

Transition metal imido catalysts for ethylene polymerisation

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Abstract

The imido complexes $\text{CpV}(\text{N}-2\text{-MeC}_6\text{H}_4)\text{Cl}_2$ (**1**), $\text{Cr}(\text{N}-i\text{-Bu})_2\text{Cl}_2$ (**2**), $\text{CpNb}(\text{N}-2\text{-}i\text{-BuC}_6\text{H}_4)\text{Cl}_2$ (**3**) and $\text{Mo}(\text{N}-i\text{-Bu})_2\text{Cl}_2$ (**4**) have been tested as precatalysts for the polymerisation of ethylene in combination with diethylaluminium chloride or methylaluminoxane (MAO) co-catalysts. The vanadium precursors give the highest activities but are short-lived, while the chromium system gives a long-lived catalyst of moderate activity. The niobium and molybdenum derivatives gave relatively low activities under all test conditions. The polyethylene generated by the vanadium and chromium catalysts is of high molecular weight with little branching. The dialkyl complexes $\text{Cr}(\text{N}-i\text{-Bu})_2(\text{CH}_2\text{Ph})_2$ (**5**), $\text{Cr}(\text{N}-2,6\text{-Pr}_2\text{C}_6\text{H}_3)_2(\text{CH}_2\text{Ph})_2$ (**6**), $\text{Cr}(\text{N}-2,6\text{-Pr}_2\text{C}_6\text{H}_3)_2\text{Me}_2$ (**7**), $\text{Mo}(\text{N}-i\text{-Bu})_2(\text{CH}_2\text{Ph})_2$ (**8**), $\text{Mo}(\text{N}-2,6\text{-Pr}_2\text{C}_6\text{H}_3)_2(\text{CH}_2\text{Ph})_2$ (**9**), $(\text{C}_5\text{Me}_5)\text{Nb}(\text{N}-2,6\text{-Pr}_2\text{C}_6\text{H}_3)\text{Me}_2$ (**10**) and $(\text{C}_5\text{Me}_5)\text{Ta}(\text{N}-i\text{-Bu})(\text{CH}_2\text{Ph})_2$ (**11**) have been prepared by treatment of the dihalide precursors with appropriate alkylating reagents and investigated as precursors to well-defined cationic alkyl catalysts. Treatment of (**5**) with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ affords the cationic η^2 -benzyl species $[\text{Cr}(\text{N}-i\text{-Bu})_2(\eta^2\text{-CH}_2\text{Ph})][\text{B}(\text{C}_6\text{F}_5)_4]$ (**12**) while its reaction with $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ liberates toluene to give a mixture of the mono and bis(dimethylaniline) adducts $[\text{Cr}(\text{N}-i\text{-Bu})_2(\eta^2\text{-CH}_2\text{Ph})(\text{NMe}_2\text{Ph})][\text{B}(\text{C}_6\text{F}_5)_4]$ (**14**) and $[\text{Cr}(\text{N}-i\text{-Bu})_2(\eta^2\text{-CH}_2\text{Ph})(\text{NMe}_2\text{Ph})_2][\text{B}(\text{C}_6\text{F}_5)_4]$ (**15**). Complex **12** reacts with trimethylphosphine to give the mono-phosphine adduct $[\text{Cr}(\text{N}-i\text{-Bu})_2(\eta^2\text{-CH}_2\text{Ph})(\text{PMe}_3)][\text{B}(\text{C}_6\text{F}_5)_4]$ (**13**). Solutions containing cationic species (**12**, **14**, **15**) are active for ethylene polymerisation in the absence of co-catalyst, affording high-molecular-weight polyethylene with relatively broad molecular-weight distributions. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Transition metals; Imido complexes; Ethylene polymerisation

1. Introduction

In recent years there has been increasing interest in the discovery and development of new families of catalysts for α -olefin polymerisation [1], driven by a desire to access polyolefinic materials with new or improved performance parameters. A wide variety of ligand types have been investigated, ranging from mono through to tetradentate coordination and bearing either neutral or charged donor groups.

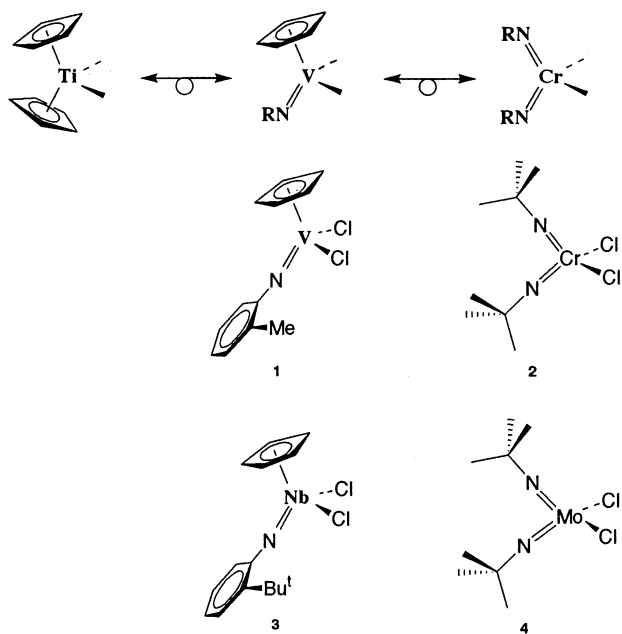
Dianionic ligands (L^{2-}) that can bind to a metal using a combination of 1σ and 2π orbital interactions present an interesting case, since an isolobal relation-

ship can be drawn with the mono-anionic cyclopentadienide moiety [2]. Examples of $1\sigma, 2\pi$ ligands include borollide [3,4], dicarbollide [5,6], imide [7–10] and butadienide [11–15]. It is thus possible using these ligands to synthesise isolobal Group 5 and Group 6 metal analogues of the Group 4 metallocenes, thereby offering an opportunity to extend the horizon of metallocene-like reactivity further to the right in the transition series.

Over the past few years we have been investigating the isolobal relationship for half-sandwich metal imido complexes of the Group 5 metals [16–22] and bis(imido)metal complexes of the Group 6 metals [23–27] — the isolobal relationship between imido complexes and Group 4 metallocenes is shown in Scheme 1. Within this series, chromium holds a special place due to its widespread use in the commercial production of

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Scheme 1.

polyethylene [28–31]. An additional attraction of this study, therefore, was the possibility for developing a homogeneous, well-defined chromium polymerisation catalyst system. Molecular chromium systems have recently been reviewed [32,33].

Here we describe the ethylene polymerisation characteristics of a series of transition metal imido procatalysts, both as conventional dual component systems and in the case of chromium a more well-defined system. Aspects of this work have been communicated [7,10].

2. Results

2.1. Dichloride procatalysts

The prototypical Group 5 and Group 6 metal imido dichloride compounds **1–4** were selected for initial screening. The results of Schlenk-scale 1 atm ethylene polymerisation tests using dual component catalyst systems (metal dihalide procatalyst + co-catalyst) are collected in Table 1. It should be noted that these tests were employed primarily to establish the presence of activity for the imido procatalyst and to identify catalysts for a more in-depth study; the results reported in Table 1 were reproduced several times, though not optimised beyond the conditions reported. First, it is evident that the half-sandwich vanadium tolylimido procatalyst is intrinsically the most active of these metal imido systems when either diethylaluminium chloride or methylaluminoxane (MAO) is employed (runs 1 and 2, cf. 3–6). It is also evident that a large excess of MAO does not lead to a vast increase in activity for the vanadium system and MAO leads to a decrease in activity for the chromium procatalyst. Although the niobium and molybdenum procatalysts showed some activity under the same conditions, they were far inferior to their first row congeners.

