Catalytic polymerisation of ethylene with tris(pyrazolyl)borate complexes of late transition metals

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Dedicated to the memory of Roberto Santi, who was an irreplaceable teacher and friend for all of us.

Abstract

Various 3,5-substituted tris(pyrazolyl)borate nickel(II) and palladium(II) complexes have been prepared and characterised in both the solid state and solution [tris(pyrazolyl)borate = tris(3,5-dimethylpyrazolyl)borate (Tp*), tris(3-*t*-butyl-5-methylpyrazolyl)borate (Tp$^{t\text{-Bu,Me}}$) or tris(3-cumyl-5-methyl pyrazolyl)borate (Tp^{Cum,Me})]. The crystal structures of the tetrahedral complex [k^3*N,N′,N″*-Tp$^{t\text{-Bu,Me}}$NiCl] and of the trigonal–bipyramidal derivative [k^3*N,N′,N″*-Tp^{Cum,Me}NiCl(3-methyl-5-cumylpyrazole)] have been determined by X-ray diffraction analysis. The catalytic performance of all compounds has been tested in ethylene polymerisation. The nickel catalysts activated with methylaluminoxane (MAO) produce polyethylene with moderate to good activity, while the palladium compounds show scarce activity.
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1. Introduction

The development of efficient and selective late transition metal catalysts for the polymerisation and copolymerisation of ethylene [1], α-olefins [2] and functionalised olefins [3] under mild conditions is one of the major goals in homogeneous catalysis. The first examples of Ni[II] and Pd[II] catalysts capable of effectively polymerising ethylene and α-olefins to give high-molecular-weight polymers were reported by Brookhart and coworkers who employed square–planar cationic alkyl precursors stabilised by sterically demanding α-diimine ligands [1a]. By simply varying the pressure, the temperature and the substituents on the nitrogen atoms, the selectivity of the α-diimine nickel catalysts may change to give either highly branched amorphous ethylene homopolymers or linear high-density materials [4].

Recent achievements in the field of ethylene polymerisation by single-site late transition metal catalysis comprise the application of 2,6-bis(imino)pyridyl Ni[II] complexes [5] and of halide-free combinations of Ni(acac)$_2$ and diazadiene, ArN=CH–CH=NAr [Ar = 2,6-C$_6$H$_3$(i-Pr)$_2$] [6]. Catalyst systems based on nickel (II) dialkyl 1,4-diazadiene complexes have also been reported to be effective catalysts for the polymerisation of ethylene [7]. Most important advances in ethylene polymerisation technology, however, are those independently obtained by Brookhart [1b] and Gibson [1c] through the use of Fe[II] and Co[II] halides supported by bis(imino)pyridyl ligands (**I**) bearing bulky substituents on the imino nitrogen atoms. Indeed, irrespective of the catalyst composition, the steric constraints imposed by the substituents on the nitrogen donor atoms are recognised to play a crucial role in determining both the activity and selectivity of the polymerisation process [4].

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As part of an ongoing research project aimed at discovering new ligand systems for the polymerisation and copolymerisation of ethylene and α-olefins via soluble late transition metal catalysts [8], we have focused our attention also on the tris(pyrazolyl)borate (Tp) structure (**II**).
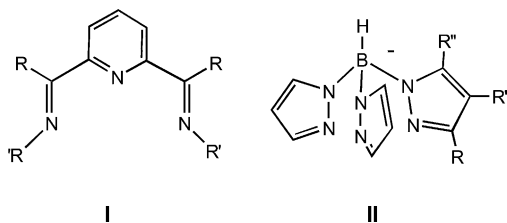
Since their discovery in 1966 by Trofimenko [9], Tp ligands have been largely employed in organometallic chemistry to study, in combination with various transition metal ions, many elementary steps occurring in olefin polymerisation (e. g. C–C and C–H bond formation/cleavage/coordination) [10]. Unlike 2,6-bis(imino)pyridines, Tp ligands can coordinate metal centres in facial fashion (commonly known as k^3N,N',N''). The occurrence of this bonding mode implies that all the pyrazole units are bound to the same metal centre, which for Tp is not a mandatory rule as k^2N,N', k^2N,H and k^3N,N',H forms have also been observed [11]. In the most common k^3N,N',N'' bonding mode, the metal centre, besides having three *cis* sites for coordination and reactivity, may adopt coordination geometries (such as the tetrahedral one) and spin states that are inaccessible to bis(imino)pyridines. Moreover, Tp's offer the additional advantage over 2,6-bis(imino)pyridines of a more efficient and easier spatial control around the metal centre because as many as three positions in the pyrazole ring (3, 4 and 5) are available for substitution [9]. The important role of pyrazole substituents in tailoring the steric and electronic environment around the metal centre in Tp complexes has been recently highlighted by the thermal stability of the alkyl ligand in $Tp^{i-Pr}MCH_2CH_3$ (M = Co, Fe, Ni) towards β-hydride elimination which represents one of the most efficacious pathways to polymer termination [12].

