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2-*tert*-Butyl and 2-phenylphenylimido complexes of titanium(IV) and their olefin polymerisation activity

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Reaction of 7 equivalents of *tert*-butylamine with $TiCl_4$ in hexane at 0 °C gave $[TiCl_2(NCMe_3)(NH_2CMe_3)_2]_2$ **1** which on thermalisation with 2,6-diisopropylaniline in toluene gave $[TiCl_2(NC_6H_3Pr^i_2\text{-}2,6)(NH_2CMe_3)_2]_x$ **2**. Imido exchange of $[TiCl_2(NCMe_3)(NH_2CMe_3)]_x$ with *o*-toluidine or 2-*tert*-butylaniline and addition of pyridine gave $[TiCl_2(NC_6H_4Me\text{-}2)(py)_3]$ and $[TiCl_2(NC_6H_4CMe_3\text{-}2)(py)_3]$ which crystallised to give $[TiCl_2(NC_6H_4Me\text{-}2)(py)_2]_2$ **3** and $[TiCl_2(NC_6H_4CMe_3\text{-}2)(py)_2]_2$ **4**. 2-Phenylaniline and $[TiCl_2(NCMe_3)(py)_3]$ gave $[TiCl_2(NC_6H_4Ph\text{-}2)(py)_2]_2$ **5** on crystallisation and reaction of *tert*-butylaniline or 2-phenylaniline with $[TiCl_2(NCMe_3)(tmeda)]$ gave $[TiCl_2(NC_6H_4CMe_3\text{-}2)(tmeda)]$ **6** and $[TiCl_2(NC_6H_4Ph\text{-}2)(tmeda)]_2$ **7**. Complexes **1, 3, 4, 5, 6,** and **7** were characterised by X-ray crystallography and the possibility of imdo ligand C–N bond rotation taking place analysed and compared with the NMR spectra. $[TiCl_2(NCMe_3)(tmeda)]$ and $MAO{\cdot}(MeAlO)_n$, polymerises ethylene at low pressure with low activity (3.2 g $mmol^{-1}$ h^{-1} bar^{-1}), $[TiCl_2(NC_6H_4CMe_3)(tmeda)]$ or $[TiCl_2(NC_6H_4Ph\text{-}2)(tmeda)]$ and MAO gives a 4-fold increase in activity whereas propene is not polymerised but 1-hexene is. Heterogenisation by addition of $[TiCl_2(NCMe_3)(NH_2CMe_3)_2]_2$ **1** to tmeda-functionalised crosslinked polystyrene or imido exchange of $[TiCl_2(NCMe_3)(tmeda)]$ with NH_2-functionalised crosslinked polystyrene gives supported complexes which do not polymerise ethylene at low pressure in the presence of MAO.

Since our work on the reaction of $TiCl_4$ and *tert*-butylamine[1] which showed that an imido ligand was generated and not two amido ligands,[2] the reaction has been used to produce compounds for vapour deposition[3,4] and the precursor to the complex $[TiCl_2(NCMe_3)(py)_3]$ which has generated an extensive and unique chemistry.[5] We have taken renewed interest in the reaction as addition of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda) to the reaction mixture gives $[TiCl_2(NCMe_3)(tmeda)]$ cleanly and in high yield.[1] The crystal structure shows a 5-coordinate monomeric complex with *cis*-orientated dichloro ligands[3] similar to that found in both $[TiCl_2(NPh)(tmeda)]$ and $[(TiCl_2)_2\{trans\text{-}NC(Me)(Me)CN\}]$,[6] and does not have the imido-bridged dimeric structure we originally proposed.[1] In view of the prominence of *cis*-dichloro ligands in catalysis involving the 16-electron complexes $[TiCl_2(Cp)_2]$[7] and $[TiCl_2(OAr)_2]$,[8] the dichloro ligands in the 14-electron tmeda imides are an attractive prospect for homogeneous catalysis and the imido and other nitrogen donor ligands present opportunities for heterogenisation. We have also been interested in using phenylimido ligands substituted in the 2 position with a *tert*-butyl or phenyl group to influence regiospecifically sections of a complex when imido ligand C–N bond rotation is impeded.[9] We report here the results of studies directed towards an understanding of these features in the titanium imide system.

Results and discussion

When $TiCl_4$ is treated with an excess of *tert*-butylamine in benzene solution an orange crystalline solid can be obtained which depending on the degree of drying corresponds to the formulation $[TiCl_2(NCMe_3)(NH_2CMe_3)_3]$ or $[TiCl_2(NCMe_3)(NH_2CMe_3)_2]$.[3] Osmometric molecular weight determinations of the tris-amine complex indicate a trimer for which a cyclic bridging imido structure has been proposed.[3] Although the orange complexes are crystalline the crystal quality has generally been found to be poor. In addition, the reaction apparently does not go to completion in solution as amine hydrochloride is sometimes produced as the reaction medium is removed.[10] In the present work a reaction of $TiCl_4$ and 4 equivalents of *tert*-butylamine in CH_2Cl_2 initiated at −78 °C and then allowed to warm to room temperature gave an orange complex which analysed close to the formulation $[TiCl_2(NCMe_3)(NH_2CMe_3)_2]_2{\cdot}5\ Me_3CNH_3Cl$. Poor quality X-ray data were obtained for a crystal of the sample but this did show the presence of amine hydrochloride in the unit cell. From a reaction using 7 equivalents of *tert*-butylamine in hexane at 0 °C a sample analysing as $[TiCl_2(NCMe_3)(NH_2CMe_3)_2]$ was obtained which gave crystals suitable for X-ray crystallography.

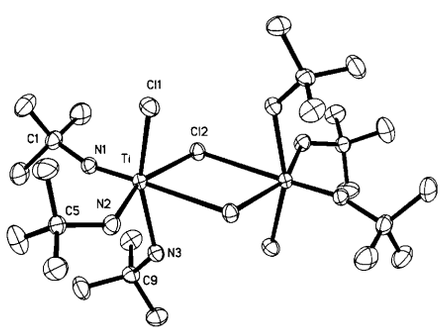

Fig. 1 Molecular structure of complex **1**; without H atoms and with key atoms labelled.

The structure (Fig. 1) shows the complex is a chloro-bridged dimer with terminal imido ligands conforming to the formulation $[TiCl(\mu\text{-}Cl)(NCMe_3)(NH_2CMe_3)_2]_2$ **1**. This solid state

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Table 1 Selected bond lengths (Å) and bond angles (°) for $[TiCl_2(NCMe_3)(NH_2CMe_3)_2]_2$ **1**

Ti–N(1)	1.695(2)	Ti–N(2)	2.264(2)
Ti–N(3)	2.662(2)	Ti–Cl(1)	2.4332(6)
Ti–Cl(2)	2.4639(6)	Ti–Cl(2′)	2.8142(6)
N(1)–C(1)	1.470(3)		
Ti–N(1)–C(1)	164.4(2)	N(1)–Ti–N(2)	104.8(1)
N(1)–Ti–N(3)	102.2(1)	N(2)–Ti–N(3)	86.9(1)
N(1)–Ti–Cl(1)	98.8(1)	N(2)–Ti–Cl(1)	87.8(1)
N(3)–Ti–Cl(1)	159.1(1)	N(1)–Ti–Cl(2)	98.7(1)
N(2)–Ti–Cl(2)	156.3(1)	N(3)–Ti–Cl(2)	85.4(1)
Cl(1)–Ti–Cl(2)	91.7(1)	N(1)–Ti–Cl(2′)	176.7(1)
N(2)–Ti–Cl(2′)	76.6(1)	N(3)–Ti–Cl(2′)	74.8(1)
Cl(1)–Ti–Cl(2′)	84.3(1)	Cl(2)–Ti–Cl(2′)	79.8(1)
Ti–Cl(2)–Ti′	100.2(1)	Ti–N(2)–C(5)	131.2(1)
Ti–N(3)–C(9)	128.3(1)		

Table 2 Selected bond lengths (Å) and bond angles (°) for $[TiCl_2(NC_6H_4Me\text{-}2)(py)_2]_2$ **3**

Ti–N(1)	1.711(2)	Ti–N(2)	2.230(2)
Ti–N(3)	2.220(2)	Ti–Cl(1)	2.3788(6)
Ti–Cl(2)	2.4529(6)	Ti–Cl(2′)	2.7123(6)
N(1)–C(11)	1.385(3)		
Ti–N(1)–C(11)	170.4(2)	N(1)–Ti–N(2)	93.2(1)
N(1)–Ti–N(3)	93.2(1)	N(2)–Ti–N(3)	170.8(1)
N(1)–Ti–Cl(1)	97.8(1)	N(3)–Ti–Cl(1)	92.5(1)
N(2)–Ti–Cl(2)	93.1(1)	N(1)–Ti–Cl(2)	100.9(1)
N(3)–Ti–Cl(2)	86.1(1)	N(2)–Ti–Cl(1)	86.3(1)
Cl(1)–Ti–Cl(2)	161.3(1)	N(1)–Ti–Cl(2′)	179.6(1)
N(3)–Ti–Cl(2′)	86.7(1)	N(2)–Ti–Cl(2′)	86.8(1)
Cl(1)–Ti–Cl(2′)	82.6(1)	Cl(2)–Ti–Cl(2′)	78.7(1)
Ti–Cl(2)–Ti′	101.3(1)	C(11)–C(12)–C(17)	120.8(2)
		C(13)–C(12)–C(17)	120.7(2)

structure thus differs from the trimer indicated by osmometry in CH_2Cl_2 and proposed as a cyclic bridging imide.[3] Bond distances and angles for the complex are contained in Table 1. Each titanium atom has a distorted octahedral geometry consisting of the imido and amine ligands and terminal and bridging chloro ligands. The Ti–N(1) and Ti–Cl(1) bond lengths [1.695(2) and 2.4332(6) Å respectively] are similar to those in a variety of other titanium imides.[11] In the asymmetric chlorine bridge the Ti–Cl(2) bond length [2.4639(6) Å] is longer than the terminal Ti–Cl(1) bond length but the Ti–Cl(2′) bond length [2.8142(6) Å] where Cl(2′) lies *trans* to the imido function is very long and must nearly represent the limit for this type of bonding. In $CDCl_3$ solution the NMR spectra become more complex with time but there is evidence in the $^{13}C\text{-}\{^1H\}$ spectrum that the solid state structure is present initially, as the major features are one imido ligand quaternary (δ 72.2) and two non-equivalent amine ligand quaternaries (δ 52.6 and 52.2). The long Ti–Cl(2′) bond length in the crystal structure indicates that dissociation into two monomers would be facile and other work has shown that dissociation of the amine ligands can occur,[3] so that these processes could give rise to the solution dynamics observed.