In the case of vanadium, the polyethylene forms rapidly over the first few minutes of the polymerisation after which the catalyst is inactive, whereas for the chromium catalyst the flocculent polyethylene product is formed over the 60 min duration of the run. Indeed, filtration of the supernatant solution from this polymerisation run followed by exposure to ethylene (1 atm) over a further 60 min period gave a similar quantity of polyethylene. GPC analysis of the PE generated from run 1 showed a broad molecular weight distribution with a main peak (*M_p*) value of 2×10^5 .

Table 1
Results of 1 atm ethylene polymerisation tests using dichloride procatalysts

Run	Procatalyst (mmol)	Activator (mmol equiv. ⁻¹)	Yield PE (g)	Activity (g mmol ⁻¹ h ⁻¹ b ⁻¹)
1	VCp(Ntol)Cl ₂ ^a 1 (0.175)	Et ₂ AlCl (3.50/20)	0.44	15.1 ^b
2	VCp(Ntol)Cl ₂ ^a 1 (0.007)	MAO (12/1715)	0.19	27.1 ^b
3	Cr(N- <i>t</i> -Bu) ₂ Cl ₂ 2 (0.007)	Et ₂ AlCl (3.86/20)	1.73	9.0
4	Cr(N- <i>t</i> -Bu) ₂ Cl ₂ 2 (0.040)	MAO (12/300)	0.19	4.4
5	NbCp(NAr ^c)Cl ₂ 3 (0.120)	Et ₂ AlCl (3.60/30)	0.06	0.6
6	Mo(N- <i>t</i> -Bu) ₂ Cl ₂ 4 (0.160)	Et ₂ AlCl (3.20/20)	<0.03	<0.2

^a Ntol = N-2-MeC₆H₄.

^b Catalyst deactivation within minutes.

^c Ar = 2-*t*-BuC₆H₄ [41].

The polymer derived from the chromium catalyst (run 3) gave a main peak (*M_p*) value of 1.2×10^6 . In both cases there was little evidence of branching (< 1 branch per 1000 carbons) by NMR spectroscopy.

2.2. Dialkyl procatalysts

Having identified promising candidates for ethylene polymerisation, particularly the vanadium and chromium procatalyst systems, our next objective was to synthesise dialkyl versions of these complexes and to investigate them as precursors to well-defined 'single-site' cationic alkyl catalysts. Attempts to synthesise dialkyl derivatives of the vanadium system were unsuccessful due to a propensity for reductive dimerisation [34–36], an observation that is most likely relevant to the short lifetime of the vanadium system. Teuben and co-workers [34,35] have isolated and structurally characterised the binuclear V(IV) species, $[\text{CpV}(\mu\text{-N-2-MeC}_6\text{H}_4\text{Me})_2]$, and in a separate study on the sterically hindered imido complex, $\text{CpV}(\text{N-2,6-Pr}_2\text{C}_6\text{H}_3)\text{Cl}_2$, we have isolated two other highly unusual divanadium species that arise from reductive dimerisation [36]. Supporting the vanadium procatalyst on a polystyrene support has been shown to increase the lifetime of the system [37].

By contrast, the bis(imido)chromium system is well behaved towards alkylation. The chromium dibenzyl complex $\text{Cr}(\text{N}^i\text{-Bu})_2(\text{CH}_2\text{Ph})_2$ (**5**) can be prepared in good yield by treatment of $\text{Cr}(\text{N}^i\text{-Bu})_2\text{Cl}_2$ with two equivalents of benzylmagnesium chloride. Despite general difficulties in obtaining crystalline samples of dialkyl complexes of this type [38] **5** can be crystallised from cold pentane. Its molecular structure has been described previously [10] and reveals η^1 - and η^2 -benzyl ligands. The ^{13}C CP MAS solid-state NMR spectrum of **5** is shown with and without non-quaternary suppression in Fig. 1 and clearly shows the two different *ipso*-carbon resonances at δ 158 and 124 ppm attributable to the η^1 - and η^2 -bonding modes, respectively. The solution ^{13}C -NMR spectrum shows an averaged resonance at δ 140 ppm. The analogous arylimido complex, $\text{Cr}(\text{N-2,6-Pr}_2\text{C}_6\text{H}_3)_2(\text{CH}_2\text{Ph})_2$ (**6**), can be prepared by a closely related procedure.

The methyl analogue of **5** has been reported by Schaverien and co-workers [38] as an impure oil. In order to obtain a crystalline species we turned our attention to the bulky bis(arylimido)chromium system [39]; treatment of $\text{Cr}(\text{N-2,6-Pr}_2\text{C}_6\text{H}_3)_2\text{Cl}_2$ with two equivalents of methylmagnesium bromide afforded $\text{Cr}(\text{N-2,6-Pr}_2\text{C}_6\text{H}_3)_2\text{Me}_2$ (**7**) as a green crystalline solid in reasonable yield.

The molybdenum analogue of **5** was prepared in a straightforward procedure from $\text{Mo}(\text{N}^i\text{-Bu})_2\text{Cl}_2(\text{dme})_2$ [40]. A comparison of the ^{13}C solution and CP MAS solid-state NMR spectra are shown in Fig. 2. As for its

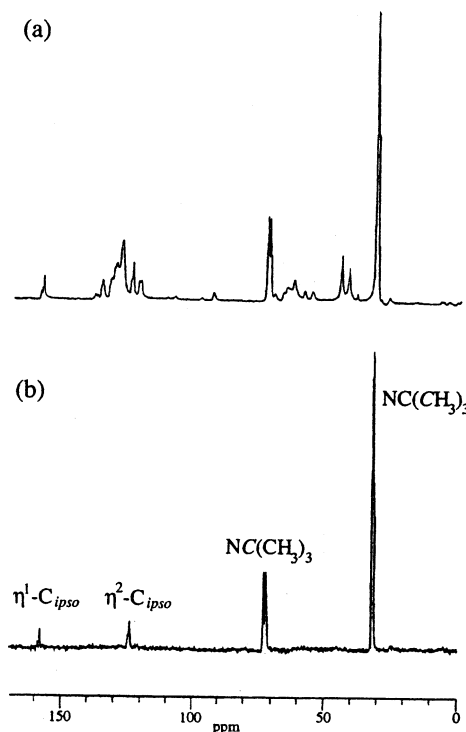


Fig. 1. The ^{13}C CP MAS solid-state NMR spectrum of **1**: (a) without non-quaternary suppression; (b) with non-quaternary suppression.

chromium analogue, characteristic shifts for the *ipso*-carbons of η^1 - and η^2 -benzyl ligands are observed, this time at δ 156 and 125 ppm, respectively, the solution NMR spectrum giving an averaged signal at ca. δ 140.

In earlier alkylation studies on the half-sandwich niobium and tantalum system [20], we found that it was necessary to use bulky cyclopentadienyl ligands in or

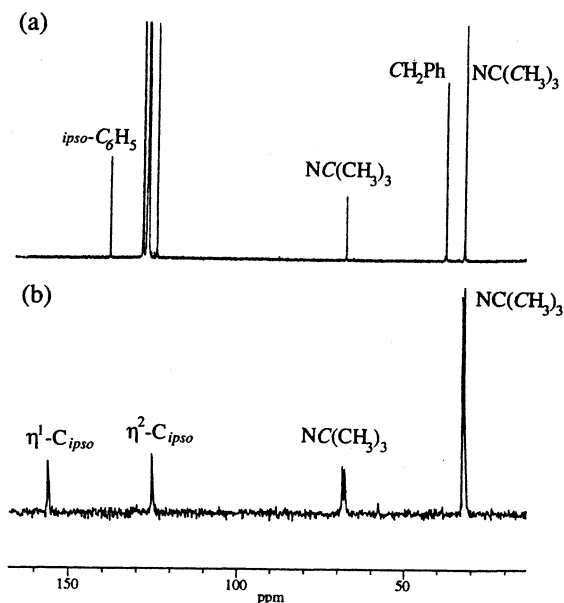


Fig. 2. ^{13}C -NMR spectra for complex **4**: (a) in solution; (b) in the solid state, with non-quaternary suppression.