Despite the great amount of fundamental work described in the relevant literature, surprisingly little has been reported on transition metal Tp complexes as polymerisation catalysts. The arylnickel(II) tris(3-phenylpyrazolyl)borate complex [Ni(*o*-tolyl)(PPh₃)(Tp^{Ph})] is a mediocre catalyst for the co-polymerisation of ethylene and carbon monoxide [13], while the polymerisation of styrene and the stereoregular polymerisation of phenylacetylene have been achieved with [TpTiCl₃] [14] and [Tp^{R2}Rh(cod)] (R = Me, Ph, i-Pr; cod = cycloocta-1,5-diene), respectively [15]. Some examples of α-olefin polymerisation reactions [16] as well as ethylene/hexene copolymerisation catalysed by Tp early transition metal complexes have been reported [17]. Jordan has investigated the correlation between the activity in ethylene polymerisation and the steric hindrance of TpR,R′TiCl₃, discovering that the best catalytic performance was obtained with R and R′ = 2,4,6-trimethyl benzene [16]. The large majority of catalysts precursors with tris(pyrazolyl)borate ligands contain either early transition metals or lanthanides, e.g. the titanium and zirconium complexes [TpMCl₃] and [TpCpMCl₂] [18], the yttrium complex [TpYCl₃] [19] and the vanadium imido complex [TpV(N-*t*-Bu)Cl₂] [20]. Polymerisation of ethylene by titanium and vanadium catalysts immobilised on MAO-modified silica has also been reported [21].

In this paper, we describe the synthesis and characterisation of new Ni[II] and Pd[II] complexes containing tris(3,5-dimethylpyrazolyl)borate (Tp*), tris(3-*t*-butyl-5-methylpyrazolyl)borate (Tp$^{t-Bu,Me}$) or tris(3-cumyl-5-methylpyrazolyl)borate (Tp^{Cum,Me}). All the compounds obtained have been tested as catalyst precursors for the polymerisation of ethylene in the presence of activators such as methylaluminoxane (MAO), magnesium dibutyl (MgBu₂), diethylaluminum chloride (AlEt₂Cl) or tris(3,5-trifluorophenyl)borane (B[C₆H₃(3,5-CF₃)₂]₃). Prior to this work, Ni[II] catalysts stabilised by 3- or 3,5-mesityl substituted pyrazolylborate ligands have been reported to be exclusively active for ethylene oligomerisation to low-molecular-weight α-olefins [22].

2. Experimental

2.1. Materials and methods

All reactions were performed under argon using Schlenk-type glassware. Methanol was distilled under argon from CaH₂, while toluene, THF and DME were distilled from sodium/benzophenone and then stored on 4 Å molecular sieves. Anhydrous NiCl₂, Tl(OCOH), KTp* and Et₂AlCl (1.8 M in toluene) were obtained from Aldrich and used as received. B[C₆H₃(3,5-CF₃)₂]₃ and [PdCl(η³-allyl)]₂ were purchased from Strem. Methylaluminoxane 10% Al (MAO) and ethylene were obtained from AKZO and Rivoira, respectively. TlTp* [6], [Tp*Pd(η³-allyl)] [23] and the potassium salts KTp$^{t-Bu,Me}$ and KTp^{Cum,Me} were prepared according to literature methods [9,10]. ¹H NMR spectra were recorded on a 200 MHz Brucker Electrospin AG 200 BZH instrument; chemical shits are relative to tetramethylsilane as external reference or calibrated against the solvent resonances. IR spectra were obtained with a Perkin Elmer 1420 instrument, while MS-FAB spectra were obtained with a Finnigan MAT M scan instrument, using *m*-nitrobenzylalcohol as matrix.