Alkylimido complexes are easily generated using $TiCl_4$ and a primary alkylamine,[1–3] but arylimido complexes are not generated by this process or other usual routes.[10] However they can be generated by imido group exchange in the $[TiCl_2(NCMe_3)(py)_3]$ system.[12,13] Our initial attempts at exchanging the *tert*-butylimido ligand in the $TiCl_4$/*tert*-butylamine reaction product using 2-*tert*-butyl- or 2-phenyl-aniline did not give a single isolatable product. $^{13}C\text{-}\{^1H\}$ NMR spectral analysis of the product obtained by addition of an excess of aniline to complex **1** in benzene or CH_2Cl_2 at room temperature showed loss of the *tert*-butylimido ligand quaternary (δ 72.2), resonances characteristic of *tert*-butylamine ligands (*ca.* δ 52) and two phenylimido *ipso*-carbon resonances (*ca.* δ 154). Refluxing in benzene for a short period gave predominantly one phenylimido species. Consequent thermalisation of 2,6-di-isopropylaniline and complex **1** in toluene for an extended period gave rise to $[TiCl_2(NC_6H_3Pr^i_2\text{-}2,6)(NH_2CMe_3)_2]_x$ **2** which was isolated in 51% yield. A dimeric chloro-bridged structure with *trans* orientated *tert*-butylamine ligands is proposed for the complex based on the crystal structure of **1** and the appearance of only one set of *tert*-butylamine resonances in the ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra. A similar structure has been proposed for the complex $[TiCl_2(NCHEt_2)(NH_2CHEt_2)_2]_x$.[3] NMR tube studies showed that addition of pyridine or tmeda to complex **2** gave rise to the adducts $[TiCl_2(NC_6H_3Pr^i_2\text{-}2,6)(py)_3]$[13] and $[TiCl_2(NC_6H_3Pr^i_2\text{-}2,6)(tmeda)]$.

NMR tube experiments indicated that the imido exchange reaction of complex **1** with substituted anilines, particularly those with a single *ortho* substituent, was facilitated by addition of pyridine or tmeda. However similar NMR studies on $[TiCl_2(NCMe_3)(NH_2CMe_3)]_x$, prepared from $TiCl_4$ and *tert*-butyl·*N*-trimethylsilylamine,[1] indicated that the imido exchange reaction in the absence of pyridine or tmeda was rapid. By adding *o*-toluidine to the $[TiCl_2(NCMe_3)(NH_2CMe_3)]_x$ reaction mixture, stirring the solution for one hour and then adding pyridine, a 70% yield of $[TiCl_2(NC_6H_4Me\text{-}2)(py)_3]$ could be obtained. This complex was characterised by NMR spectroscopy as prolonged drying *in vacuo* or recrystallisation from a hexane-layered CH_2Cl_2 solution, gave the bis-pyridine adduct $[TiCl_2(NC_6H_4Me\text{-}2)(py)_2]_2$ **3**. Its crystal structure (Fig. 2) showed a chloro-bridged dimer which compares with the monomeric structures proposed for other $[TiCl_2(NR)(py)_2]$ complexes[13] and that found by X-ray crystallography for $[TiCl_2(NCMe_3)(OPPh_3)_2]$.[3] The structure is most like the azide bridged complexes $[TiCl(N_3)(NCMe_3)(py)_2]_2$ and $[TiCl(N_3)(NCy)(py)_2]_2$ (Cy = cyclohexyl).[4]

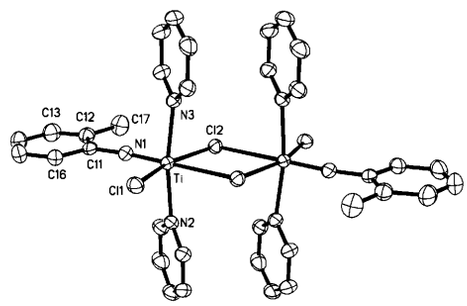


Fig. 2 Molecular structure of complex **3**; details as in Fig. 1.

Bond lengths and angles for complex **3** are shown in Table 2. The Ti–Cl(1) and Ti–Cl(2) bond lengths [2.3788(6) and 2.4529(6) Å respectively] are a little shorter than in **1** [2.4332(6) and 2.4639(6) Å respectively] where the amine ligands are *cis* to each other and not *trans* as in complex **3**, but the Ti–Cl(2′) bond length [2.7123(6) Å] is considerably shorter than in **1** [2.8142(6) Å]. The phenyl ring orientates in dimer **3** with the methyl groups of the dimer sitting directly above Cl(2) and Cl(2′). The Ti–N(1)–C(11) bond angle [170.4(2)°] is essentially linear and there is little difference in the N(1)–Ti–Cl(1) and N(1)–Ti–Cl(2) bond angles [97.8(1) and 100.9(1)° respectively] so that the methyl group appears to have little effect on the coordination geometry. Simple molecular models indicate that the methyl group could move over the pyridine ligands so that the imido ligand C–N bond rotation would not be restricted. For the d^2 molybdenum complex $[MoCl_2(NC_6H_3Me_2\text{-}2,6)(PMe_3)_3]$ NMR studies show hindered rotation of this kind at low temperature.[14]

Addition of 2-*tert*-butylaniline to $[TiCl_2(NCMe_3)(NH_2CMe_3)]_x$ followed by pyridine gave a complex which NMR spectroscopy showed to be $[TiCl_2(NC_6H_4CMe_3\text{-}2)(py)_3]$. Drying *in vacuo* or recrystallisation from a hexane-layered CH_2Cl_2 solution gave the bis-pyridine adduct $[TiCl_2(NC_6H_4CMe_3\text{-}2)(py)_2]_2$ **4**. Analytical data for a crystalline sample were obtained

Table 3 Selected bond lengths (Å) and bond angles (°) for $[TiCl_2(NC_6H_4CMe_3\text{-}2)(py)_2]_2$ **4**

Ti–N(1)	1.702(2)	Ti–N(2)	2.200(2)
Ti–N(3)	2.189(2)	Ti–Cl(1)	2.3503(6)
Ti–Cl(2)	2.4373(7)	Ti–Cl(2′)	2.6825(7)
N(1)–C(1)	1.379(3)		
Ti–N(1)–C(1)	165.9(2)	N(1)–Ti–N(2)	94.9(1)
N(1)–Ti–N(3)	93.9(1)	N(2)–Ti–N(3)	170.6(1)
N(1)–Ti–Cl(1)	95.4(1)	N(3)–Ti–Cl(1)	87.7(1)
N(2)–Ti–Cl(2)	89.4(1)	N(1)–Ti–Cl(2)	103.1(1)
N(3)–Ti–Cl(2)	91.8(1)	N(2)–Ti–Cl(1)	88.2(1)
Cl(1)–Ti–Cl(2)	161.5(1)	N(1)–Ti–Cl(2′)	172.3(1)
N(3)–Ti–Cl(2′)	84.7(1)	N(2)–Ti–Cl(2′)	86.2(1)
Cl(1)–Ti–Cl(2)	84.6(1)	Cl(2)–Ti–Cl(2′)	77.0(1)
Ti–Cl(2)–Ti′	103.0(1)	C(2)–C(7)–C(9)	109.6(2)
C(1)–C(2)–C(7)	122.2(2)	C(2)–C(7)–C(10)	110.1(2)
C(3)–C(2)–C(7)	121.1(2)	C(8)–C(7)–C(9)	108.4(2)
C(2)–C(7)–C(8)	112.2(2)	C(8)–C(7)–C(10)	106.6(2)
		C(9)–C(7)–C(10)	109.8(2)

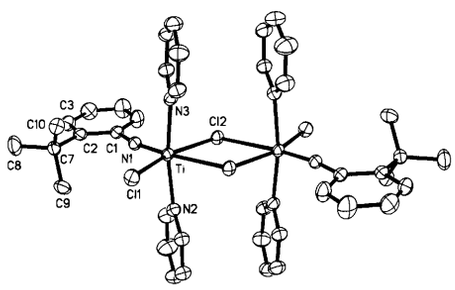


Fig. 3 Molecular structure of complex **4**; details as in Fig. 1.

by adding 2-*tert*-butylaniline to $[TiCl_2(NCMe_3)(py)_3]$.[13,15] A crystal structure determination of **4** (Fig. 3) shows a dimeric chloro-bridged structure similar to that found for complex **3**. However in **3** the methyl group sits over a bridging chloride [Cl(2)], whereas in **4** the *tert*-butyl group sits over a terminal chloro ligand [Cl(1)]. With this orientation in **4** the chloro ligand bonding tightens up somewhat in comparison to **3** [Ti–Cl(1) bond lengths 2.3503(6) and 2.3733(6) Å, Ti–Cl(2) bond lengths 2.4373(7) and 2.4529(6) Å, Ti–Cl(2′) bond lengths 2.6825(7) and 2.7123(6) Å respectively] but there is little change in the pyridine or imido ligand bond lengths (Table 3).

