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Synthesis and catalytic activity of binuclear titanium imido complexes

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Treatment of the N–P ligand Ar^{P}N(SiMe$_3$)$_2$ with TiCl$_4$ affords the imido-bridged binuclear titanium complex [TiCl$_2$(THF)(μ-NAr^P)]$_2$ (Ar^P = *m*-C$_6$H$_4$PR$_2$) which reacts with Ni(0) or Pd(II) to give heterotrinuclear compounds, while activation with methylaluminoxane generates a new type of imido-based ethene polymerisation catalyst that is tolerant of –PR$_2$ functional groups.

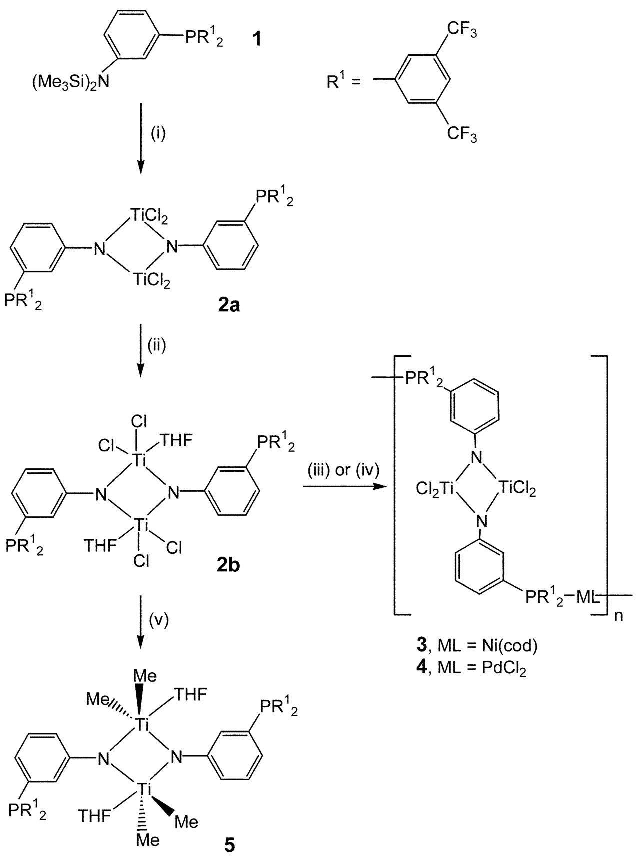
The synthesis of soluble alkene polymerisation catalysts based on non-metallocene ligand frameworks continues to attract considerable attention.[1,2] Numerous structural motifs are known, most commonly employing N,N and N,O chelate ligands, such as diamides (N–N)$^{2-}$ and iminophenoxides (O–N)$^-$. Notable examples are octahedral titanium and zirconium bis(phenoxyimine) complexes of the type (O–N)$_2$-MCl$_2$.[3] We have been interested in the possiblity of generating catalysts based on binuclear complexes and have recently reported an asymmetric example, (N–O)TiCl(μ-Cl)$_3$TiCl$_3$.[4] We report here the synthesis and reactivity of binuclear imido-bridged compounds of the type [TiCl$_2$(μ-NAr)$_2$]$_2$.

The phosphinoaryl amine ligand **1** was readily prepared from *m*-ClMgC$_6$H$_4$N(SiMe$_3$)$_2$ and R$^1_2$PCl in 85% yield [R^1 = 3,5-(CF$_3$)$_2$C$_6$H$_3$]. The ligand was chosen to explore the possibility of forming early–late transition metal heteronuclear complexes by selective coordination to the N and/or P donor. Ligand **1** reacts with TiCl$_4$ in dichloromethane at −78 °C under dehalosilylation to give the imido complex **2a** as a deep red microcrystalline solid. Recrystallising **2a** from THF or conducting the reaction in THF instead of CH$_2$Cl$_2$ affords the bis-THF complex **2b**, which is more soluble in organic solvents (Scheme 1).†

The reaction of **2b** with Ni(cod)$_2$ or PdCl$_2$(cod) (cod = 1,5-cyclooctadiene) afforded the corresponding heteronuclear complexes **2a**·Ni(cod) (**3**) and **2b**·PdCl$_2$ (**4**), respectively, as microcrystalline solids. The compounds were identified on the basis of their elemental analyses but proved insoluble in dichloromethane and are evidently coordination polymers.

Unfortunately attempts to grow crystals of **2**–**4** suitable for X-ray diffraction proved unsuccessful. The spectrocopic parameters of **2** did not allow us to distinguish unequivocally between a mononuclear structure of the type RN=TiCl$_2$(L),[5] or a dimeric chloro- or imido-bridged alternative. However, alkylation of **2b** with methyllithium in diethyl ether at 0 °C afforded the corresponding titanium dimethyl complex **5** as red crystals.