2.2. Synthesis of TlTp*

In a round-bottomed flask containing 30 mL of MeOH was dissolved 2.013 g of KTp* (2 mmol); to the resulting solution was slowly added 0.996 g of Tl(OCOH) (6 mmol) in 40 mL of MeOH. An off-white solid immediately precipitated, which was collected, and dried in vacuo to give 2.448 g (81% yield) of TlTp*. ¹H NMR (CDCl3): δ 5.75 (3H, broad s), 2.38 (9H, s), 2.29 (9H, s); IR (Nujol) 2500 cm⁻¹, ν(BH).

2.3. Synthesis of [k³N,N′,N″-Tp*NiCl] (1)

About 0.065 g of anhydrous $NiCl_2$ (0.5 mmol) was dissolved in 30 mL of MeOH. To the resulting green solution, was added 0.250 g of TlTp* (0.5 mmol). After stirring at room temperature for 24 h, the solvent was removed in vacuo, and the residue was dissolved in diethyl ether. After TlCl was removed by filtration, the solution was evaporated to give a pink solid that was dried in vacuo to give 0.17 g (87% yield) of **1**. ¹H NMR (CDCl3): δ 5.12 (3H, broad s), 1.24 (9H, s), 0.9 (9H, s); IR (Nujol): 2524 cm⁻¹, ν(BH). Anal. Calcd for $C_{15}H_{22}BClN_6Ni$: C, 46.04; H, 5.66; N, 21.47. Found: 45.87; H, 5.57; N, 21.18.

2.4. Synthesis of [k³N,N′,N″-Tp^{t-Bu,Me}NiCl] (2)

To 0.285 g of anhydrous $NiCl_2$ (2.19 mmol) in 60 mL of THF, was added 1 g of $KTp^{t-Bu,Me}$ (2.19 mmol). After stirring the reaction mixture at room temperature for 4 days, solid KCl was filtered off and the filtrate was evaporated to dryness. The blue residue was recrystallised from a mixture of heptane/CH_2Cl_2 (1:1, v/v) to give violet crystals (0.73 g, 64.4% yield). ¹H NMR (CDCl3): δ 5.25 (3H, broad s), 2.24 (27H, s), 1.3 (9H, s); IR (Nujol): 2558 cm⁻¹, ν(BH). Anal. Calcd for $C_{24}H_{40}BClN_6Ni$: C, 55.68; H, 7.79; N, 16.23. Found: C, 55.23; H, 7.48; N, 16.36.

2.5. Synthesis of [k³N,N′,N″-Tp^{Cum,Me}NiCl(3-methyl-5-cumylpyrazole)] (3)

To a yellow suspension of 0.100 g of anhydrous $NiCl_2$ (0.77 mmol) in 100 mL of 1,2-dimethoxy ethane (DME), was added 0.5 g of $KTp^{Cum,Me}$ (0.77 mmol). The suspension was stirred until complete dissolution of the solid occurred. The solvent was then removed under reduced pressure and 50 mL of CH_2Cl_2 was added. The resulting solution was evaporated in vacuo to give **3** as a green solid (0.48 g). Recrystallisa-

tion of the crude product from CH_2Cl_2/n-heptane (1:1, v/v) at −18 °C gave 0.120 g of **3** as green crystals (22% yield). ¹H NMR (CDCl3): δ 7.80 (6H, d), 7.15 (6H, d), 5.38 (3H, s), 2.43 (3H, q), 1.55 (9H, s), 1.02 (18H, d); IR (Nujol): 2442 cm⁻¹, ν(BH). m.p. = 180–83 °C. FAB⁺-MS: m/z 702 [M⁺]. Anal. Calcd for $C_{52}H_{61}BClN_8Ni$: C, 69.15; H, 6.80; N, 12.40. Found: C, 69.21; H, 6.64; N, 12.38.

2.6. Polymerisation procedure

A three-necked round-bottomed flask was connected to a reservoir containing 1 bar ethylene. Into this flask was introduced, under argon, a toluene solution of the catalyst, followed by the appropriate activator. The flask was then purged with ethylene and placed in an oil bath maintained at the desired temperature. The reaction was terminated by addition of methanol acidified with 6N HCl. The polymer obtained was washed with water and methanol, and then dried in vacuo for 8 h (see Table 1).