Although the Ti–Cl(2′) bond length in complex **4** is still long, suggesting easy dissociation in solution to a monomer, the NMR spectra in $CDCl_3$ solution indicate the presence of only one species with no solution dynamics being evident. There is little difference in the various N(1)–Ti–Cl bond angles between complexes **4** and **3** and with the Ti–N(1)–C(1) bond angle in **4** at 165.9(2)° the *tert*-butyl group sits easily over Cl(1) (straddled by the C(9) and C(10) methyls and without significant widening of the C(9)–C(7)–C(10) bond angle) and appears to have little influence on the molecule overall. In $CDCl_3$ solution at room temperature the NMR spectra show no sign of the methyl hydrogens becoming diastereotopic indicating that the *tert*-butyl group rotates. Simple molecular models suggest that movement of the *tert*-butyl group over a rotating pyridine ligand would not be easy so that this substituent is likely to be trapped in the vicinity of Cl(1). However rotation about the N–C bond of the imido ligand would be more likely to occur if dissociation of the dimer produced a 5-co-ordinate complex with widened out N(imido)–Ti–N(py) angles (see later). In general no change in the 1-σ, 2-π nature of an M–N triple bond is expected for Ti–N–C bond angles down to about 150° in organoimido complexes.[16]

The complex $[TiCl_2(NC_6H_4Ph\text{-}2)(py)_2]_2$ **5** formed when the tris-pyridine parent crystallised and a crystal structure (Fig. 4) showed a similar overall geometry to that of complex **4**. However the structure is more like that of *o*-toluimide **3** except that

Table 4 Selected bond lengths (Å) and bond angles (°) for $[TiCl_2(NC_6H_4Ph\text{-}2)(py)]_2$ **5**

Ti–N(1)	1.719(2)	Ti–N(2)	2.206(2)
Ti–N(3)	2.241(2)	Ti–Cl(1)	2.3956(7)
Ti–Cl(2)	2.4497(7)	Ti–Cl(2′)	2.6781(7)
N(1)–C(1)	1.380(3)		
Ti–N(1)–C(1)	164.1(2)	N(1)–Ti–N(2)	93.7(1)
N(1)–Ti–N(3)	102.2(1)	N(2)–Ti–N(3)	163.7(1)
N(1)–Ti–Cl(1)	98.0(1)	N(3)–Ti–Cl(1)	86.6(1)
N(2)–Ti–Cl(2)	80.4(1)	N(1)–Ti–Cl(2)	95.0(1)
N(3)–Ti–Cl(2)	84.3(1)	N(2)–Ti–Cl(1)	87.7(1)
Cl(1)–Ti–Cl(2)	166.9(1)	N(1)–Ti–Cl(2′)	170.5(1)
N(3)–Ti–Cl(2′)	92.3(1)	N(2)–Ti–Cl(2′)	89.8(1)
Cl(1)–Ti–Cl(2′)	89.2(1)	Cl(2)–Ti–Cl(2′)	77.7(1)
Ti–Cl(2)–Ti′	102.3(1)	C(1)–C(6)–C(7)	121.7(2)
		C(5)–C(6)–C(7)	119.8(2)

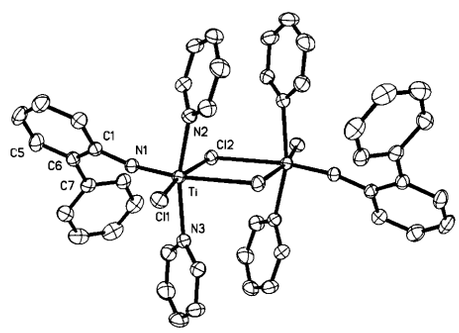


Fig. 4 Molecular structure of complex **5**; details as in Fig. 1.

the phenyl substituent sits over but between the pyridine and bridging chloro ligands. Bond lengths and angles are contained in Table 4. The Ti–N bonds in complexes **5** and **3** are similar in length but the Ti–Cl(1) bond length is larger in **5** [2.3956(7) Å] than in **3** [2.3788(6) Å] whereas the Ti–Cl(2) and Ti–Cl(2′) bonds are more similar in the respective complexes [2.4497(7) and 2.4529(6) Å; 2.6781(7) and 2.7123(6) Å]. The Ti–N(1)–C(1) bond angle [164.1(2)°] is smaller than that observed in complex **3** [170.4(2)°] but does not represent any meaningful change to the imido linkage.[16] The N(1)–Ti–Cl(1) bond angle [98.0(1)°] is similar to that in **3** [97.8(1)°] but N(1)–Ti–Cl(2) [95.0(1)°] is smaller than in **3** [100.9(1)°] where the methyl substituent sits directly over Cl(2). The effect of the phenyl substituent in **5** can also be seen in the Ti–N(3) bond length [2.241(2) Å] which is longer than Ti–N(2) [2.206(2) Å]. The N(1)–Ti–N(2) [93.7(1)°] is significantly smaller than N(1)–Ti–N(3) [102.2(1)°] and this angle is significantly larger than the equivalent bond angle in complex **3** [93.2(1)°]. With the N(1)–Ti–N(3) bond angle widened in **5** the phenyl substituent does not push away from the adjacent pyridine ligand [C(1)–C(6)–C(7) and C(5)–C(6)–C(7) bond angles 121.7(2) and 119.8(2)° respectively].

Addition of 2-*tert*-butylaniline to $[TiCl_2(NCMe_3)(tmeda)]$ in CH_2Cl_2 gave $[TiCl_2(NC_6H_4CMe_3\text{-}2)(tmeda)]$ **6** for which a crystal structure showed a monomer consisting of a pseudo square-prismatic geometry about titanium with the imido ligand occupying the apical site (Fig. 5). Bond lengths and angles are contained in Table 5. The imido ligand phenyl ring is rotated so that the *tert*-butyl group sits over a tmeda ligand methyl group and this positioning results in the Ti–N(1)–C(1) angle decreasing to 155.5(2)° but the Ti–N(1) bond length [1.715(2) Å] is no different to the others reported here. It has been shown that M–N–C bond angles in other imido complexes are somewhat flexible and can reduce to about 150° as a result of steric effects and crystal packing forces.[16] Analysis of the crystal packing in the unit cell of **6** indicates there is a pocket above the tmeda ligand that accommodates the *tert*-butyl group and there is no stacking of the phenyl rings.

Table 5 Selected bond lengths (Å) and bond angles (°) for [$TiCl_2$-($NC_6H_4CMe_3$-2)(tmeda)] **6**

Ti–N(1)	1.715(2)	Ti–N(2)	2.247(2)
Ti–N(3)	2.300(2)	Ti–Cl(1)	2.3514(8)
Ti–Cl(2)	2.3200(9)	N(1)–C(1)	1.404(3)
Ti–N(1)–C(1)	155.5(1)	N(1)–Ti–N(2)	95.9(1)
N(1)–Ti–N(3)	110.2(1)	N(2)–Ti–N(3)	77.3(1)
N(1)–Ti–Cl(1)	103.3(1)	N(1)–Ti–Cl(2)	106.0(1)
N(2)–Ti–Cl(1)	158.5(1)	N(2)–Ti–Cl(2)	87.9(1)
N(3)–Ti–Cl(1)	86.9(1)	N(3)–Ti–Cl(2)	142.0(1)
Cl(1)–Ti–Cl(2)	95.9(1)	Ti–N(2)–C(13)	111.1(2)
Ti–N(2)–C(14)	113.9(2)	Ti–N(2)–C(11)	105.4(2)
Ti–N(3)–C(15)	112.4(2)	Ti–N(3)–C(16)	110.2(2)
Ti–N(3)–C(12)	109.9(2)	C(1)–C(2)–C(7)	121.9(2)
C(8)–C(7)–C(10)	107.0(3)	C(3)–C(2)–C(7)	121.1(3)
C(9)–C(7)–C(10)	111.1(3)	C(2)–C(7)–C(8)	112.7(3)
C(2)–C(7)–C(9)	110.4(2)	C(8)–C(7)–C(9)	106.9(3)
C(2)–C(7)–C(10)	108.6(2)	C(8)–C(7)–C(10)	107.0(3)
C(9)–C(7)–C(10)	111.1(3)		

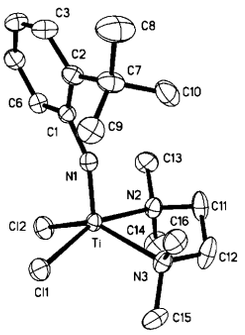


Fig. 5 Molecular structure of complex **6**; details as in Fig. 1.

The Ti–Cl(1) and Ti–Cl(2) bond lengths in complex **6** [2.3514(8) and 2.3200(9) Å] are not much different but Ti–N(3) [2.300(2) Å], which involves the nitrogen atom of the tmeda ligand that is adjacent to the imido ligand *tert*-butyl group, is a little longer than Ti–N(2) [2.247(2) Å]. However these Ti–Cl and Ti–N bonds are no different to those found in [$TiCl_2(NCMe_3)$(tmeda)].[3] The N(1)–Ti–Cl(1), N(1)–Ti–Cl(2) and N(1)–Ti–N(2) bond angles in **6** are also not much different to those in [$TiCl_2(NCMe_3)$(tmeda)]. The N(1)–Ti–N(3) bond angle in **6** [110.2(1)°] is much larger than N(1)–Ti–N(2) [95.9(1)°] and the comparable N–Ti–N bond angles in [$TiCl_2$-($NCMe_3$)(tmeda)] are 100.7(2) and 101.9(2)°.[3] Thus in **6** the *tert*-butyl substituent is mainly accommodated by distortions in the Ti–N(1)–C(1) and N(1)–Ti–N(3) bond angles.

