE{(mol M) h bar}⁻¹. ^b In 50 cm³ toluene. ^c This work. ^d In 3 L toluene.

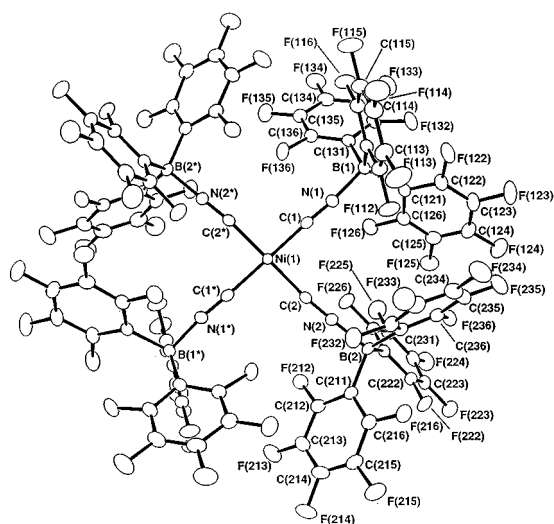


Fig. 2 Structure of the anion in **2a**. Selected bond lengths (\AA) and angles ($^{\circ}$): Ni–C(1) 1.855(2), Ni–C(2) 1.862(2), N(1)–B(1) 1.574(2), C(1)–N(1) 1.145(2); C(1)–Ni–C(2) 87.15(7), C(1)–Ni–C(2*) 92.85(7), Ni–C(1)–N(1) 176.5(2), C(1)–N(1)–B(1) 174.8(2), N(1)–B(1)–C(111) 103.65(14).

autoclave was filled with swollen polymer. Polymerisations in a 5-l autoclave at the reduced activator concentration of 6.7×10^{-8} M and an initial temperature of 60°C proceeded so rapidly that the rate of feed gas delivery could not keep pace with gas consumption; the pressure dropped to *ca.* 2 bar and only recovered after 4 min when the amount of polymer formed prevented effective gas take-up. Under these conditions, a turnover number of $53\,000\text{ s}^{-1}$ was observed. This figure represents a lower limit estimate and is to our knowledge the highest activity for an ethene polymerisation catalyst reported in the literature so far. Mixtures of **4** and **2a** also showed a good activity of $> 10^6$ g PE {(mol Zr) h bar}⁻¹.

The activity of a catalyst may be due to several factors: (i) the ligand influence on the rate of chain propagation, (ii) the concentration of active centres generated by the activator, (iii) the position of the equilibrium between active species and dormant states, (iv) the rate of irreversible deactivation of the active centre. When assessing catalysts, it is often tacitly assumed that (i) is the most important factor, and hence the search for new catalysts concentrates on ligand design.¹¹ The results reported here show that at least equally large variations in catalyst activity are achieved by varying the mode of activation: under closely comparable conditions, activation of **3** with 1/AlBu₃ gives a catalyst which is 36 times more active than **3**/MAO (entries 5 and 6).¹²

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Notes and references

† Crystal data: compound **1**: C₅₆H₁₅B₂F₃₀N, *M* = 1293.31, triclinic, space group P1, *a* = 13.3342(2), *b* = 14.8405(2), *c* = 15.8631(2) \AA , α =

116.4370(6), β = 90.9440(7), γ = 113.6410(5) $^{\circ}$, *V* = 2501.10(6) \AA^3 , *Z* = 2, *D*_c = 1.717 g cm⁻³, μ = 0.178 mm⁻¹, 9800 independent reflections were collected (*R*_{int} = 0.0304) (Nonius KappaCCD diffractometer, Mo- $\text{K}\alpha$, 150 K) solved by direct methods (SHELXS-97)¹⁵ and refined by full-matrix least squares (SHELXL-97)¹⁶ on *F*² of all unique data to *R*₁ = 0.0355 [8664 observed data with *F*² > 2 σ (*F*²)], *wR*₂ = 0.0972 (all data), *S* = 1.034. Compound **2a**: C₁₁₄H₃₀B₄F₆₀N₄Ni₂CH₂Cl₂, *M* = 2867.22, monoclinic, space group *P*2₁/*c*, *a* = 12.0340(1), *b* = 14.6297(1), *c* = 31.8468(3) \AA , β = 100.6920(6) $^{\circ}$, *V* = 5509.41(8) \AA^3 , *Z* = 2, *D*_c = 1.728 g cm⁻³, μ = 0.430 mm⁻¹, 10807 independent reflections were collected (*R*_{int} = 0.0540), solved by direct methods (SHELXS-97) and refined by full-matrix least squares (SHELXL-97) on *F*² of all unique data to *R*₁ = 0.0344 [9064 observed data with *F*² > 2 σ (*F*²)], *wR*₂ = 0.0857 (all data), *S* = 1.006.

CCDC 182/1312. See <http://www.rsc.org/suppdata/cc/1999/1533/> for crystallographic files in .cif format.

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