2.7. X-ray diffraction studies

Summaries of crystal and intensity data for the Ni^{II} complexes **2** and **3** are presented in Tables 2 and 3. Experimental data were recorded at room temperature on a Enraf-Nonius CAD4 diffractometer. A set of 25 carefully centered reflections in the range of $7.5° \leq \theta \leq 10°$ (**1**) and $8.5° \leq \theta \leq 12°$ (**2**), respectively, was used for determining the lattice constants. As a general procedure, the intensities of three standard reflections were measured periodically every 2 h for orientation and intensity control. This procedure did not reveal any decay of intensities. The data were corrected for Lorentz and polarisation effects. Atomic scattering factors were those tabulated by Cromer and Waber [24] with anomalous dispersion correction taken from Ref. [25]. An empirical absorption correction was applied via Ψ scan for both compounds with transmission factors in the range

Table 1
Ethylene polymerisation catalysed by precursors **1–4** in the presence of various activators[a]

Run	Catalyst (mmol)	Activator	Molar Ratio [Act]/[Cat]	T (°C)	t (h)	Yield (g PE)	Productivity (g PE)/(mol M)	T_m (°C)[b]
1	**1** (0.038)	MAO	50	55	2	0.08	2057	131
2	**2** (0.014)	MAO	50	55	2	0.13	13020	129
3	**2** (0.010)	MAO	1000	55	2	0.21	20700	123
4	**3** (0.014)	MAO	50	55	2	0.25	17600	112
5	**3** (0.010)	MAO	1000	55	2	0.24	23600	102
6	**3** (0.014)	$MgBu_2$	1	25	24	0.05	3571	132
7	**3** (0.007)	$MgBu_2$	10	25	24	0.04	5643	130
8	**3** (0.007)	$MgBu_2$	200	25	4	0.10	14080	129
9	**3** (0.014)	$AlEt_2Cl$	50	25	4	0	0	–
10	**4** (0.043)	MAO	50	25	24	0	0	–
11	**4** (0.043)	MAO	1000	25	12	0.05	1145	128
12	**4** (0.043)	$MgBu_2$	1	25	24	0	0	–
13	**4** (0.043)	$AlEt_2Cl$	25	25	12	0	0	–
14	**4** (0.043)	$B[C_6H_3(3,5-CF_3)_2]_3$	1	25	12	0	0	–
15	**4** (0.043)	$B[C_6H_3(3,5-CF_3)_2]_3$	1	45	12	0.03	688	130

[a] Polymerisation conditions: $P(C_2H_4) = 1$ bar; toluene 50 ml; 1200 rpm.

[b] T_m determined by DSC (heating rate: 10 °C/min).

Table 2
Crystal data and structure refinement for **2**

Identification code	[k3N,N',N''-Tp$^{t\text{-Bu,Me}}$NiCl]
Empirical formula	$C_{24}H_{40}B_1C_{11}N_6Ni$
Formula weight	517.60
Temperature (K)	293(2)
Wavelength (Å)	0.71069
Crystal system	Trigonal
Space group	$R3$
Unit cell dimensions	$a = 9.7160(10)$ Å, $\alpha = 109.990(10)°$
	$b = 9.7160(10)$ Å, $\beta = 109.990(10)°$
	$c = 9.7160(10)$ Å, $\gamma = 109.990(10)°$
Volume (m^3)	692.16(12)
z	I
Density (calculated) (Mg/m^3)	1.242
Absorption coefficient (mm^{-1})	0.820
$F(0\,0\,0)$	276
Crystal size (mm^3)	$0.25 \times 0.30 \times 0.40$
Theta range for data collection	2.56–29.97°
Index ranges	$0 \le h \le 12$, $0 \le k \le 12$, $\sim13 \le l \le 10$
Reflections collected	1794
Independent reflections	1494 [R(int) = 0.2387]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1494/1/106
Goodness of fit on F^2	1.016
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0667$, $wR2 = 0.1781$
R indices (all data)	$R1 = 0.0730$, $wR2 = 0.1857$
Absolute structure parameter	0.71(4)
Largest diff. peak and hole	1.231 and $\sim$0.816 e Å^{-3}

0.94–0.99 (**1**) and 0.44–99 (**2**). The computational work was performed with a Digital Dec 5000/200 workstation using the programs SHELX93 [26]. The program ZORTEP was also used.