The Ti–N–C bond angles involving the tmeda ligand are all very similar and the imido ligand *tert*-butyl group is not pushed upwards to any extent [C(1)–C(2)–C(7) and C(3)–C(2)–C(7) bond angles 121.9(2) and121.1(3)° respectively]. However the two methyl groups of this substituent that straddle the tmeda ligand methyl do open out a little but the effect is small [C(8)–C(7)–C(10) and C(8)–C(7)–C(9) bond angles 107.0(3) and 106.9(3)° respectively; C(9)–C(7)–C(10) 111.1(3)°]. The ^{1}H NMR spectrum of the complex in $CDCl_3$ solution shows a sharp resonance for these methyls indicating rotation is not restricted. The spectum also shows that full rotation of the imido ligand C–N bond might occur as there is a sharp singlet for the tmeda ligand methylene protons and not the expected AB quartet if the solid state asymmetric structure is locked. However if the *tert*-butyl group sits above and between Cl(1) and Cl(2) [or over C(11) and C(12) of the tmeda ligand] in solution a symmetrical structure results in which the tmeda methylenes are equivalent.

A crystal structure determination showed that after crystallisation the reaction of 2-phenylaniline and [$TiCl_2$-($NCMe_3$)(tmeda)] gave a chloro-bridged dimer, [$TiCl_2(NC_6$-H_4Ph-2)(tmeda)]$_2$ **7** (see Fig. 6), with a distorted octahedral co-ordination geometry about each titanium atom similar to that found for complex **1**. Bond lengths and angles for **7** are contained in Table 6. The imido ligand phenyl ring orientates in a similar manner to that in complex **6**, but with the face of the aromatic ring substituent lying above a tmeda ligand methyl group. Even with this "closed up" 6-co-ordinate geometry the phenyl substituent is easily accommodated above the tmeda methyl group with the Ti–N(1)–C(1) bond angle at 165.0(1)° [*cf*. 155.5(1)° in 5-co-ordinate complex **6**], N(1)–Ti–N(2) at 100.0(1) [*cf*. 95.9(1)° in **6**] and C(1)–C(2)–C(7) and C(3)–C(2)–C(7) at 122.7(2) and 118.9(2)° [*cf*. 121.9 and 121.1(3)° in **6**]. The Ti–N(1) bond lengths in **6** and **7** are similar [1.715(2) and 1.717(2) Å] but the Ti–N(2) and Ti–N(3) bond lengths in **7** [both 2.312(2) Å] are similar to the longer Ti–N(3) [2.300(2) Å] in complex **6**. In **7** the N(1)–Ti–Cl(1) and N(1)–Ti–Cl(2) bond angles are 98.7(1) and 92.6(1)° which compare with 98.8(1) and 98.7(1)° in dimer **1** and 103.3(1) and 106.0(1)° in monomer **6**. The Ti–Cl(2′) bond distance in **7** [2.7060(8) Å] is shorter than in dimer **1** [2.8142(6) Å] but similar to those found in the other dimeric complexes reported.

Table 6 Selected bond lengths (Å) and bond angles (°) for [$TiCl_2$-(NC_6H_4Ph-2)(tmeda)]$_2$ **7**

Ti–N(1)	1.717(2)	Ti–N(2)	2.312(2)
Ti–N(3)	2.312(2)	Ti–Cl(1)	2.3699(8)
Ti–Cl(2)	2.4350(8)	Ti–Cl(2′)	2.7060(8)
N(1)–C(1)	1.390(3)		
Ti–N(1)–C(1)	165.0(2)	N(1)–Ti–N(2)	100.0(1)
N(1)–Ti–N(3)	92.4(1)	N(2)–Ti–N(3)	76.0(1)
N(1)–Ti–Cl(1)	98.7(1)	N(2)–Ti–Cl(1)	89.1(1)
N(3)–Ti–Cl(1)	162.8(1)	N(1)–Ti–Cl(2)	92.6(1)
N(2)–Ti–Cl(2)	163.3(1)	N(3)–Ti–Cl(2)	92.6(1)
Cl(1)–Ti–Cl(2)	99.97(3)	N(1)–Ti–Cl(2′)	168.9(1)
N(2)–Ti–Cl(2′)	90.7(1)	N(3)–Ti–Cl(2′)	87.4(1)
Cl(1)–Ti–Cl(2′)	84.20(3)	Cl(2)–Ti–Cl(2′)	76.4(1)
Ti–Cl(2)–Ti′	103.62(3)	Ti–N(2)–C(15)	113.7(1)
Ti–N(2)–C(16)	108.1(1)	Ti–N(2)–C(13)	110.6(1)
Ti–N(3)–C(17)	112.5(2)	Ti–N(3)–C(18)	118.7(2)
Ti–N(3)–C(14)	101.9(2)	C(1)–C(2)–C(7)	122.7(2)
C(7)–C(2)–C(3)	118.9(2)		

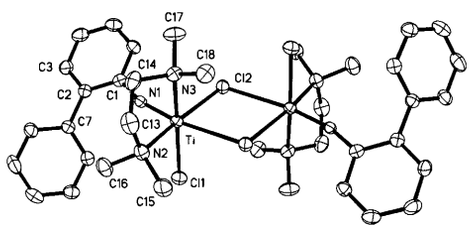


Fig. 6 Molecular structure of complex **7**; details as in Fig. 1.

In $CDCl_3$ solution the ^{1}H NMR spectrum of complex **7** suggests one species is present but over the time taken to accumulate the ^{13}C-{^{1}H} NMR spectrum a second species is evident, there being double the expected number of carbon resonances. This was not observed in the spectrum of 2-*tert*-butylimido complex **6** and probably results from the dimeric form observed in the solid state converting into a monomer when the 2-phenylimido ligand is present.

Catalysis

Some preliminary results of olefin polymerisations are reported which demonstrate the ability of the imido-*cis*-dichloro system to act in catalysis. The solid state structures of [$TiCl_2(NCMe_3)$-(tmeda)] and [$TiCl_2(NC_6H_4CMe_3$-2)(tmeda)] **6** show that the Cl–Ti–Cl bond angles [93.9(1)[3] and 95.9(1)° respectively] are similar to that found in [$TiCl_2Cp_2$] [94.4(1)°[17]] which is catalytically active towards olefin polymerisation.[7] Initially we attempted to prepare [$Ti(CH_3)_2(NCMe_3)$(tmeda)] for olefin

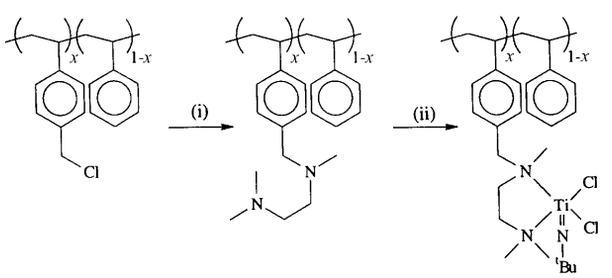
Table 7 Polymerisations with MAO co-catalyst[a]

Complex	Amount/μmol	Monomer	Al : Ti	Time/min	Yield/g	Activity[b]
$[TiCl_2(NCMe_3)(tmeda)]$	117	Ethene	137	20	0.18	3.2
1	99	Ethene	116	20	0.47	7.1
6	46	Ethene	142	10	0.17	13.0
6	64.5	Ethene	102	20	0.46	11.2
6	47	Propene	140	30	0.00	0.0
6	67.9	1-Hexene	68	30	0.14	4.1
7	12.5	Ethene	1024	20	0.09	12.7
trimedaPS–$[TiCl_2(NCMe_3]_x$	[c]	Ethene	130	30	0.01	0.1
trimedaPS–$[TiCl_4]_x$	[c]	Ethene	130	30	0.01	0.1
amPS–$[TiCl_2(NCMe_3)(tmeda)]_x$	[c]	Ethene	100	30	0.00	0.0

[a] Conditions: toluene–CH_2CH_2, 20–23 °C, ethene 1.7 bar, propene 1 bar. [b] g $mmol^{-1}$ h^{-1} bar^{-1}. [c] Estimated to be less than 100 μmol.