Table 2
Results of high pressure/temperature ethylene polymerisation tests using dialkyl procatalysts

Run	Catalyst precursor (mmol)	Activator (equiv.)	Temp (°C)	Solvent	Pressure (bar) C ₂ H ₄	Yield PE (g)	Activity (g mmol ⁻¹ h ⁻¹ bar ⁻¹)
1	(5) (0.133)	[PhNMe ₂ H] [B(C ₆ F ₅) ₄] (1)	30	Toluene/ <i>i</i> C ₄	10	65.2	50
2	(5) (0.133)	[PhNMe ₂ H] [B(C ₆ F ₅) ₄] (1)	50	Toluene/ <i>i</i> C ₄	10	75.2	57
3	(5) (0.133)	[PhNMe ₂ H] [B(C ₆ F ₅) ₄] (1)	75	Toluene/ <i>i</i> C ₄	10	42.1	32
4	(5) (0.133)	[PhNMe ₂ H] [B(C ₆ F ₅) ₄] (1)	50	CH ₂ Cl ₂ / <i>i</i> C ₄	10	77.2	58
5	(5) (0.133)	[Ph ₃ C] [B(C ₆ F ₅) ₄] (1)	50	CH ₂ Cl ₂ / <i>i</i> C ₄	10	75.4	57
6	(5) (0.021)	[PhNMe ₂ H] ^a [B(C ₆ F ₅) ₄] (1)	50	Toluene/ <i>i</i> C ₄	10	6.7	32
7	(5) (0.021)	[PhNMe ₂ H] ^b [B(C ₆ F ₅) ₄] (1)	50	Toluene/ <i>i</i> C ₄	10	2.5	20
8	(5) (0.133)	B(C ₆ F ₅) ₃ (1)	50	CH ₂ Cl ₂ / <i>i</i> C ₄	10	Negligible	–
9	(6) (0.051)	[PhNMe ₂ H] [B(C ₆ F ₅) ₄] (1)	50	CH ₂ Cl ₂ / <i>i</i> C ₄	10	33.8	44
10	(7) (0.12)	[PhNMe ₂ H] [B(C ₆ F ₅) ₄] (1)	50	CH ₂ Cl ₂ / <i>i</i> C ₄	10	77.0	66
11	(8) (0.071)	[PhNMe ₂ H] [B(C ₆ F ₅) ₄] (1)	50	CH ₂ Cl ₂ / <i>i</i> C ₄	15	3.1	3
12	(9) (0.079)	[PhNMe ₂ H] [B(C ₆ F ₅) ₄] (1)	50	CH ₂ Cl ₂ / <i>i</i> C ₄	15	4.8	4
13	(10) (0.087)	[PhNMe ₂ H] [B(C ₆ F ₅) ₄] (1)	50	CH ₂ Cl ₂ / <i>i</i> C ₄	10	Negligible	–
14	(11) (0.087)	[PhNMe ₂ H] [B(C ₆ F ₅) ₄] (1)	50	CH ₂ Cl ₂ / <i>i</i> C ₄	10	Negligible	–

^a Ten equivalents PhNMe₂ added.

^b 25 equivalents PhNMe₂ added.

der to stabilise dialkyl derivatives. Thus, rather than employing the cyclopentadienyl niobium complex used for the screening reactions outlined in Table 1, the study was continued using a pentamethylcyclopentadienyl analogue. (C₅Me₅)Nb(N-2,6-Prⁱ₂C₆H₃)Me₂ (**10**) [20] and (C₅Me₅)Ta(N-*i*-Bu)(CH₂Ph)₂ (**11**) [41] can be synthesised straightforwardly from their dichloride precursors.

The results of polymerisation tests on **5–11** using boron activators are shown in Table 2. These runs were carried out in a 1 l autoclave fitted with temperature control and a mass-flow sensor to allow ethylene uptake to be monitored. Results for the chromium procatalysts are reported using the three boron activators [PhNMe₂H][B(C₆F₅)₄], [CPh₃][B(C₆F₅)₄] and B(C₆F₅)₃. A general feature of all the runs is a remarkably stable rate of ethylene uptake for the chromium systems, affording stable kinetic profiles for in excess of 3 h. The effect of temperature on activity using [PhNMe₂H][B(C₆F₅)₄] as the activator can be seen from runs 1–3. While there is a modest increase upon raising the temperature from 30 to 50°C, the activity falls off at 75°C, presumably due to catalyst deactivation. For runs 1–3, the chromium catalyst mixture was injected into the reactor as an immiscible suspension in toluene. The

catalyst is fully miscible in methylene chloride and this can also be used as the injector solvent without loss of activity (run 4). The trityl activator [CPh₃][B(C₆F₅)₄] gave an activity comparable to that found for the anilinium reagent (run 5) but all attempts to activate the chromium procatalyst using the neutral borane, B(C₆F₅)₃ (run 8), were unsuccessful. The arylimido dibenzyl complex (**6**) gave a slightly lower activity compared to its *t*-butyl analogue (run 9) while the dimethyl procatalyst (run 10) gave an activity figure comparable to **5**. Procatalyst **7**, however, can also be activated by B(C₆F₅)₃ (see Section 2.3). The molybdenum, niobium and tantalum procatalysts were investigated using [PhNMe₂H][B(C₆F₅)₄]. The molybdenum procatalysts, Mo(N-*i*-Bu)₂(CH₂Ph)₂ (**8**) and Mo(N-2,6-Prⁱ₂C₆H₃)₂(CH₂Ph)₂ (**9**) (runs 11 and 12) gave much lower activities compared to chromium, with the arylimido derivative giving a slightly higher activity than its *t*-butylimido counterpart. The half-sandwich niobium and tantalum imido species (C₅Me₅)Nb(N-2,6-Prⁱ₂C₆H₃)Me₂ (**10**) and (C₅Me₅)Ta(N-*i*-Bu)(CH₂Ph)₂ (**11**) gave negligible amounts of polymer (typically < 100 mg). A report by Stryker and coworkers indicates that silyl-substituted imido ligands attached to niobium or tantalum are capable of giving higher activities [8].

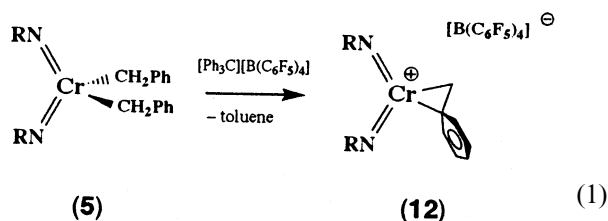
The polyethylene generated using the chromium catalysts was found to be similar to that obtained from the conventional dual component catalyst system, i.e. high molecular weight (10^5 – 10^6) and with very little branching (< 1 per 1000 carbons by ^{13}C -NMR spectroscopy).

2.3. Cationic alkyl complexes of chromium

In order to obtain a better understanding of the species that form upon treatment of $\text{Cr}(\text{N}^t\text{Bu})_2(\text{CH}_2\text{Ph})_2$ with the anilinium and trityl boron activators, these reactions were studied by high-field ^1H - and ^{13}C -NMR spectroscopy. The product is an air- and moisture-sensitive red oil that is immiscible in hydrocarbon solvent, but readily miscible in methylene chloride and therefore amenable to NMR spectroscopic studies in this solvent.