Table 3
Crystal data and structure refinement for **3**

|	
Identification code	[k3N,N',N''-Tp$^{\text{Cum,Me}}$NiCl(3-methyl-5-cumylpyrazole)]
Empirical formula	$C_{52}H_{61}BClN_8Ni$
Formula weight	903.06
Temperature (K)	293(2)
Wavelength (Å)	0.71069
Crystal system	Triclinic
Space group	$P–1$
Unit cell dimensions	$a = 14.053(2)$ Å, $\alpha = 90.67(3)°$
	$b = 14.324(6)$ Å, $\beta = 107.16(5)°$
	$c = 14.395(5)$ Å, $\gamma = 112.88(2)°$
Volume (m^3)	2524.4(14)
z	2
Density (calculated) (Mg/m^3)	1.188
Absorption coefficient (mm^{-1})	0.479
$F(0\,0\,0)$	958
Crystal size (mm^3)	$0.25 \times 0.45 \times 0.40$
Theta range for data collection	2.50–23.00°
Index ranges	$-15 \le h \le 14$, $-15 \le k \le 15$, $0 \le l \le 15$
Reflections collected	7342
Independent reflections	7013 [R(int) = 0.0285]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7013/0/534
Goodness-of-fit on F^2	1.036
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0547$, $wR2 = 0.1388$
R indices (all data)	$R1 = 0.0950$, $wR2 = 0.1582$
Largest diff. peak and hole	0.392 and -0.29 e Å^{-3}

The structures were solved by using the heavy atom technique, and all non-hydrogen atoms were found through a series of F_o Fourier maps. Refinement was done by full-matrix least-squares calculation, initially with isotropic thermal parameters, and then, during the last stage with anisotropic thermal parameters for all the atoms but the hydrogens. Phenyl rings were treated as rigid bodies and the hydrogen atoms were introduced in calculated positions.

3. Results and discussion

3.1. Synthesis and characterisation of the nickel and palladium complexes

The complexes [k$^3N,N',N''$-Tp*NiCl] (**1**), [k$^3N,N',N''$-Tp$^{t\text{-Bu,Me}}$NiCl] (**2**) and [k$^3N,N',N''$-Tp$^{\text{Cum,Me}}$NiCl(3-methyl-5-cumylpyrazole)] (**3**) were prepared as illustrated in Scheme 1, while the Pd^{II} allyl complex [Tp*Pd(η^3-allyl)] (**4**) was obtained following a literature method [23].