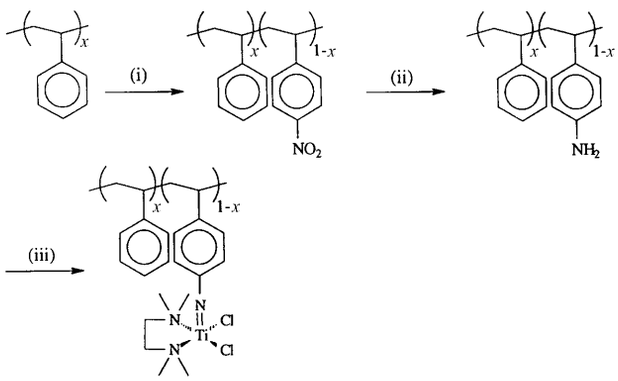
polymerisation studies with $B(C_6F_5)_3$ co-catalyst[7] but reactions of $[TiCl_2(NCMe_3)(tmeda)]$ with MeLi or MeMgI gave tars when diethyl ether solutions were warmed above −40° C. $[TiCl_2(NCMe_3)(py)_3]$[12] gave a similar result. Addition of methylaluminoxane $[(MeAlO)_n$, MAO] to $[TiCl_2(NCMe_3)(tmeda)]$ using a Ti : Al ratio of 1 : 100–150 gave much less decomposition and the mixture was found to polymerise ethylene but with very low activity[18] (3.2 g $mmol^{-1}$ h^{-1} bar^{-1}) (see Table 7) compared to $[ZrCl_2Cp_2]$ or other complexes containing cyclopentadienyl ligands where activities of up to 2000 g $mmol^{-1}$ h^{-1} atm^{-1} have been found (1 bar = 0.987 atm) when much larger Ti : Al ratios (*e.g.* 1 : 1000) are used.[7] With $[TiCl_2(NCMe_3)(NH_2CMe_3)_2]_2$ **1** the activity doubled and with $[TiCl_2(NC_6H_4CMe_3\text{-}2)(tmeda)]$ **6** a 4-fold increase in activity was found, the overall activity being comparable to the moderate activity[18] systems $[VCl_2(NC_6H_3Pr^i_2\text{-}2,6)(Tp)]$–MAO (14 g $mmol^{-1}$ h^{-1} atm^{-1})[19] and $[TaCl_2(NSiBu^t_3)(Cp^*)]$–MAO (13.8 g $mmol^{-1}$ h^{-1} atm^{-1}),[20] but much less than for $[VCl_2(NCMe_3)(Cp)]$–MAO (27 g $mmol^{-1}$ h^{-1} atm^{-1}).[21] Propene was not polymerised by complex **5**–MAO under the conditions used but a small activity was found for 1-hexene. $[TiCl_2(NC_6H_4Ph\text{-}2)(tmeda)]_2$ **7** and MAO polymerised ethylene slightly more than did complex **6**.

Heterogenisations were carried out *via* the tmeda addition and imido exchange processes already studied, using modified polystyrene resins. For the tmeda ligand a model system was produced by adding *N*-benzyl-*N*,*N*′,*N*′-trimethylethylenediamine (tbeda) to complex **1** giving $[TiCl_2(NCMe_3)(tbeda)]$ which showed a single set of resonances for the tbeda and imido ligands in the ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra. *N*,*N*,*N*′,*N*′-(trimethylmethylene)ethylenediamine functionalised crosslinked polystyrene was prepared and treated with complex **1** (Scheme 1). $TiCl_4$ was also supported in this way. For the imido



Scheme 1 (i) $LiNMeCH_2CH_2NMe_2$, thf; (ii) $[TiCl(\mu\text{-}Cl)(NCMe_3)(NH_2CMe_3)_2]_2$, benzene.

attachment NH_2-functionalised crosslinked polystyrene was prepared and an imido exchange reaction carried out with $[TiCl_2(NCMe_3)(tmeda)]$ (Scheme 2). Preliminary studies of the ethylene polymerisation capability of these solids in the presence of MAO, using similar conditions to those of the homogeneous equivalents, show there is little or no activity. This result compares with the increase in activity observed



Scheme 2 (i) HNO_3, AcOH; (ii) $SnCl_2{\cdot}2H_2O$, EtOH; (iii) $[TiCl_2(NCMe_3)(tmeda)]$, toluene.

when $[VCl_2(imido)(Cp)]$ is supported in a similar manner on uncrosslinked polystyrene.[21,22] Other studies have shown that polystyrene supported catalysts may lose activity in comparison to their unsupported counterparts due to the active center becoming unavailable in the matrix.[23]

Conclusion

The results of this work show that when the solid state product of a reaction between $TiCl_4$ and *tert*-butylamine is a chloro-bridged dimer with terminal imido ligands solution dynamics occur to give other species. Tris-pyridine phenylimido complexes formed by imido exchange lose a pyridine ligand on crystallisation giving 6-co-ordinate chloro-bridged dimers in which imido ligand C–N bond rotation may be impeded when the substituent is 2-*tert*-butyl or 2-phenyl but not 2-methyl. With the tmeda ligand present a monomeric 5-co-ordinate complex forms when the substituent is 2-*tert*-butyl and imido ligand C–N bond rotation appears not to be impeded. When the substituent is 2-phenyl a six-co-ordinate dimer forms which shows solution dynamics. The *cis*-dichloro ligands in the monomer or dimer lead to systems that are catalytically active, polymerising ethylene in the presence of MAO with an activity to the low end of that recognised as moderate but similar to that found for some other imido complexes. Heterogenisation on crosslinked polystyrene achieved by functionalising with the tmeda equivalent or by imido exchange gives rise to loss of ethylene polymerisation activity in the presence of MAO, compared to an increase observed when vanadium imido complexes are immobilised on uncrosslinked linear NH_2-functionalised polystyrene.

Experimental

Syntheses

All preparations and manipulations were carried out under dry

oxygen-free nitrogen using standard bench-top techniques for air-sensitive substances. Light petroleum (bp 40–60 °C), hexane, benzene, toluene and diethyl ether were distilled from sodium wire–benzophenone and dichloromethane and pyridine from freshly ground CaH_2. Solid amines were used as received and liquid amines dried over and distilled from freshly ground CaH_2. MAO was prepared in toluene with a modification of a literature procedure[24] using a 1:1.6 ratio of $AlMe_3$ to water. Polymer grade ethylene, propylene and 1-hexene were used as received. Literature procedures were used to prepare $[TiCl_2(NCMe_3)(NH_2CMe_3)]_x$,[1] $[TiCl_2(NCMe_3)(tmeda)]$,[1,3] $[TiCl_2(NCMe_3)(py)_3]$[12] and nitro-functionalised polystyrene.[25] ^1H and ^{13}C-{^1H} NMR spectra were recorded at 400 and 100 MHz respectively on a Bruker AM400 spectrometer (b = broad, bs = broad singlet, bt = broadened triplet, d = doublet, dd = doublet of doublets, m = multiplet, obsc = obscured, s = singlet, sept = septet, t = triplet, td = triplet of doublets). $CDCl_3$ was dried over, and distilled from, freshly ground CaH_2. C, H and N analyses were determined by Dr A. Cunninghame and associates, University of Otago, New Zealand.

Preparations

$[TiCl_2(NCMe_3)(NH_2CMe_3)_2]_2$ 1. A rapidly stirred solution of $TiCl_4$ (5.2 g, 27.4 mmol) in hexane (100 cm^3) was cooled to 0 °C and *tert*-butylamine (20 cm^3, 190 mmol) added dropwise. The mixture was stirred for 4 h, filtered through Celite which was washed with hexane (20 cm^3) and the volume reduced. On standing at −20 °C for several h large orange crystals were formed which were dried *in vacuo*. Yield 6.7 g (70%). Analytical data show that the material corresponds closely to the bis-amine complex [Found: C, 41.8; H, 9.4; N, 12.5. $C_{12}H_{31}Cl_2N_3Ti$ requires C, 42.9; H, 9.3; N. 12.5%]. ^1H NMR: δ 1.00 (s, Me), 1.15 (s, Me), 1.37 (bs, Me), 1.50 (s, Me), 1.58 (s, Me), 2.69 (s, NH), 3.40 (s, NH), 4.25 (s, NH), 4.56 (s, NH) and 8.20 (bs, NH). ^{13}C-{^1H} NMR: δ 28.2 (CMe_3), 30.4 (CMe_3), 30.7 (CMe_3), 31.0 (CMe_3), 31.2 (CMe_3), 31.4 (CMe_3), 31.5 (CMe_3), 51.8 (C), 52.2 (C), 52.6 (C), 72.2 (C) and 73.9 (C).

$[TiCl_2(NC_6H_3Pr^i_2\text{-}2,6)(NH_2CMe_3)_2]_x$ 2. 2,6-Diisopropylaniline (2.8 g, 15.8 mmol) was added to a solution of complex **1** (5.4 g. 8.03 mmol) in toluene (30 cm^3) and the mixture stood for 3 h and then refluxed for 14 h. The solution was cooled to −20 °C and the solid filtered off, washed with hexane (5 cm^3) and dried *in vacuo* giving the complex as a yellow powder. Yield 1.8 g (51%).The analytical sample was obtained by recrystallisation from hexane [Found: C, 54.8; H, 9.3; N, 9.6. $C_{20}H_{39}Cl_2N_3Ti$ requires C, 54.6; H, 8.9; N, 9.5%]. ^1H NMR: δ 1.24 [d, ^3J(HH) 6.9, 12 H, $CHMe_2$], 1.41 (s, 18 H, CMe_3), 3.65 (bs, 4 H, NH_2), 4.44 [sept, ^3J(HH) 6.9, 2 H, CH], 6.81 [t, ^3J(HH) 7.0, 1 H, *p*-H] and 6.90 [d, ^3J(HH) 7.0 Hz, 2 H, *m*-H]. ^{13}C-{^1H} NMR: δ 24.1 ($CHMe_2$), 27.1 (CH), 31.3 (CMe_3), 53.0 (C), 122.9 (CH), 123.5 (CH), 144.8 (*o*-C) and 157.5 (*ipso*-C).

$[TiCl_2(NC_6H_3Pr^i_2\text{-}2,6)(py)_3]$. Complex **2** (*ca*. 0.03 g, 0.07 mmol) and pyridine (*ca*. 0.05 g, 0.6 mmol) were dissolved in $CDCl_3$ (*ca*. 0.5 cm^3) and the mixture transferred to an NMR tube. The NMR spectra were identical to those reported.[13]

$[TiCl_2(NC_6H_3Pr^i_2\text{-}2,6)(tmeda)]$. Complex **2** (*ca*. 0.03 g, 0.07 mmol) and tmeda (*ca*. 0.05 g, 0.4 mmol) were dissolved in $CDCl_3$ (*ca*. 0.5 cm^3) and the mixture transferred to an NMR tube. ^1H NMR: δ 1.14 [d, ^3J(HH) 6.7, 12 H, $CHMe_2$], 2.21 (s, 12 H, Me), 2.36 (s, 4 H, CH_2), 5.13 [sept, ^3J(HH) 6.7 Hz, CH] and 6.82 (m, 3 H, *m* and *p*-H). ^{13}C-{^1H} NMR: δ 24.5 ($CHMe_2$), 25.9 (CH), 45.6 (CH_3), 57.3 (CH_2), 122.3 (*p*-C), 126.1 (*m*-C), 147.4 (*ortho*-C) and 157.5 (*ipso*-C).