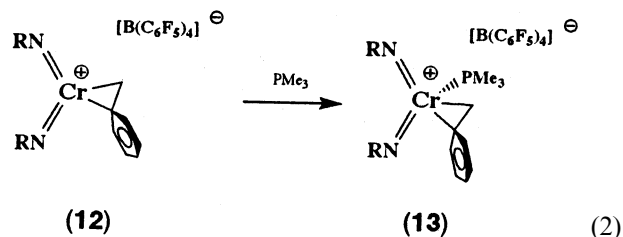
The ^1H -NMR spectrum resulting from an equimolar mixture of $\text{Cr}(\text{N}^t\text{Bu})_2(\text{CH}_2\text{Ph})_2$ and $[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ (recorded in CD_2Cl_2) reveals a clean transformation to a single new chromium species and the singlet methylene resonance of the 1,1,1,2-tetraphenylethane by-product can be observed at δ 3.98. For the chromium species, a singlet resonance at δ 1.59 is observed attributable to the hydrogens of the *t*-butyl groups (shifted from δ 1.20 for the neutral dibenzyl precursor), and a new singlet signal at δ 4.21 is assignable to the metal-bound methylene protons of a new benzyl ligand (shifted from δ 2.49 for **5**). Integration of these signals versus the methyl hydrogens of the *t*-butylimido ligand indicates that one benzyl ligand is attached to the metal centre.

The ^1H decoupled ^{13}C -NMR spectrum shows a resonance at δ 59.3 due to the metal-bound methylene carbon and significantly a resonance at δ 128.8 attributable to the *ipso*-carbon of an η^2 -benzyl ligand. This compares with a value of δ 124.4 recorded in the solid state spectrum of $\text{Cr}(\text{N}^t\text{Bu})_2(\text{CH}_2\text{Ph})_2$. These data are consistent with the formation of the cationic η^2 -benzyl species (**12**) shown in Eq. (1). As drawn, **12** may be regarded as a three-coordinate chromium species and therefore it is possible that coordinated NMR solvent or the counterion may play a role in stabilising the cationic chromium centre.

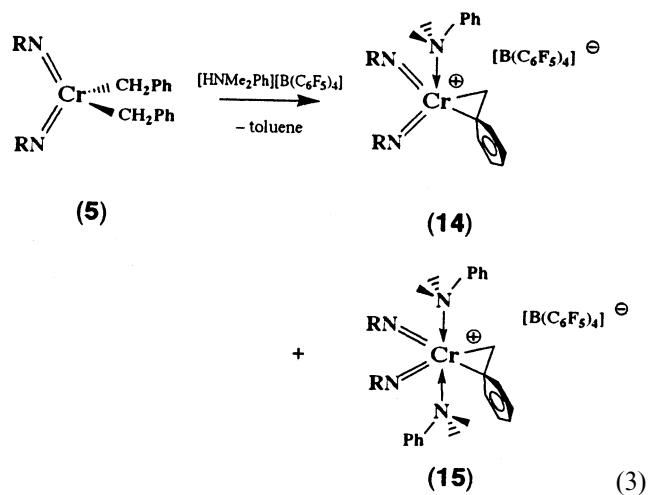


Some support for the chromium centre in **12** being able to accommodate another ligand is provided by treatment of **12** with one equivalent of trimethylphosphine. This gives a PMe_3 adduct whose NMR data support the four-coordinate, pseudo-tetrahedral structure shown in Eq. (2). The methylene hydrogens of the η^2 -benzyl ligand

show a coupling of 2 Hz to the adjacent phosphorus, while the methylene carbon appears as a doublet resonance at δ 52.9 ($^2J_{\text{CP}} = 4.5$ Hz). The *ipso*-carbon resonance at δ 128.8, by contrast, shows no coupling to phosphorus, though a small triplet splitting (5.3 Hz) due to the methylenic hydrogens is observable in the proton coupled spectrum. These observations are consistent with the benzyl methylene group lying adjacent to the PMe_3 ligand by comparison with the spectral features of $[\text{Mo}(\text{N}^t\text{Bu})_2(\text{L})(\text{PMe}_3)]$ complexes [25], where L is an alkene or alkylne.



The reaction of $\text{Cr}(\text{N}^t\text{Bu})_2(\text{CH}_2\text{Ph})_2$ with one equivalent of $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ gives a more complicated product mixture. One equivalent of toluene is generated via protonation of one of the benzyl ligands; free dimethylaniline, however, is not observed. The ^1H -NMR spectrum reveals a major species **14** containing resonances attributable to the *t*-butyl hydrogens of the imido ligands (δ 1.67), a benzyl-methylene signal (δ 3.84) and a resonance at δ 2.87 which integrates for the methyls of one metal-bound dimethylaniline. A second series of resonances, at δ 1.55, 3.64 and 2.97 in the ratio 9:1:6 are assignable to a bis(dimethylaniline) adduct **15** (Eq. (3)). Due to the multiplicity of signals arising from this mixture it did not prove possible to assign the ^{13}C -NMR spectrum and so we are unable to conclude anything about the bonding mode of the remaining chromium-bonded benzyl group. Addition of one equivalent of dimethylaniline to the cationic benzyl species formed upon treatment of $\text{Cr}(\text{N}^t\text{Bu})_2(\text{CH}_2\text{Ph})_2$ with $[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ affords this same product mixture.



We have also used ^1H -NMR spectroscopy to investigate the reactions of these mixtures towards ethylene. Notably, exposure of the cationic alkyl species to 1 atm pressure of ethylene did not result in formation of polyethylene. It was found necessary to increase the ethylene pressure to ca. 2–3 atm before any polyethylene was generated; the solid polymer, however, quickly obscured and broadened the NMR signals preventing further information from being obtained. Reaction of $\text{Cr}(\text{N}-2,6\text{-Pr}_2\text{C}_6\text{H}_3)_2\text{Me}_2$ and $\text{B}(\text{C}_6\text{F}_5)_3$ under an atmosphere of ethylene produces rapid conversion to polymer, qualitatively faster than the benchmark $\text{Cr}(\text{N}-i\text{Bu})_2(\text{CH}_2\text{Ph})_2/[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ catalyst system. For comparison purposes, the previously reported molybdenum analogue, $\text{Mo}(\text{N}-2,6\text{-Pr}_2\text{C}_6\text{H}_3)_2(\text{CH}_3)_2$, was studied with all three boron species. In all cases, dark red solutions are formed identical in appearance to the chromium systems, but the resulting spectra exhibit several septet signals attributable to the isopropyl methine hydrogens of a number of different unidentified arylimido products. Dimeric $[\text{Mo}(\text{N}-i\text{Bu})_2(\text{CH}_3)_2]_2$ also shows a reaction with all three boron species and when formed in the presence of ethylene in an NMR tube, polymer is produced, but only very slowly (days). Given the propensity of molybdenum to form imido-bridged dimeric species, this may account for the extremely low catalytic activities generally observed for the molybdenum systems. Neither the chromium nor the molybdenum catalysts showed activity for propylene polymerisation under analogous conditions.

Of the Nb and Ta complexes, $(\text{C}_5\text{Me}_5)\text{Nb}(\text{N}-2,6\text{-Pr}_2\text{C}_6\text{H}_3)\text{Me}_2$ (**10**) and $(\text{C}_5\text{Me}_5)\text{Ta}(\text{N}-i\text{Bu})(\text{CH}_2\text{Ph})_2$ (**11**) did not react with $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$, even after 24 h, but they did react swiftly with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ to give a complicated mixture of products that could not be identified. A similarly complicated product mixture was obtained using $\text{B}(\text{C}_6\text{F}_5)_3$. These systems were not investigated further.