Treatment of anhydrous NiCl$_2$ with 1 equiv. of Tp*Tl in methanol at room temperature gave pink crystals of **1**, which was straightforwardly characterised by elemental analysis
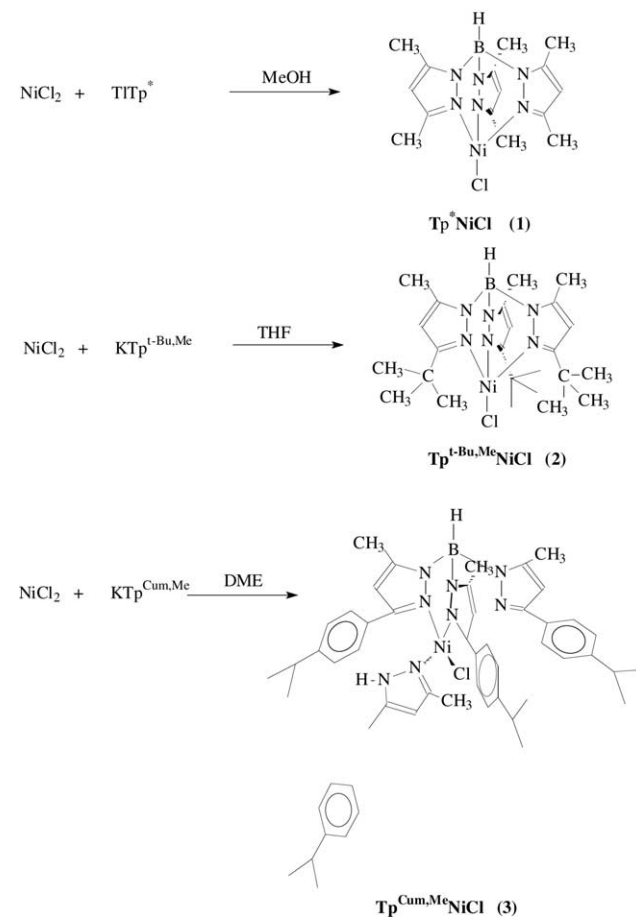
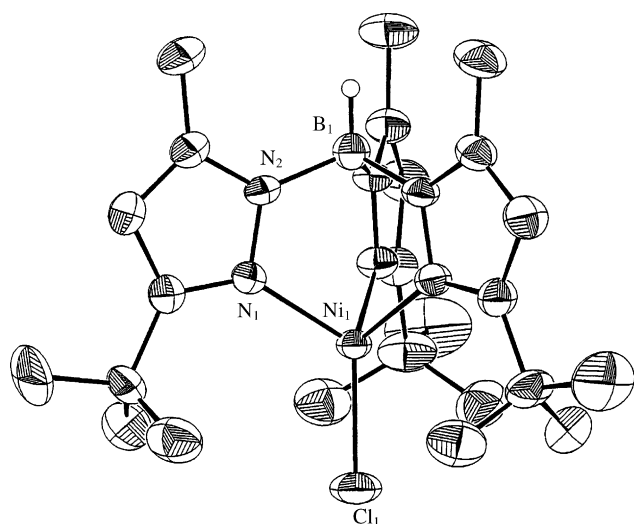Scheme 1. Schematic procedure for the synthesis of Tp*NiCl, Tp$^{t\text{-Bu,Me}}$NiCl and Tp$^{\text{Cum,Me}}$NiCl.

Fig. 1. ZORTEP drawing of [k³*N*,*N'*,*N''*-Tp*^t-Bu,Me*NiCl]. All the hydrogen atoms are omitted for clarity. Selected bond distances (Å): Ni—N1(N3, N7), 1.995(4); Ni—Cl, 2.219(3); N1—N, 21.355(6); N2—B, 1.538(6). Selected bond angles (°): N1—Ni—N3(N7), 93.52(18); Cl—Ni—N1(N3, N7), 122.74(13).

and by IR and ¹H NMR spectroscopy (CDCl₃). The ¹H NMR spectrum shows a broad signal at 5.12 ppm, due to the protons on the pyrazole rings, and two singlets at 1.24 and 0.9 ppm assigned to the methyl substituents. The IR contains a ν(BH) band at 2524 cm⁻¹ [27].

Well-shaped single crystals of **2** were obtained by recrystallisation from heptane–methylene chloride (1:1, v/v). An X-ray analysis demonstrates the tridentate coordination of the Tp*^t-Bu,Me* ligand. Fig. 1 shows a ZORTEP view of a molecule of this compound, while important bond lengths and angles are collected in the caption to the figure. The nickel centre adopts a tetrahedral coordination geometry with no apparent deviation from an ideal C₃-symmetrical structure, all the Ni—N bonds (1.995(4) Å) and N—Ni—Cl angles (122.74(13)°) being equal. The molecular structure is quite similar to that of the thiocyanate derivative [Tp*^t-Bu,Me*Ni(NCS) reported by Trofimenko et al. [28].

Complexes **2** and **3** have been prepared by reacting anhydrous NiCl₂ with the potassium salt of the corresponding pyrazolylborate anion in the appropriate solvent (Tp*^t-Bu,Me*K in THF or Tp*^Cum,Me*K [29], in 1,2-dimethoxyethane).