The X-ray structure of **5** (Fig. 1) confirms the binuclear structure, with a core Ti$_2$N$_2$ four-membered ring.‡ The formation of a cyclic structure is in contrast to the formation of the mononuclear imido compound Ti(NBu^t)Cl$_2$(py)$_3$ or the exclusively chloride-bridged [TiCl$_2$(NBu^t)(H$_2$NBu^t)]$_4$, both products of the reaction of TiCl$_4$ with Bu^{t}N(H)SiMe$_3$.[6,7] It is also noted that the the phosphinoaniline *m*-Ph$_2$PC$_6$H$_4$N(H)SiMe$_3$ has been reported to react with TiCl$_4$ to afford an amido complex, TiCl[N(SiMe$_3$)C$_6$H$_4$PPh$_2$]$_3$.[8] Each titanium atom in **5** occupies the centre of a trigonal bipyramid, with one imido-N *trans* to the THF ligand, while the other N atom occupies an equatorial position. The Ti–N distances within the ring are almost



Scheme 1 *Reagents and conditions*: (i), TiCl$_4$, CH$_2$Cl$_2$, −78 °C to room temperature; (ii), THF; (iii), Ni(cod)$_2$, dichloromethane, 16 h, 23 °C; (iv) PdCl$_2$(cod), dichloromethane, 16 h, 23 °C; (v) MeLi, Et$_2$O, 0 °C to room temperature, 5 h.

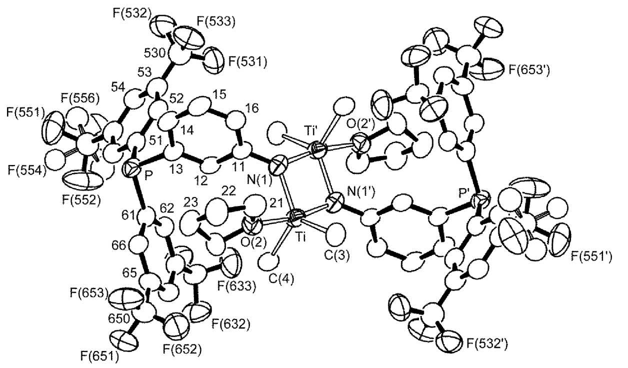


Fig. 1 Structure of compound **5**, showing the atomic numbering scheme. Ellipsoids are drawn at 50% probability. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ti–C(3) 2.147(7), Ti–C(4) 2.125(8), Ti–N(1) 1.971(6), Ti–N(1′) 1.921(6), Ti–O(2) 2.188(5); N(1)–Ti–N(1′) 83.4(2), Ti–N(1)–Ti′ 96.6(2), C(3)–Ti–N(1) 122.3(3), C(4)–Ti–N(1) 120.0(3), C(3)–Ti–C(4) 117.2(3), N(1′)–Ti–O(2) 169.1(2), N(1)–Ti–O(2) 87.8(2), C(3)–Ti–N(1′) 92.6(3), C(4)–Ti–N(1′) 101.8(3).

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Table 1 Ethene polymerisations with titanium imido complexes[a]

Complex	Ti/μmol	Al/Ti ratio	Activity[b]	M_w
2b	5	1000	5.5	n.d.
2b	10	1000	4.2	n.d.
2b	20	1000	6.2	190,000
3	20	2000	4.0	n.d.[c]

[a] *Conditions:* 50 mL toluene, 20 °C, 15 min, 1 bar ethene. Reactions were terminated by methanol injection. [b] In 10^5 g-PE (mol Ti)$^{-1}$ h^{-1} bar^{-1}. [c] Insufficiently soluble for GPC analysis.

identical, 1.971(6) and 1.921(6) Å, slightly longer than the Ti–N distances of 1.904(2) and 1.916(2) Å in the structurally related mono-Cp complex $[Cp^RTi(Cl)(\mu\text{-}NBu^t)]_2$ $[Cp^R = C_5H_4B(C_6F_5)_2(H_2NBu^t)]$.[9] The $TiC_2N(1)$ moiety deviates little from planarity (angle sum 359.5°). The Ti–C bond lengths are slightly longer than those found in $TiMe_4(THF)$ (average 2.096 Å).[10] The Ti–O(THF) bond in **5** of 2.188(5) is 0.2 Å shorter than in $TiMe_4(THF)$ but longer than in $[Cp^*_2TiMe(THF)]^+$ (2.154(6) Å).[11]

On activation with methylaluminoxane (MAO), complex **2b** catalyses the polymerisation of ethene under mild conditions (Table 1). Within the test range productivities are independent of [Ti], and hence not mass-transport limited. In some cases high molecular weight polyethene was obtained which proved to be insufficiently soluble for gel permeation chromatography at 160 °C. Very similar productivities were obtained with the heterobinuclear complex **3**, *i.e.* the catalysts are unaffected by the presence of complexed or uncomplexed diarylphosphine substituents.[12]

The results show that titanium imido complexes constitute a new type of readily accessible and comparatively robust polymerisation catalysts. The formation of well-defined alkyls suggests that the Ti_2N_2 framework is likely to be unaffected by activators such as MAO under polymerisation conditions, and high molecular weight polymers are obtained without the need for sterically highly hindered or specifically tailored ligand environments. Studies exploring this versatile class of catalysts in more detail are in progress.