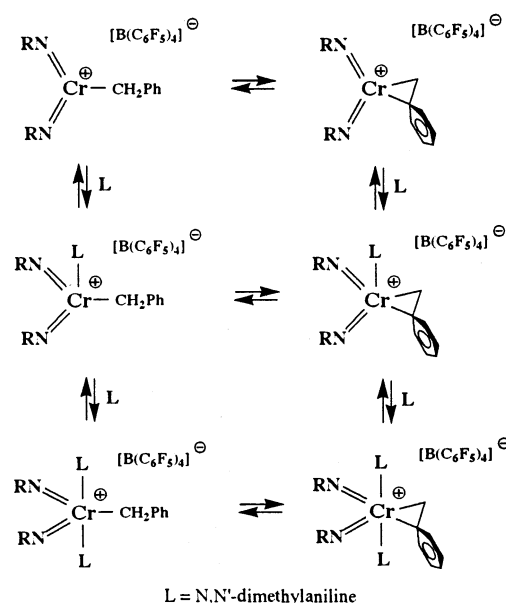
3. Discussion

A significant and surprising feature of the well-defined chromium system is the remarkably robust nature of the catalyst. Although the absolute activities are not particularly high, the catalyst system does not appear to undergo significant deactivation over a 3 h polymerisation run. Interestingly, the activity drops to zero upon exposure of the catalyst solution to an atmosphere of carbon monoxide and no CO is incorporated into the product. However, once the CO has been purged from the system, the activity recovers to its former level. The polyethylene generated has very little branching and, in its general properties, resembles the

polyethylene generated by heterogeneous chromium catalysts [28–31]. The molecular-weight distributions of the products, however, are generally broad and often bi-modal indicating that these are not ‘single-site’ catalysts. The reaction of **5** with the dimethylanilinium borate may hold the answer to the other active sites that might be present in the reaction mixture. These possibilities are outlined in Scheme 2.

In the presence of a base such as dimethylaniline, mono(aniline) and bis(aniline) adducts are generated. Experiments in which excess dimethylaniline is added to the catalyst mixture expectedly lowers the activity (Table 2, runs 6 and 7), and also changes the molecular-weight distribution from essentially broad unimodal when no excess base is present (run 2), to progressively bimodal as base is added (runs 6 and 7). In the absence of a base, such as arises in the reaction of **1** with the tritylborate reagent, it is not possible to rule out solvent adducts even though they are not observable. It also has to be recognised that agostic $\text{C}-\text{H}\cdots\text{Cr}$ interactions involving the growing polymer may also be involved since the η^2 -benzyl species is only relevant to the initiating species.

In summary, transition metal imido complexes of the Group 5 and 6 metals are active for ethylene polymerisation and the chromium system is surprisingly robust. Scope may remain for improving the performance of these imido catalyst systems through judicious further modifications to the imido ligand substituents.



Scheme 2. Possible initiating species arising from the reaction of $(\text{RN})_2\text{Cr}(\text{CH}_2\text{Ph})_2$ with $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$.

4. Experimental

4.1. General

All manipulations were performed under an atmosphere of dry nitrogen using standard Schlenk and cannula techniques, or in a conventional nitrogen-filled glovebox. Solvents were dried by reflux and distillation from an appropriate drying agent and degassed prior to use. Elemental analyses were performed by the micro-analytical services of the Department of Chemistry at Durham. NMR spectra were recorded on Varian VXR 400 S and Bruker WM250 spectrometers at 400.0 MHz (^1H); 100.6 MHz (^{13}C) and 250.0 MHz (^1H), respectively; chemical shifts are referenced to the residual protio impurity of the deuterated solvent; IR spectra (Nujol mulls, CsI windows), Perkin–Elmer 577 and 457 grating spectrophotometers; mass spectra, VG 7070E [70 eV (ca. 1.12×10^{17} J), 100 mA emission]. $\text{Cr}(\text{N}^i\text{Bu})_2\text{Cl}_2$ was synthesised via the procedure described by Wilkinson and co-workers [42]. $\text{Mo}(\text{N}-2,6\text{-Pr}_2\text{C}_6\text{H}_3)_2\text{Cl}_2(\text{dme})$ [25] was prepared from Na_2MoO_4 . $\text{VCp}(\text{N}-2\text{-MeC}_6\text{H}_4)\text{Cl}_2$ [43], $\text{VCp}(\text{N}^i\text{Bu})\text{Cl}_2$ [43], $\text{Mo}(\text{N}^i\text{Bu})_2\text{Cl}_2$ [44], $\text{Cr}(\text{N}-2,6\text{-Pr}_2\text{C}_6\text{H}_3)_2\text{Cl}_2$ [39] and the boron reagents $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$, $[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ and $\text{B}(\text{C}_6\text{F}_5)_3$ [45–47] were prepared by literature procedures. CrO_2Cl_2 , BCl_3 (1.0 M solution in heptane), $\text{MgCl}\cdot\text{CH}_2\text{Ph}$ (1.0 M solution in diethyl ether), MgBrCH_3 (3.0 M solution in diethyl ether), Et_2AlCl (1.8 or 1.0 M solution in toluene) and 2,6-diisopropylaniline were purchased from Aldrich Chemical Co.; the aniline was distilled under a dinitrogen atmosphere prior to use. All other chemicals were obtained commercially and used as received unless stated otherwise.

4.2. Ambient temperature/pressure polymerisation procedure

Ethylene was dried by passing through a column of CaCl_2 , molecular sieves and P_2O_5 , which had previously been flushed with N_2 for at least 1 h. Further drying was achieved by passing through a bubbler containing silicone oil (30 ml) to which 2 ml of 1.8 M deac in toluene had been added.

In a typical polymerisation procedure, diethylaluminiumchloride (deac, 20 equivalents) was added via syringe to a stirred solution of the catalyst (50 mg) in toluene (ca. 75 ml), and the mixture was left to stir for 10 min. The catalyst solution was then purged with ethylene for 1 h, after which time the polymerisation was terminated by purging with N_2 . Any polymer formed was isolated, washed in turn MeOH, dil. HCl–MeOH (ca. 1:10), toluene, filtered and dried in vacuo.

4.3. High-pressure polymerisation procedure

The rig consists of a 1 or 3 l stainless steel autoclave with a water-fed temperature regulation system, gas feed lines, an overhead stirrer and a liquid injection system. Pressure and temperature sensors allow specific conditions to be maintained throughout the test and a mass-flow controller monitors the flow of ethylene into the autoclave, ensuring that the required overpressure is maintained.

The autoclave is dried by raising the temperature of the water jacket to 95°C and purging with a flow of 1 l min $^{-1}$ of N_2 for at least 1 h. The temperature of the water is then set to that required for the experiment and the jacket allowed to cool. Fifty percent of the required co-catalyst and ca. 1.5 l of *iso*-butane ($i\text{C}_4$) is introduced to the autoclave, with stirring, via the liquid injection system.

The catalyst is pre-weighed into a Schlenk tube and dissolved in ca. 50 ml solvent, and the remaining 50% of co-catalyst is added. The autoclave is then charged with (typically) 10 bar overpressure of ethylene and allowed to reach equilibrium, and the data collection system is activated. The catalyst/co-catalyst system is passed via syringe into the injection system and then injected into the autoclave using an over pressure of N_2 . After the desired time (typically 1 h) the polymerisation is terminated by closing the ethylene supply and venting the autoclave to atmosphere.

The isolated polymer is washed in turn with MeOH–dil. HCl, EtOH–water and dried overnight in vacuo.