$[TiCl_2(NC_6H_4Me\text{-}2)(py)_2]_2$ 3. *tert*-Butyl-*N*-trimethylsilylamine (4.33 g, 29.8 mmol) in CH_2Cl_2 (15 cm^3) was added to $TiCl_4$ (2.83 g, 14.9 mmol) in hexane (35 cm^3) at 0 °C and the mixture stirred for 14 h and refluxed for 2 h. *o*-Toluidine (1.5 g, 14.0 mmol) was added, the mixture stirred for 1 h, pyridine (5.5 cm^3, 68.3 mmol) added and the mixture stirred for 48 h. The solution was filtered through Celite and concentrated whereupon crystals of the tris-pyridine complex were deposited which were washed with CH_2Cl_2 (7 cm^3) and hexane (15 cm^3) and dried *in vacuo* to give a green-brown powder. Yield 4.8 g (70%). This complex was characterised by NMR spectroscopy. ^1H NMR: δ 2.36 (s, 3 H, Me), 6.65 [td, ^3J(HH) 7.4, ^4J(HH) 1.1, 1 H, *p*-H(imido)], 6.87 [m, 2 H, *m*-H(imido)], 7.18 [d, ^3J(HH) 7.4, 1 H, *o*-H(imido)], 7.18 [obsc, 2 H, *m*-H(py)], 7.29 [t, ^3J(HH) 6.9, 4 H, *m*-H(py)], 7.64 [bt, 1 H, *p*-H(py)], 7.77 [t, ^3J(HH) 7.6, 2 H, *p*-H(py)], 8.76 (b, 2 H, *o*-H(py)] and 9.08 [d, ^3J(HH) 7.6 Hz, 4 H, *o*-H(py)]. ^{13}C-{^1H} NMR: δ 18.2 (Me), 121.6 [*p*-CH(imido)], 123.4 [*o*-CH(imido)], 123.9 [*m*-CH(*trans*-py)], 125.3 [*m*-CH(imido)], 126.1 [*m*-CH(*cis*-py)], 129.1 [*m*-CH(imido)], 132.7 [*o*-C(imido)], 137.0 [*p*-CH(*cis*-py)], 138.5 [*p*-CH(*trans*-py)], 150.8 [*o*-CH(*cis*-py)], 151.5 [*o*-CH(*trans*-py)] and 158.5 (*ipso*-C). {Assignments made by COESY and comparison with the spectrum of $[TiCl_2(NCMe_3)(py)_3]$.} The complex was dissolved in CH_2Cl_2 and layered with hexane to give crystals of the bis-pyridine complex [Found: C, 46.3; H, 4.1; N, 9.1. $C_{34}H_{34}Cl_4N_6Ti_2{\cdot}2CH_2Cl_2$ requires C, 46.3; H, 4.1; N, 9.0%]. Two molecules of CH_2Cl_2 per dimeric unit were found in the unit cell of the crystal structure. The complex was insufficently soluble to obtain NMR spectra.

$[TiCl_2(NC_6H_4CMe_3\text{-}2)(py)_2]_2$ 4. *tert*-Butyl-*N*-trimethylsilylamine (0.63 g, 4.34 mmol) was added dropwise to $TiCl_4$ (2.83 g, 14.9 mmol) in CH_2Cl_2 (20 cm^3) at 0 °C and the mixture stirred for 14 h. 2-*tert*-Butylaniline (0.33 g, 2.21 mmol) was added and the mixture refluxed for 1 h and stirred for 14 h. The solution was filtered, the precipitate washed with CH_2Cl_2 (3 times 10 cm^3) and pyridine (*ca*. 5 cm^3) added to the combined filtrates. The solution was stirred for 14 h and an excess of hexane added giving the tris-pyridine complex as a yellow-brown powder after drying for a short period *in vacuo*. Yield 0.5 g (46%). This complex was characterised by NMR spectroscopy. ^1H NMR: δ 1.38 (s, 9 H, CMe_3), 6.73 [td, ^3J(HH) 7.4, ^4J(HH) 1.4, 1 H, *p*-H(imido)], 7.02 [m, 2 H,], 7.20 [bs, 2 H,], 7.31 [t, ^3J(HH) 6.9, 4 H, *m*-H(py)], 7.65 [bt, ^3J(HH) 6.9, 1 H, 7.77 [t, ^3J(HH) 7.6, 2 H,], 7.88 [d, ^3J(HH) 7.6, 1 H], 8.72 [b, 2 H, *o*-H(py)] and 9.10 [d, ^3J(HH) 7.6 Hz, 4 H, *o*-H(py)]. ^{13}C-{^1H} NMR: δ 30.2 (CMe_3), 35.1 (C), 122.1 [*p*-CH(imido)], 123.6 [*o*-CH(imido)], 124.0 [*m*-CH(*trans*-py)], 124.6 [*m*-CH(imido)], 125.9 [*m*-CH(*cis*-py)], 132.8 [*m*-CH(imido)], 136.7 [*p*-CH(*cis*-py)], 138.6 [*p*-CH(*trans*-py)], 140.8 [*o*-C(imido)], 150.7 [*o*-CH(*cis*-py)], 151.4 [*o*-CH(*trans*-py)] and 158.7 (*ipso*-C). (Assignments made by comparison with spectrum of complex **3**.) A solution of this complex in CH_2Cl_2 was concentrated and layered with hexane to give yellow-brown crystals of the bis-pyridine complex [Found: C, 53.0; H, 5.3; N, 9.2. $C_{40}H_{46}Cl_4N_6Ti_2{\cdot}CH_2Cl_2$ requires C, 52.8; H, 5.2; N, 9.0%]. One molecule of CH_2Cl_2 per dimeric unit was found in the unit cell of the crystal structure. ^1H NMR: δ 1.39 (s, 9 H, CMe_3), 6.79 [td, ^3J(HH) 7.6, ^4J(HH) 1.4, 1 H, *p*-H(imido)], 7.08 [m, 2 H, *m*-H(imido)], 7.24 [t, ^3J(HH) 6.4, 4 H, *m*-H(py)], 7.73 [td, ^3J(HH) 6.4, ^4J(HH) 1.5, 2 H, *p*-H(py)], 7.90 [dd, ^3J(HH) 7.6, ^4J(HH) 0.9, 1 H, *o*-H(imido)] and 9.08 [dd, ^3J(HH) 6.4, ^4J(HH) 1.5 Hz, 4 H, *o*-H(py)]. ^{13}C-{^1H} NMR: δ 30.1 (CMe_3), 35.1 (C), 122.7 [*p*-CH(imido)],124.1 [*m*-CH(py)], 125.0 [*m*-CH(imido)], 126.1 [*m*-CH(imido)], 132.5 [*o*-CH(imido)], 138.6 [*p*-CH(py)], 131.3 [*o*-C(imido)], 150.9 [*o*-CH(py)] and 159.1 (*ipso*-C). (Assignments made by COESY spectrum.)

$[TiCl_2(NC_6H_4Ph\text{-}2)(py)]_2$ 5. The complex $[TiCl_2(NCMe_3)(py)_3]$ (1.07 g, 2.5 mmol) and 2-phenylaniline (0.39 g, 2.3 mmol) were dissolved in CH_2Cl_2 (45 cm^3) and the mixture was stirred for 14 h. The solution volume was reduced and hexane (30 cm^3)

added giving the tris-pyridine complex as a yellow-brown powder after drying *in vacuo*. Yield 1.1 g (91%). This complex was characterised by NMR spectroscopy. ^{1}H NMR: δ 6.60–7.30 (m, 15 H), 7.47 [td, ^3J(HH) 7.6, ^4J(HH) 1.5, 1 H], 7.78 [d, ^3J(HH) 7.6, 2 H], 8.48 [d, ^3J(HH) 5.0, 2 H, *o*-H(py)] and 8.72 [d, ^3J(HH) 5.0 Hz, 4 H, *o*-H(py)]. ^{13}C-{^{1}H} NMR: δ 115.1 (CH), 117.9 (CH), 121.1 (CH), 123.2 [*m*-CH(*trans*-py)], 126.0 [*m*-CH(*cis*-py)], 128.0 (CH), 128.3 (CH), 128.6 (CH), 129.9 (CH), 135.5 [*p*-CH(*cis*-py)], 137.7 [*p*-CH(*trans*-py)], 139.2 (C), 143.4 (C), 149.4 [*o*-CH(*cis*-py)], 151.3 [*o*-CH(*trans*-py)] and 156.3 (*ipso*-C). A solution of this complex in CH_2Cl_2 was concentrated and layered with hexane to give yellow-brown crystals of the bis-pyridine complex [Found: C, 58.3; H, 4.5; N, 9.1. $C_{22}H_{19}Cl_2N_3Ti$, requires C, 59.4; H, 4.3; N, 9.5%]. The complex was insufficiently soluble to obtain NMR spectra.