A tridentate coordination of the Tp*^Cum,Me* ligand is observed also for **3** which was obtained as large green crystals by recrystallisation from dichloromethane/*n*-pentane at −18 °C. In this case, however, the five-coordinate, 18e⁻ nickel(II) centre has a distorted trigonal–bipyramidal environment, which is made up of the Tp*^Cum,Me* ligand, a chloride ion and a molecule of 3-methyl-5-cumylpyrazole. Fig. 2 shows a ZORTEP view of a molecule of this compound; important bond lengths and angles are collected in the caption to the figure. The equatorial plane contains two of the N atoms of the Tp*^Cum,Me* group, N(3) and N(5), and the chloride ligand. The third Tp*^Cum,Me* nitrogen and 3-methyl-5-cumylpyrazole
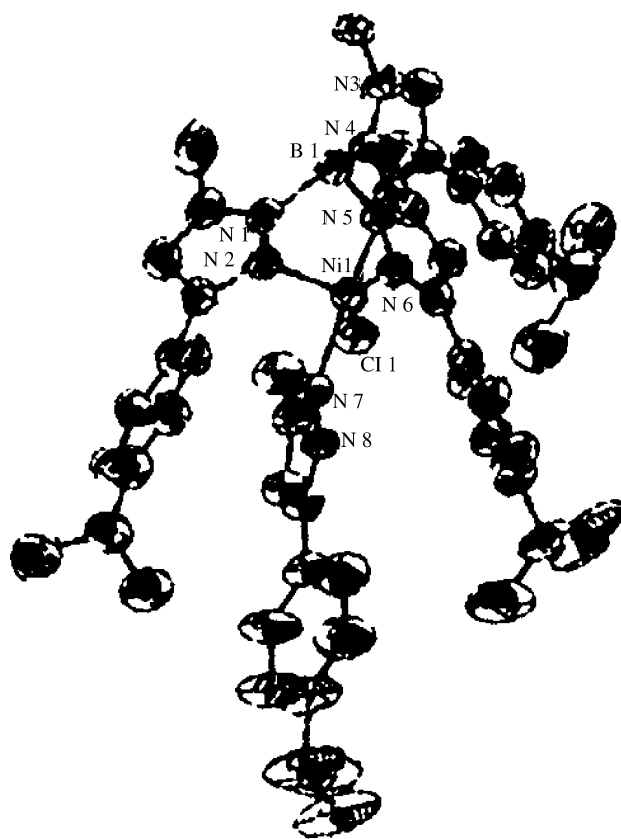

Fig. 2. ZORTEP drawing of [k³*N*,*N'*,*N''*-Tp*^Cum,Me*NiCl(3-methyl-5-cumylpyrazole)]. All the hydrogen atoms are omitted for clarity. Selected bond distances (Å): Ni—N5, 2.020(4); Ni—N, 32.029(3); Ni—N, 72.102(3); Ni—N, 12.157(3); Ni—Cl, 2.2911(14). Selected bond angles (°): N5—Ni—N, 396.08(15); N5—Ni—N, 789.37(14); N3—Ni—N, 790.27(14); N5—Ni—N, 192.43(14); N3—Ni—N, 181.23(13); N7—N1—N, 1171.45(13); N5—Ni—Cl, 117.56(11); N3—Ni—Cl, 146.35(11); N7—Ni—Cl, 90.77(10); N1—Ni—Cl, 95.80(10).

nitrogen occupy axial positions. The equatorial Ni—N distances, 2.020(4) and 2.029(3) Å, compare well to those of the trigonal–bipyramidal Tp* derivative Tp*NiCysEt [30]. Like the latter complex, a weaker axial ligand field is indicated by the longer axial Ni—N distances (Ni—N(1), 2.157(3) and 2.102(3) Å). Distortions of in-plane angles from idealised values reflect the geometrical constraints of the tripodal ligand. The bond distances within the axial pyrazole ring are in the normal range for this class of unidentate ligands [31].

Tetrahedral Ni^II complexes with Tp's ligands bearing a phenyl substituent in the 3-position are generally unstable and tend to accept a fifth ligand forming five-coordinate chromophores [28]. This tendency is most likely the driving force leading to the formation of **3** via electrophilic attack by a four-coordinate [k³*N*,*N'*,*N''*-Tp*^Cum,Me*NiCl] species to free Tp*^Cum,Me*.

3.2. Catalytic ethylene polymerisation

All of the experiments were performed in toluene and the pressure was kept constant to 1 bar of ethylene. In Table 1

are collected polymerisation results with both Ni[II] and Pd[II] catalysts.