4.3.1. $\text{Cr}(\text{N}^i\text{Bu})_2(\text{CH}_2\text{Ph})_2$ (5)

$\text{Cr}(\text{N}^i\text{Bu})_2\text{Cl}_2$ (1.0 g, 3.76 mmol) was dissolved in diethyl ether (75 ml) and cooled in a dry-ice–acetone slush bath. To this very dark red–black solution was then added two equivalents of MgClCH_2Ph (1.0 M Et_2O , 7.52 ml, 7.52 mmol) dropwise via syringe over 10 min. The solution became progressively more red during the addition. The mixture was allowed to warm to room temperature (r.t.) and stirred for 18 h. The resultant blood-red solution was filtered from the white precipitate and the volatile components were removed under reduced pressure to give a red oily solid. Extraction with pentane (30 ml) followed by concentration and cooling of the filtrate to ca. –30°C afforded crystalline $\text{Cr}(\text{N}^i\text{Bu})_2(\text{CH}_2\text{Ph})_2$. Yield 1.08 g, 76%. Anal. Calc. for $\text{C}_{22}\text{H}_{32}\text{N}_2\text{Cr}$: C, 70.18; H, 8.57; N, 7.44. Found: C, 70.49; H, 8.66; N, 7.42%. IR: 1593m, 1352m(sh), 1260w, 1223s(br), 1173w, 1092m(br), 1019m(br), 888w, 806s, 759m, 690vs, 597w, 534m, 513m, 466m cm $^{-1}$. NMR (C_6D_6): ^1H (400 MHz), δ 6.99 (m, 10H, CH_2Ph), 2.49 (s, 4H, CH_2Ph), 1.20 (s, 18H, $\text{C}(\text{CH}_3)_3$); ^{13}C (100.6 MHz), δ 140.34 (s, $\text{C}_6\text{H}_5\text{--C}_{\text{ipso}}$), 131.60 (d, $^1J_{\text{CH}}$ 157.1 Hz, $\text{C}_6\text{H}_5\text{--C}_{\text{ortho}}$), 128.94 (d*, $\text{C}_6\text{H}_5\text{--C}_{\text{meta}}$), 125.65 (d, $^1J_{\text{CH}}$ 160.5 Hz,

$C_6H_5-C_{para}$), 71.97 (s, $C(CH_3)_3$), 44.50 (t, $^1J_{CH}$ 141.9 Hz, CH_2Ph), 31.63 (q, $^1J_{CH}$ 127.0 Hz, $C(CH_3)_3$). (* $^1J_{CH}$ value obscured by overlap with solvent resonance). MS (CI^+ , m/z , ^{35}Cl) 377 [$M+H$] $^+$, 303 [$M-N^iBu-2H$] $^+$, 286 [$M-CH_2Ph+H$] $^+$.

NMR characterising data for $[Cr(N^iBu)_2(\eta^2-CH_2Ph)][B(C_6F_5)_4]$ and $[Cr(N^iBu)_2(\eta^2-CH_2Ph)(PMe_3)][B(C_6F_5)_4]$ have been reported previously [10].

4.3.2. $Cr(N-2,6-Pr^i_2C_6H_3)_2(CH_2Ph)_2$ (**6**)

$Cr(NAr)_2Cl_2$ (0.25 g, 0.53 mmol) was dissolved in diethyl ether (75 ml) and cooled in a dry-ice–acetone slush bath. To this bright red solution was then added two equivalents of $PhCH_2MgCl$ (1.06 ml, 1.0 M solution in diethyl ether; 1.06 mmol). The mixture was allowed to warm to r.t. and stirred for 18 h. The resultant red–green solution was filtered from the white precipitate and the volatile components were removed under reduced pressure. Extraction and recrystallisation from pentane at $-30^\circ C$ afforded green crystals of $Cr(NAr)_2(CH_2Ph)_2$. Yield 0.18 g, 69%. Anal. Calc. for $C_{38}H_{48}N_2Cr$: C, 78.05; H, 8.27; N, 4.79. Found: C, 78.12; H, 8.39; N, 4.46%. IR: 1590w, 1318m(br), 1266m(sh), 1175w, 1099w(br), 1058w, 1026m, 984w, 933w, 796s, 753vs, 722s, 692s, 530w, 475m, 452m. NMR (C_6D_6): 1H (400 MHz), δ 7.17–6.88 (m, 16H, C_6H_3 and CH_2Ph), 3.85 (sept, $^3J_{HH}$ 6.60 Hz, 4H, $CH(CH_3)_2$), 3.41 (s, 4H, CH_2Ph), 1.12 (d, $^3J_{HH}$ 7.20 Hz, 24H, $CH(CH_3)_2$); ^{13}C (100.6 MHz), δ 158.00 (s, $C_6H_3-C_{ipso}$), 146.03 (s, $C_6H_3-C_{ortho}$), 140.15 (s, CH_2Ph-C_{ipso}), 132.69 (d, $^1J_{CH}$ 158.3 Hz, CH_2Ph-C_{ortho}), 128.78 (d*, CH_2Ph-C_{meta}), 127.12 (d*, $C_6H_3-C_{para}$), 126.24 (d, $^1J_{CH}$ 160.2 Hz, CH_2Ph-C_{para}), 122.79 (d, $^1J_{CH}$ 156.4 Hz, $C_6H_3-C_{meta}$), 59.88 (t, $^1J_{CH}$ 139.6 Hz, CH_2Ph), 28.48 (d, $^1J_{CH}$ 129.35 Hz, $CH(CH_3)_2$), 23.87 (q, $^1J_{CH}$ 125.90 Hz, $CH(CH_3)_2$). (* $^1J_{CH}$ value obscured by overlap with solvent resonance).

4.3.3. $Cr(N-2,6-Pr^i_2C_6H_3)_2(CH_3)_2$ (**7**)

$Cr(NAr)_2Cl_2$ (0.390 g, 0.83 mmol) was dissolved in diethyl ether (75 ml) and cooled in a dry-ice–acetone slush bath. To this bright red solution was then added two equivalents of an $MeMgBr$ solution (0.58 ml of a 3 M solution in diethyl ether; 1.65 mmol). The mixture was allowed to warm to r.t. and stirred for 18 h. The resultant green solution was filtered from the white precipitate and the volatile components were removed under reduced pressure. Extreme solubility precluded recrystallisation from pentane. However, green microcrystalline $Cr(NAr)_2(CH_3)_2$ was isolated from a concentrated acetonitrile solution at $-30^\circ C$. Yield 0.18 g, 51%. Anal. Calc. for $C_{26}H_{40}N_2Cr$: C, 72.19; H, 9.32; N, 6.48. Found: C, 71.70; H, 9.24; N, 6.49%. IR: 1919w, 1583w, 1271m, 1157w(br), 1110m(sh), 1058w, 994w,

933w, 795m, 722s, 515m(sh), 446w(br). NMR (C_6D_6): 1H (400 MHz), δ 6.91 (m, 6H, C_6H_3), 3.73 (sept, $^3J_{HH}$ 6.90 Hz, 4H, $CH(CH_3)_2$), 1.83 (s, 6H, Me), 1.12 (d, $^3J_{HH}$ 6.80 Hz, 24H, $CH(CH_3)_2$); ^{13}C (100.6 MHz), δ 157.81 (s, $C_6H_3-C_{ipso}$), 145.24 (s, $C_6H_3-C_{ortho}$), 127.60 (d*, $C_6H_3-C_{para}$), 122.74 (d, $^1J_{CH}$ 156.4 Hz, $C_6H_3-C_{meta}$), 49.73 (q, $^1J_{CH}$ 130.45 Hz, CH_3), 28.80 (d, $^1J_{CH}$ 125.12 Hz, $CH(CH_3)_2$), 23.52 (q, $^1J_{CH}$ 126.03, $CH(CH_3)_2$). (* $^1J_{CH}$ value obscured by overlap with solvent resonance). MS (CI^+ , m/z , ^{35}Cl) 433 [M] $^+$, 418 [$M-CH_3$] $^+$, 402 [$M-2CH_3$] $^+$.