[TiCl$_2$(NC$_6$H$_4$CMe$_3$-2)(tmeda)] 6. *Procedure A. tert*-Butylamine (4.5 cm^3, 42.8 mmol) was added dropwise to $TiCl_4$ (1.0 g, 5.1 mmol) in benzene (40 cm^3) and the mixture stirred for 8 h after which 2-*tert*-butylaniline (0.77 g, 5.16 mmol) was added and the mixture refluxed for 1.5 h. After cooling to room temperature tmeda (0.59 g, 5.08 mmol) was added and the mixture stirred for 14 h. The solution was filtered, the volume reduced, hexane (50 cm^3) added and the solution cooled to −20 °C overnight giving brown crystals which were washed with cold hexane and dried *in vacuo*. Yield 1.3 g (67%) [Found: C, 48.8; H, 8.2; N, 10.7. $C_{16}H_{29}Cl_2N_3Ti$ requires C, 50.2; H, 7.7; N, 11.0%]. ^{1}H NMR: δ 1.59 (s, 9 H, CMe_3), 2.89 (s, 12 H, Me), 3.15 (s, 4 H, CH_2), 6.76 [td, ^3J(HH) 8.0, ^4J(HH) 1.0, 1 H, *p*-H], 6.95 [td, ^3J(HH) 7.7, ^4J(HH) 1.0, 1 H, *m*-H], 7.11 [dd, ^3J(HH) 7.7, ^4J(HH) 1.0, 1 H, *m*-H] and 7.30 [d, ^3J(HH) 7.7 Hz, 1 H, *o*-H]. ^{13}C-{^{1}H} NMR: δ 30.9 (CMe_3), 35.5 (C), 51.2 (Me), 58.8 (CH_2), 124.2 (*m*-CH), 125.6 (*m*-CH), 125.7 (*m*-CH), 129.9 (*o*-CH), 141.3 (*o*-C) and 160.8 (*ipso*-C).

Procedure B. 2-*tert*-Butylaniline (1.16 g, 7.8 mmol) was added to [TiCl$_2$(NCMe$_3$)(tmeda)] (2.46 g, 8.0 mmol) and the mixture stirred for 14 h and worked up as under procedure A. Crystals suitable for X-ray analysis were obtained by layering a CH_2Cl_2 solution with hexane and leaving to stand overnight.

[TiCl$_2$(NC$_6$H$_4$Ph-2)(tmeda)]$_2$ 7. A mixture of [TiCl$_2$(NCMe$_3$)(tmeda)] (1.17 g, 3.8 mmol) and 2-phenylaniline (0.63 g, 3.7 mmol) was dissolved in CH_2Cl_2 (30 cm^3) and stirred for 14 h. Hexane (40 cm^3) was layered on top and the solution allowed to stand for 2 d. The crystals were filtered off, one was removed for X-ray crystallography, and the remainder were washed with hexane and dried *in vacuo*. Yield 0.6 g (39%) [Found: C, 53.4; H, 6.5; N, 10.4. $C_{18}H_{25}Cl_2N_3Ti$ requires C, 53.8; H, 6.3; N, 10.5%]. ^{1}H NMR: δ 2.62 (s, 12 H, Me), 2.78 (s, 4 H, CH_2), 6.80 (m, 1 H), 6.98 [d, ^3J(HH) 7.3, 1 H], 7.15 (m, 2 H), 7.29 (m, 1 H), 7.42 (m, 2 H) and 7.60 [d, ^3J(HH) 7.4 Hz, 2 H]. ^{13}C-{^{1}H} NMR: δ 44.7 (Me), 51.2 (Me), 54.2 (CH_2), 58.4 (CH_2), 115.7 (CH), 118.7 (CH), 122.1 (CH), 126.7 (CH), 127.1 (CH), 127.6 (CH), 128.0 (CH), 128.4 (CH), 128.8 (CH), 129.1 (CH), 129.2 (CH), 130.3 (CH), 130.4 (CH),139.5 (C), 141.0 (b, C), 143.5 (CH) and 156.0 (*ipso*-C) [2C and an *ipso*-C not observed in the accumulation].

Me$_2$NCH$_2$CH$_2$NMe(CH$_2$Ph) (tbeda). *N*,*N*,*N*′-Trimethylethylenediamine (trimeda) (1.45 g, 14.2 mmol) in diethyl ether (25 cm^3) was cooled to 0 °C and n-butyllithium (7.0 cm^3, 2.15 M solution, 15.1 mmol) added dropwise. The solution was stirred overnight at room temperature, recooled to 0 °C and benzyl chloride (1.9 g, 15.0 mmol) added. After stirring for 2 d the solution was filtered through Celite and the volatiles removed to give a yellow oil which NMR spectroscopy showed to be essentially pure. Yield 1.9 g (70%). Distillation gave a colourless liquid. Yield 1.2 g (44%) ^{1}H NMR: δ 2.11 (s, 6 H, NMe_2), 2.14 (s, 3 H, NMe), 2.36 (m, 4 H, CH_2CH_2), 3.42 (s, 2 H, CH_2) and 7.16 (m, 5 H, Ph). ^{13}C-{^{1}H} NMR: δ 42.3 (NMe), 45.7 (NMe_2), 55.0 (CH_2), 57.3 (CH_2), 62.7 (CH_2), 126.7 (*p*-C), 127.9 (*m*-C), 128.9 (*o*-C) and 138.8 (*ipso*-C).

[TiCl$_2$(NCMe$_3$)(tbeda)]. tbeda (0.27 g, 1.4 mmol) in CH_2Cl_2 (20 cm^3) was added to complex **1** (0.47 g, 0.7 mmol) in CH_2Cl_2 (20 cm^3) and the mixture stirred for 14 h. The solution was filtered, the solvent removed and the yellow complex dried *in vacuo*. Yield 0.5 g (94%) [Found: C, 49.6; H, 7.7; N, 10.4. $C_{16}H_{29}Cl_2N_3Ti$ requires C, 50.3; H, 7.7; N, 11.0%]. ^{1}H NMR: δ 1.16 (s, 9 H, CMe_3), 2.22 (s, 6 H, NMe_2), 2.25 (s, 3 H, NMe), 2.47 (m, 4 H, CH_2CH_2), 3.53 (s, 2 H, CH_2) and 7.30 (m, 5 H, Ph). ^{13}C-{^{1}H} NMR: δ 30.4 (CMe_3), 42.1 (NMe), 45.5 (NMe_2), 54.8 (CH_2), 57.1 (CH_2), 62.5 (CH_2), 72.6 (C), 126.5 (*p*-C), 127.8 (*m*-C), 128.7 (*o*-C) and 138.6 (*ipso*-C).

trimeda functionalised polystyrene (trimedaPS). *N*,*N*,*N*′-Trimethylethylenediamine (0.52 g, 5.1 mmol) in THF (25 cm^3) was cooled to −40 °C and n-butyllithium (2.4 cm^3, 2.15 M solution, 5.2 mmol) added dropwise. The mixture was stirred for 1 h at room temperature, then added to chloromethylated polystyrene (2% crosslinked, 2 mequivalents Cl g^{-1}, 1.06 g, 2.12 mmol Cl) and the suspension heated at reflux for 44 h. Further trimeda (0.60 g, 5.9 mmol) was lithiated as above but in diethyl ether (20 cm^3) and hexane (20 cm^3) and the solution added to the polystyrene from the previous functionalisation and refluxed for 12 h. The solid was filtered off, washed with water, ethanol and CH_2Cl_2 and dried *in vacuo* to give pale orange beads. Yield 1.15 g [Found: C, 83.7; H, 8.6; N, 4.4%. This corresponds to more than 90% substitution of Cl by trimeda (concentration *ca.* 1.32 mmol g^{-1})].

trimedaPS-[TiCl$_2$(NCMe$_3$)]$_x$. trimedaPS [0.17 g (*ca.* 0.22 mmol trimeda)] and complex **1** (0.21 g, 0.297 mmol) were refluxed in benzene (30 cm^3) for 2 d. A further portion of complex **1** (0.4 g, 0.60 mmol) was added and the mixture refluxed for 1 d. The cooled solution was filtered and the orange-brown beads washed with CH_2Cl_2 and dried *in vacuo*.

trimedaPS-[TiCl$_4$]$_x$. trimedaPS [0.21 g (*ca.* 0.28 mmol trimeda)] was suspended in CH_2Cl_2 (20 cm^3) and $TiCl_4$ (1 cm^3, 9.1 mmol) added *via* a syringe. After refluxing the solution for 14 h the brown beads were washed with CH_2Cl_2 and dried *in vacuo*. Yield 0.27 g.

Amino functionalised polystyrene (amPS). Nitro-functionalised polystyrene (2.25 g, *ca.* 21.6 mmol, 28% NO_2) and tin(IV) chloride dihydrate (25.4 g, 113 mmol) in ethanol (40 cm^3) were refluxed for 66 h and the yellow-orange polymer beads filtered off and washed with ethanol. The beads were suspended in hydrochloric acid (8 M) for 1 h and then filtered off, washed successively with water, ethanol–water (1 : 1), ethanol, soaked in aqueous KOH (2 M) for 40 minutes and washed with aqueous KOH (1 M). The washing and soaking process was repeated and the beads were then washed with water, ethanol–water (1 : 1), ethanol and finally with CH_2Cl_2. They were dried at 130 °C and again *in vacuo*. Yield 1.95 g [Found: C, 83.0; H,6.9; N, 2.5%. This corresponds to *ca.* 71% reduction of the nitro functionality]. IR (cm^{-1}): 3450 (NH_2) and 1600 (NH_2).

amPS–[TiCl$_2$(NCMe$_3$)(tmeda)]$_x$. A solution of complex **1** (0.80 g, 1.19 mmol) and tmeda (1.08 g, 9.29 mmol) in toluene (10 cm^3) was added to amPS (0.8 g) and the heterogeneous mixture refluxed for 7 d. The dark brown polymer beads were washed with toluene followed by CH_2Cl_2, dried *in vacuo* and used in the polymerisation reaction without further characterisation.