Depending on the concentration of MAO, **1**–**3** exhibit an activity, which increases linearly in ethylene polymerising at 55 °C. In comparable experimental conditions, the catalytic activity increases remarkably with the size of the 3-substituent in the pyrazole ring. As shown in runs 1–4, the plain substitution of either *t*-butyl or cumyl for methyl increases the productivity of polyethylene (PE) by six and eight times, respectively. The greater activity of **2** as compared to **1** is apparently due to steric effects, the basicity of the N donor being quite comparable in the two Tp ligands. As proposed by Brookhart [1b,4] and Gibson [1a] for the polymerisation of ethylene with bis(imino)pyridyl iron(II) and cobalt(II) complexes, robust steric hindrance at the metal centre is required to disfavour β-H elimination mechanisms leading to undesired termination [12], and hence allow for efficient polymerisation. The increased catalytic activity of **3** versus both **1** and **2** is more difficult to explain since **3** is a five-coordinate species in the solid state. In catalytic conditions, ethylene should easily displace the 3-cumyl-5-methylpyrazole ligand and then insert into the M–C bond of the propagating polymer. 3-Cumyl-5-methylpyrazole is actually a weaker ligand than each arm of Tp^{Cum,Me} due to the absence of both chelate effect and negative charge. A clear-cur explanation for the superior activity of **3** is also hampered by the hierarchies of steric hindrance (Me < Ph < *t*-Bu) and nitrogen basicity (Ph < Me < *t*-Bu) as a function of the 3-R group in the Tp's ligands. Tentatively, it may be proposed that the inhibiting effect caused by the relatively scarce steric hindrance of the cumyl substituent in the 3-position is more than compensated by the reduced basicity of the nitrogen donor, which should favour the coordination of the electron-rich ethylene molecule (notice that the N–Ni distances in **3**, 2.050 Å, are appreciably longer than those in **2**, 1.995 Å).

Increasing the MAO to catalyst ration from 50 to 1000 (run 3 versus 2 and 5 versus 4) has been found to increase the PE productivity of **2** by ca. 35% and of **3** by 20%, which has previously been observed for bis(imino)pyridyl metal complexes [1]. No attempt to correlate the molecular weight distribution with MAO concentration was made. The polymers obtained were analysed by DSC; the T_m of all runs were well below the T_m for a linear PE (136 °C), demonstrating they were branched PE, as just reported for nickel catalysts [3,4].

In addition to MAO, other alkylating agents have been employed to activate **3** for ethylene polymerisation. MgBu$_2$ proved to be less efficient than MAO (runs 6–8), while AlEt$_2$Cl was totally inactive (run 9).

Consistent with previous reports [3,4], the substitution of Pd[II] for Ni[II] resulted in the formation of much worst polymerisation catalysts as shown in Table 1 for **4** which gave a modest productivity of PE only in the presence of a high concentration of MAO (run 10). Neither MgBu$_2$ nor Et$_2$AlCl were able to activate the palladium precursor (runs 12 and 13) which, however, became slightly active in the presence

of a stoichiometric amount of B[C$_6$H$_3$(3,5-CF$_3$)$_2$]$_3$ at 45 °C (run 15).

4. Conclusion

This study has shown that the presence of a bulky substituent in the 3-position of the pyrazolyl groups is of mandatory importance to generate active Ni[II] catalysts for ethylene polymerisation. Either alkyl (as in Tp$^{t-Bu,Me}$NiCl) or aryl (as in Tp^{Cum,Me}NiCl) groups in the 3-position may be equally effective, yet their size seems to play a major role in governing the catalytic activity. Indeed, under comparable conditions, we have found that the cumyl substituent gives a better catalyst as compared to the bulkier *t*-butyl substituent, while a previous study has shown that mesityl groups in the 3-position lead to Ni[II] catalysts that are selective for the oligomerisation of ethylene to short chain α-olefins [22]. Apparently, some steric hindrance, close to the nickel centre, is required to slow down the chain transfer rate, yet it must be finely tuned because too bulky substituents such as the mesityl group may further disfavour chain propagation, ultimately yielding oligomers instead of PE.

Irrespective of the Ni[II] chloride precursor, MAO proved more efficacious than any other activator investigated, while the Pd[II] complex [Tp*Pd(η^3-allyl)] showed little activity with either Lewis acid or MAO activator.

Appendix A. Support information available

CCDC 237633 and 237634 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB21EZ, UK; fax: +44-1223-336-033; or deposit@ccdc.cam.ac.uk).

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