4.3.4. $Mo(N^iBu)_2(CH_2Ph)_2$ (**8**)

$Mo(N^iBu)_2Cl_2 \cdot dme$ (2.00 g, 5.03 mmol) was dissolved in diethyl ether (75 ml) and cooled in a dry-ice–acetone slush bath. To this deep yellow solution was then added two equivalents of $PhCH_2MgCl$ (10.1 ml, 1.0 M solution in diethyl ether; 10.1 mmol). After addition of 50% of the Grignard reagent a colour change from yellow to deep orange was observed. The mixture was allowed to warm to r.t. and stirred for 18 h. The resultant deep orange solution was filtered from the white precipitate and the volatile components were removed under reduced pressure. Extraction and recrystallisation from acetonitrile at $-30^\circ C$ afforded orange crystals of $Mo(N^iBu)_2(CH_2Ph)_2$. Yield 1.62 g, 77%. Anal. Calc. for $C_{22}H_{32}N_2Mo$: C, 62.85; H, 7.67; N, 6.66. Found: C, 62.27; H, 7.67; N, 6.41%. NMR (C_6D_6): 1H (400 MHz), δ 6.98 (m, 10H, CH_2Ph), 2.21 (s, 4H, CH_2Ph), 1.24 (s, 18H, $C(CH_3)_3$); ^{13}C (100.6 MHz), δ 139.37 (s, $C_6H_5-C_{ipso}$), 129.55 (d, $^1J_{CH}$ 157.1 Hz, $C_6H_5-C_{ortho}$), 129.46 (d*, $C_6H_5-C_{meta}$), 125.26 (d, $^1J_{CH}$ 160.7 Hz, $C_6H_5-C_{para}$), 67.94 (s, $C(CH_3)_3$), 37.65 (t, $^1J_{CH}$ 137.7 Hz, CH_2Ph), 31.98 (q, $^1J_{CH}$ 126.8 Hz, $C(CH_3)_3$). (* $^1J_{CH}$ value obscured by overlap with solvent resonance).

4.3.5. $Mo(N-2,6-Pr^i_2C_6H_3)_2(CH_2Ph)_2$ (**9**)

$Mo(NAr)_2Cl_2 \cdot dme$ (2.00 g, 3.3 mmol) was dissolved in diethyl ether (75 ml) and cooled in a dry-ice–acetone slush bath. To this burgundy solution was then added two equivalents of $PhCH_2MgCl$ (6.6 ml, 1.0 M solution in diethyl ether; 6.6 mmol). After addition of 50% of the Grignard reagent a colour change from burgundy to deep orange was observed. The mixture was allowed to warm to r.t. and stirred for 18 h. The resultant deep orange solution was filtered from the white precipitate and the volatile components were removed under reduced pressure. Extraction and recrystallisation from acetonitrile at $-30^\circ C$ afforded orange crystals of $Mo(NAr)_2(CH_2Ph)_2$. Yield 1.45 g, 60%. Anal. Calc. for $C_{38}H_{48}N_2Mo$: C, 72.59; H, 7.69; N, 4.46. Found: C, 72.36; H, 7.61; N, 4.20%. NMR (C_6D_6): 1H (250 MHz), δ 7.03–6.93 (m, 16H, C_6H_3 and CH_2Ph), 3.81 (sept,

$^3J_{\text{HH}}$ 6.9 Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 2.83 (s, 4H, CH_2Ph), 1.13 (d, $^3J_{\text{HH}}$ 6.87 Hz, 24H, $\text{CH}(\text{CH}_3)_2$); ^{13}C (100.6 MHz), δ 153.35 (s, $\text{C}_6\text{H}_3\text{--C}_{\text{ipso}}$), 143.26 (s, $\text{C}_6\text{H}_3\text{--C}_{\text{ortho}}$), 136.74 (s, $\text{CH}_2\text{Ph--C}_{\text{ipso}}$), 132.69 (d, $^1J_{\text{CH}}$ 158.3 Hz, $\text{CH}_2\text{Ph--C}_{\text{ortho}}$), 129.39 (d*, $\text{CH}_2\text{Ph--C}_{\text{meta}}$), 126.51 (d*, $\text{C}_6\text{H}_3\text{--C}_{\text{para}}$), 125.59 (d, $^1J_{\text{CH}}$ 160.69 Hz, $\text{CH}_2\text{Ph--C}_{\text{para}}$), 122.42 (d, $^1J_{\text{CH}}$ 157.55 Hz, $\text{C}_6\text{H}_3\text{--C}_{\text{meta}}$), 47.49 (t, $^1J_{\text{CH}}$ 135.75 Hz, CH_2Ph), 28.27 (d, $^1J_{\text{CH}}$ 128.21 Hz, $\text{CH}(\text{CH}_3)_2$), 23.35 (q, $^1J_{\text{CH}}$ 125.24 Hz, $\text{CH}(\text{CH}_3)_2$). (* $^1J_{\text{CH}}$ value obscured by overlap with solvent resonance).

4.3.6. $(\text{C}_5\text{Me}_5)\text{Nb}(\text{N-2,6-Pr}^i_2\text{C}_6\text{H}_3)\text{Me}_2$ (**10**)

A THF solution of methylmagnesium chloride (20 ml, 3.0 M) was reduced to dryness to give a white solid. $(\text{C}_5\text{Me}_5)\text{Nb}(\text{N-2,6-Pr}^i_2\text{C}_6\text{H}_3)\text{Cl}_2$ (2.50 g, 5.27 mmol) was then added and Et_2O (30 ml) condensed onto the vessel at -196°C . The mixture was then allowed to warm to 0°C and stirred for 4 h. The volatile components were then removed under reduced pressure and the resultant residue was extracted with pentane (3×30 ml) to give an orange solution. This solution was left to stand for 6 h to allow magnesium residues to precipitate. After filtration, concentration to ca. 20 ml and cooling to -78°C , yellow needle crystals of $(\text{C}_5\text{Me}_5)\text{Nb}(\text{NAr})\text{Me}_2$ were precipitated. Yield 1.49 g, 72%. Anal. Calc. for $\text{C}_{24}\text{H}_{38}\text{NNb}$: C, 66.50; H, 8.84; N, 3.23. Found: C, 66.33; H, 8.86; N, 2.96%. For NMR data: see Ref. [20]

4.3.7. $(\text{C}_5\text{Me}_5)\text{Ta}(\text{N-}^t\text{Bu})(\text{CH}_2\text{Ph})_2$ (**11**)

Benzylmagnesium chloride (1.0 M in Et_2O , 4.09 ml, 4.09 mmol) was added via syringe to a stirred solution of $\text{Cp}^*\text{Ta}(\text{N-}^t\text{Bu})\text{Cl}_2$ (0.89 g, 1.95 mmol) in diethyl ether (50 ml) at -78°C . The mixture was allowed to warm up to r.t. to give a yellow solution and white precipitate. After 11 h, all volatile components were removed under reduced pressure to leave a yellow solid. Extraction with pentane followed by removal of solvent in vacuo afforded a bright yellow solid. Yield: 0.89 g, 88%. Anal. Calc. for $\text{C}_{28}\text{H}_{38}\text{NTa}$: C, 59.05; H, 6.73; N, 2.46. Found: C, 58.58; H, 6.88; N, 2.52%. IR: 3075w, 3055w, 3015m, 2730w, 1925w, 1595s, 1485s, 1350s, 1305w, 1265vs, 1205s, 1180w, 1095m, 1055m, 1030m, 950w, 890w, 800s, 745vs, 695vs, 560w, 535w, 495w, 430w, 405w. NMR (C_6D_6): ^1H (400 MHz), δ 7.20 (t, 4H, $^3J_{\text{HH}}$ 7.2 Hz, *m*-Ph), 7.05 (d, 4H, $^3J_{\text{HH}}$ 7.2 Hz, *o*-Ph), 6.93 (t, 2H, $^3J_{\text{HH}}$ 7.2 Hz, *p*-Ph), 2.07 (d, 2H, $^2J_{\text{HH}}$ 12.0 Hz, CH_2Ph), 1.77 (s, 15H, C_5Me_5), 1.38 (d, 2H, $^2J_{\text{HH}}$ 12.0 Hz, CH_2Ph), 1.09 (s, 9H, CMe_3); ^{13}C (100.6 MHz), δ 149.35 (s, *ipso*-Ph), 128.85 (d, $^1J_{\text{CH}}$ 160 Hz, *o*-Ph), 128.05 (d, $^1J_{\text{CH}}$ 158 Hz, *m*-Ph), 122.82 (d, $^1J_{\text{CH}}$ 158 Hz, *p*-Ph), 115.91 (s, C_5Me_5), 71.28 (t, $^1J_{\text{CH}}$ 119 Hz, CH_2Ph), 65.17 (s, CMe_3), 33.20 (q, $^1J_{\text{CH}}$ 126 Hz, CMe_3), 11.36 (q, $^1J_{\text{CH}}$ 127 Hz, C_5Me_5). MS (EI, *m/z*): 570 $[\text{M}]^+$.