Polymerisations

Polymerisations were performed in a 400 cm^3 flame-dried pressure bottle equipped with a head containing inlet and outlet

Table 8 Crystallographic data for complexes **1**, **3**, **4**, **5**, **6** and **7**

	1	**3**	**4**	**5**	**6**	**7**
Formula	$C_{24}H_{62}Cl_4N_6Ti_2$	$C_{34}H_{62}Cl_4N_6Ti_2$	$C_{40}H_{46}Cl_4N_6Ti_2$	$C_{44}H_{38}Cl_4N_6Ti_2$	$C_{16}H_{29}Cl_2N_3Ti$	$C_{36}H_{50}Cl_4N_6Ti_2$
M	672.4	932.1	1188.14	888.4	382.22	804.42
Crystal symmetry	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P\bar{1}$
a/Å	13.6191(2)	9.90300(9)	8.042(2)	10.1087(4)	15.1800(4)	7.7374(5)
b/Å	10.4143(2)	15.9595(2)	10.73410(10)	17.1958(6)	7.5428(2)	10.4470(7)
c/Å	14.51000(10)	13.57730(10)	16.4281(2)	12.4949(5)	17.0488(5)	12.5090(9)
a/°			77.0130(10)			75.8640(10)
b/°	117.7330(10)	101.1590(10)	77.14(10)	111.42	90.7510(10)	80.6930(10)
c/°			84.5900(10)			77.2650(10)
U/Å^3	1821.59(5)	2105.32(3)	1345.67(2)	2021.97(13)	1951.93(9)	950.15(11)
Z	2	4	2	4	4	2
μ/mm^{-1}	0.754	0.921	0.930	0.700	0.713	0.736
T/K	203(2)	203(2)	203(2)	203(2)	203(2)	203(2)
$R1$	0.0355	0.0366	0.0638	0.0612	0.0974	0.0436
$wR2$ (F^2, all data)	0.0821	0.0948	0.0616	0.0992	0.0967	0.1124
Data parameters	4027, 172	4717, 236	6103, 292	4557, 253	4337, 207	3830, 217

taps and a pressure guage. Homogeneous reactions were carried out by dissolving a weighed amount of catalyst in CH_2Cl_2 (10 cm^3) and transferring the solution to the pressure bottle. A toluene solution of MAO was added *via* a syringe, the mixture stirred for 10 minutes, the vessel flushed 3 times with ethylene or propene and the pressure then maintained at 1.7 atm. 1-Hexene was dissolved in CH_2Cl_2 (10 cm^3) and added after the 10 minute induction period. The polymerisation was quenched with acidified ethanol and the polymer washed with CH_2Cl_2 and dried *in vacuo* to constant weight. Heterogeneous reactions were carried out by suspending the polystyrene supported catalyst (0.1 g) in toluene (10 cm^3), adding a toluene solution of MAO and allowing an initiation time of 10 minutes before introducing the olefin monomer and working up as for the homogeneous reactions. The mass of polymer was obtained by subtracting the initial weight of polystyrene supported catalyst from the dry weight of the insoluble product.

Crystallography

Data were collected on a Siemens SMART diffractometer using Mo-Kα radiation ($\lambda = 0.71073$ Å). The data collection covered a nominal sphere of reciprocal space, by a combination of 4 sets of exposures. Each set had a different ϕ angle for the crystal and each exposure covered 0.3° in a. Coverage of the unique data sets was at least 98% complete to 56° in 2θ. Crystal decay was monitored by repeating the initial frames at the end of the data collection and analysing the duplicate reflections. Unit cell parameters were obtained by least-squares fit of all the data with $I > 10\sigma(I)$. Lorentz and polarisation reflections were applied and absorption corrections made by the method of Blessing.[26] The structures were solved by Patterson and Fourier techniques and refined by full-matrix least squares. All non-hydrogen atoms were allowed to assume anisotropic thermal motion. Hydrogen atoms were placed geometrically and refined with a riding model with U_{iso} constrained to 1.2 times U_{eq} of the carrier atom. Crystallographic data for the complexes are contained in Table 8. Programs used were SHELXS[27] for structure solution and SHELXL 93[28] for refinement.

CCDC reference number 186/2279.

See http://www.rsc.org/suppdata/dt/b0/b008232p/ for crystallographic files in .cif format.

References

1 A. J. Nielson, *Inorg. Chim. Acta*, 1988, **154**, 177.
2 R. T. Cowdell and G. W. A. Fowles, *J. Chem. Soc.*, 1960, 2522.
3 T. S. Lewkebandara, P. H. Sheridan, M. J. Heeg, A. P. Rheingold and C. H. Winter, *Inorg. Chem.*, 1994, **33**, 5879; C. H. Winter, P. H. Sheridan, T. S. Lewkebandara, M. J. Heeg and J. W. Proscia, *J. Am. Chem. Soc.*, 1992, **114**, 1095.
4 C. J. Carmalt, S. R. Whaley, P. S. Lall, A. H. Cowley, R. A. Jones, B. G. McBurnett and J. G. Ekerdt, *J. Chem. Soc.*, *Dalton Trans.*, 1998, 553.
5 P. Mountford, *Chem. Commun.*, 1997, 2127.
6 R. Duchateau, A. J. Williams, S. Gambarotta and M. Y. Chiang, *Inorg. Chem.*, 1991, **30**, 4863.
7 W. Kaminsky, *J. Chem. Soc.*, *Dalton Trans.*, 1998, 1413; M. Bochmann, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 255; H. H. Brintzinger, D. Fischer, R. Mulhaupt, B. Rieger and R. Waymouth, *Angew. Chem.*, *Int. Ed. Engl.*, 1995, **34**, 1143.
8 B. P. Santora, P. S. White and M. R. Gagne, *Organometallics*, 1999, **18**, 2557; B. P. Santora, A. O. Larsen and M. R. Gagne, *Organometallics*, 1998, **17**, 3138; E. S. Johnson, G. J. Balaich, P. E. Fanwick and I. P. Rothwell, *J. Am. Chem. Soc.*, 1997, **119**, 11086; M. G. Thorn, J. E. Hill, S. A. Waratuke, E. S. Johnson, P. E. Fanwick and I. P. Rothwell, *J. Am. Chem. Soc.*, 1997, **119**, 8630; E. S. Johnson, G. J. Balaich and I. P. Rothwell, *J. Am. Chem. Soc.*, 1997, **119**, 7685; G. J. Balaich, J. E. Hill, S. A. Waratuke, P. E. Fanwick and I. P. Rothwell, *Organometallics*, 1995, **14**, 656.
9 A. J. Nielson, M. W. Glenny, C. E. F. Rickard and J. M. Waters, *J. Chem. Soc.*, *Dalton Trans.*, 2000, 4569.
10 A. J. Nielson, unpublished work.
11 D. E. Wigley, *Prog. Inorg. Chem.*, 1994, **42**, 239.
12 P. E. Collier, S. C. Dunn, P. Mountford, O. V. Shishkin and D. Swallow, *J. Chem. Soc.*, *Dalton Trans.*, 1995, 3743.
13 A. J. Blake, P. E. Collier, S. C. Dunn, W.-S. Li, P. Mountford and O. V. Shishkin, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 1549.
14 F. Montilla, A. Galindo, E. Carmona, E. Gutierrez-Puebla and A. Monge, *J. Chem. Soc.*, *Dalton Trans.*, 1998, 1299.
15 S. C. Dunn, A.S. Batsanov and P. Mountford, *J. Chem. Soc.*, *Chem. Commun.*, 1994, 2007.
16 P. Barrie, T. A. Goffey, G. D. Forster and G. Hogarth, *J. Chem. Soc.*, *Dalton Trans.*, 1999, 4519; A. Bell, W. Clegg. P. W. Dyer, M. R. J. Elsegood, V. C. Gibson and E. L Marshall, *J. Chem. Soc.*, *Dalton Trans.*, 1994, 2247.
17 A. Clearfield, D. K. Warner, C. H. Saldarriaga-Molina, R. Ropal and I. Bernal, *Can. J. Chem.*, 1975, **53**, 1622.
18 G. J. P. Britovsek. V. C. Gibson and D. F. Wass, *Angew. Chem.*, *Int. Ed.*, 1999, **38**, 429.
19 S. Scheuer, J. Fischer and J. Kress, *Organometallics*, 1995, **14**, 2627.
20 D. M. Antonelli, A. Leins and J. M. Stryker, *Organometallics*, 1997, **16**, 2500.
21 M. P. Coles and V. C. Gibson, *Polym. Bull.*, 1994, **33**, 529.
22 M. C. W. Chan, K. C. Chew, C. I. Dalby, V. C. Gibson, A. Kohlmann, I. R. Little and W. Reed, *J. Chem. Soc.*, *Dalton Trans.*, 1998, 1673.
23 Q. H. Fan, C. Y. Ren, C. H. Yeung, W. H. Hu and A. S. C. Chan, *J. Am. Chem. Soc.*, 1999, **121**, 7407; D. C. Sherrington. *Chem. Commun.*, 1998, 2275; A. Akela and D. C. Sherrington, *Chem. Rev.*, 1981, **81**, 557.
24 E. G. M. Tornqvist and H. C. Welborn, Jr., *Eur. Pat.*, 208 561, 1987.
25 R. B. King and E. M. Sweet, *J. Org. Chem.*, 1979, **44**, 389.
26 R. H. Blessing, *Acta Crystallogr.*, *Sect. A*, 1995, **51**, 33.
27 G. M. Sheldrick, SHELXS, Institut für Anorganische Chemie, Universität Göttingen, 1990.
28 G. M. Sheldrick, SHELXL 93, Institut für Anorganische Chemie, Universität Göttingen, 1993.