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References

- [1] G.J.P. Britovsek, V.C. Gibson, D.F. Wass, *Angew. Chem. Int. Ed. Engl.* 38 (1999) 428.
- [2] See for example: V.C. Gibson, *J. Chem. Soc. Dalton Trans.* (1994) 1607.
- [3] A. Pastor, A.F. Kiely, L.M. Henling, M.W. Day, J.E. Bercaw, *J. Organomet. Chem.* 528 (1997) 65.
- [4] G.C. Bazan, S.J. Donnelly, G. Rodriguez, *J. Am. Chem. Soc.* 117 (1995) 2671.
- [5] D.J. Crowther, N.C. Baenziger, R.F. Jordan, *J. Am. Chem. Soc.* 113 (1991) 1455.
- [6] C. Kreuder, R.F. Jordan, H. Zhang, *Organometallics* 14 (1995) 2993.
- [7] M.P. Coles, V.C. Gibson, *Polym. Bull.* 33 (1994) 529.
- [8] D.M. Antonelli, A. Leins, J.M. Stryker, *Organometallics* 16 (1997) 2500.
- [9] S. Scheuer, J. Fischer, J. Kress, *Organometallics* 14 (1995) 2627.
- [10] M.P. Coles, C.I. Dalby, V.C. Gibson, W. Clegg, M.R.J. Elsegood, *J. Chem. Soc. Chem. Commun.* (1995) 1709.
- [11] G. Jiménez Pindado, M. Thornton-Pett, M. Bochmann, *J. Chem. Soc. Dalton Trans.* (1997) 3115.
- [12] B. Hessen, H. van der Heijden, *J. Am. Chem. Soc.* 118 (1996) 11 670.
- [13] K. Mashima, S. Fujikawa, H. Urata, E. Tanaka, A. Nakamura, *J. Chem. Soc. Chem. Commun.* (1994) 1623.
- [14] K. Mashima, S. Fujikawa, Y. Tanaka, H. Urata, T. Oshiki, E. Tanaka, A. Nakamura, *Organometallics* 14 (1995) 2633.
- [15] K. Mashima, Y. Tanaka, M. Kaidzu, A. Nakamura, *Organometallics* 15 (1996) 2431.
- [16] D.N. Williams, J.P. Mitchell, A.D. Poole, U. Siemeling, W. Clegg, D.C.R. Hockless, P.A. O'Neil, V.C. Gibson, *J. Chem. Soc. Dalton Trans.* (1992) 739.
- [17] J.K. Cockcroft, V.C. Gibson, J.A.K. Howard, A.D. Poole, U. Siemeling, C. Wilson, *J. Chem. Soc. Chem. Commun.* (1992) 1668.
- [18] U. Siemeling, V.C. Gibson, *J. Organomet. Chem.* 426 (1992) C25.
- [19] U. Siemeling, V.C. Gibson, *J. Chem. Soc. Chem. Commun.* (1992) 1670.
- [20] V.C. Gibson, A.D. Poole, U. Siemeling, D.N. Williams, W. Clegg, D.C.R. Hockless, *J. Organomet. Chem.* 462 (1993) C12.
- [21] V.C. Gibson, A.D. Poole, *J. Chem. Soc. Chem. Commun.* (1995) 2261.
- [22] M.C.W. Chan, J.M. Cole, V.C. Gibson, J.A.K. Howard, C. Lehmann, A.D. Poole, U. Siemeling, *J. Chem. Soc. Dalton Trans.* (1998) 103.
- [23] P.W. Dyer, V.C. Gibson, J.A.K. Howard, B. Whittle, C. Wilson, *J. Chem. Soc. Chem. Commun.* (1992) 1666.
- [24] P.W. Dyer, V.C. Gibson, J.A.K. Howard, C. Wilson, *J. Organomet. Chem.* 462 (1993) C15.

- [25] P.W. Dyer, V.C. Gibson, J.A.K. Howard, B. Whittle, C. Wilson, *Polyhedron* 14 (1995) 103.
- [26] P.W. Dyer, V.C. Gibson, W. Clegg, *J. Chem. Soc. Dalton Trans.* (1995) 3313.
- [27] V.C. Gibson, C. Redshaw, W. Clegg, M.R.J. Elsegood, U. Siemeling, T. Türk, *J. Chem. Soc. Dalton Trans.* (1996) 4513.
- [28] M.P. McDaniel, *Adv. Catal.* 33 (1985) 47.
- [29] A. Clark, *Catal. Rev.* 3 (1969) 145.
- [30] F.J. Karol, G.L. Brown, J.M. Davidson, *J. Polym. Sci. Polym. Chem. Ed.* 11 (1973) 413.
- [31] F.J. Karol, G.L. Karapinka, C. Wu, A.W. Dow, R.N. Johnson, W.L. Carrick, *J. Polym. Sci. Part A-1* 10 (1972) 2621.
- [32] K.H. Theopold, *Eur. J. Inorg. Chem.* (1998) 15.
- [33] K.H. Theopold, *CHEMTECH*, October (1997) 26.
- [34] J.-K.F. Buijink, J.H. Teuben, H. Kooijman, A.L. Spek, *Organometallics* 13 (1994) 2922.
- [35] J.-K.F. Buijink, A. Meetsma, J.H. Teuben, H. Kooijman, A.L. Spek, *J. Organomet. Chem.* 497 (1995) 161.
- [36] M.C.W. Chan, J.M. Cole, V.C. Gibson, J.A.K. Howard, *Chem. Commun. (Cambridge)* (1997) 2345.
- [37] M.C.W. Chan, K.C. Chew, C.I. Dalby, V.C. Gibson, A. Kohlmann, I.R. Little, W. Reed, *Chem. Commun. (Cambridge)* (1998) 1673.
- [38] N. Meijboom, C.J. Schavarien, A.G. Orpen, *Organometallics* 9 (1990) 774.
- [39] M.P. Coles, C.I. Dalby, V.C. Gibson, W. Clegg, M.R.J. Elsegood, *Polyhedron* 14 (1995) 2455.
- [40] P.W. Dyer, V.C. Gibson, J.A.K. Howard, B. Whittle, C. Wilson, *J. Chem. Soc. Chem. Commun.* (1992) 1666.
- [41] M.C.W. Chan, Ph.D. Thesis, University of Durham, UK, 1995.
- [42] A.A. Danopoulos, W. Leung, G. Wilkinson, B. Hussain-Bates, M.B. Hursthouse, *Polyhedron* 21 (1990) 2625.
- [43] F. Preuss, H. Becker, H.J. Häusler, *Z. Naturforsch.* 42b (1987) 881.
- [44] G. Schoettel, J. Kress, J.A. Osborn, *J. Chem. Soc. Chem. Commun.* (1989) 1062.
- [45] F.E. Crane, *Anal. Chem.* 28 (1956) 1794.
- [46] J.C.W. Chien, W.M. Tsai, M.D. Rausch, *J. Am. Chem. Soc.* 113 (1991) 8570.
- [47] A.G. Massey, A.J. Park, *J. Organomet. Chem.* 2 (1964) 245.