Acknowledgements

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Notes and references

† Synthesis and spectroscopic data: **1**: To a 1.0 M THF solution of 3-*N*,*N*-bis(trimethylsilyl)amino)phenylmagnesium chloride (23.75 mL) was added bis-[(3,5-bis(trifluoromethyl)phenyl] chlorophosphine (11.7 g, 23.75 mmol) *via* a syringe at ambient temperature. After 1 h of stirring, volatiles were removed *in vacuo* and the residue extracted with diethyl ether (70 mL). The filtrate was concentrated and light petroleum (30 mL) was added. Cooling to −20 °C gave solid **1**, yield 14 g (85%). ^{1}H NMR (300.13 MHz, C_6D_6): δ −0.031 (s, $SiMe_3$), 7.05–7.85 (Ph). $^{13}C\{^1H\}$ NMR (75.46 MHz, C_6D_6): δ 1.95 (s, $SiMe_3$), 123.36–150.30 (Ph + CF_3). ^{31}P NMR (121.49 MHz, C_6D_6): δ −4.45. Anal.: Found (calcd.): C, 48.57 (48.48); H, 4.15 (4.07); N, 2.17 (2.02).

2a: To a cold (−78 °C) solution of **1** (2.20 g, 3.17 mmol) in dichloromethane (20 mL) was added dropwise $TiCl_4$ with continued stirring. Product **2a** precipitated as a deep red solid which was collected by filtration and dried *in vacuo*, yield 1.50 g (71%). ^{1}H NMR (300.13 MHz, THF-d_8): δ 6.66–8.07 (Ph). $^{13}C\{^1H\}$ NMR (75.46 MHz, CD_2Cl_2): δ 120.00–162.37 (Ph + CF_3). ^{31}P NMR (121.49 MHz, THF-d_8): δ 1.39. Anal.: Found (calcd.): C, 39.42 (39.67); H, 1.47 (1.51); N, 2.05 (2.10); Cl, 10.92 (10.65). **2b**: Recrystallisation of **2a** from THF or conducting the reaction in THF instead of CH_2Cl_2 led to the formation of **2b** which is more soluble in aromatic solvents. Anal.: Found (calcd.): C, 42.95 (42.30); H, 3.09 (2.46); N, 1.86 (1.90); Cl, 10.15 (9.61).

3: A mixture of **2b** (1.0 g, 0.65 mmol) and $Ni(cod)_2$ (0.18 g, 0.65 mmol) was stirred in dichloromethane (30 mL) overnight at room temperature. The resulting precipitate was collected on a sintered glass funnel, washed with dichloromethane (5 mL) and dried *in vacuo*, yield 0.55 g (57%). Anal.: Found (calcd.): C, 41.47 (41.66); H, 2.62 (2.16); N, 1.97 (1.87); Cl, 10.19 (9.47).

4: Following the procedure for **3**, a solution of **2b** (0.4 g, 0.27 mmol), was treated with $PdCl_2(cod)$ (0.08 g, 0.27 mmol) to give a deep red precipitate, yield 0.3 g (67%). Anal.: Found (calcd.): C, 38.45 (37.77); H, 2.88 (2.19); N, 1.56 (1.69); Cl, 12.57 (12.86).

5: To a cold solution (0 °C) of **2b** (1.02 g, 0.69 mmol) in Et_2O was added dropwise MeLi (2.76 mmol, 1.6 M in Et_2O). When the addition was complete, the solution was allowed to warm to room temperature and stirred for 5 h. The filtrate was concentrated to one third and light petroleum (5 mL, bp 40–60 °C) was added. Cooling to −20 °C yielded red crystals, 0.55 g (57%), some of which were suitable for crystallography. Anal.: Found (calcd.): C, 48.58 (48.23); H, 3.59 (3.47); N, 2.30 (2.01). ^{1}H NMR (300.13 MHz, CD_2Cl_2): δ 0.84 (s, TiMe), 1.73 (br, THF), 3.68 (br, THF), 6.23–8.22 (Ph). $^{13}C\{^1H\}$ NMR (75.46 MHz, CD_2Cl_2): δ 27.63 (s, TiMe), 123.52–143.60 (Ph, CF_3). ^{31}P NMR (121.49 MHz, THF-d_8): δ −0.50.

‡ *Crystal data* for **5**: $C_{56}H_{48}F_{24}N_2O_2P_2Ti_2$, M = 1394.7. Triclinic, space group $P\bar{1}$ (no. 2), a = 9.572(4), b = 9.754(10), c = 16.736(14) Å, α = 77.03(7), β = 86.91(2), γ = 87.63(1)°, V = 1520(2) Å^3. Z = 1, D_c = 1.524 g cm^{-3}, $F(000)$ = 704, T = 140(1) K, μ(Mo-Kα) = 4.3 cm^{-1}, λ(Mo-Kα) = 0.71069 Å, 7860 reflections measured, 4957 unique (R_{int} = 0.144), F^2 refinement, R_1 = 0.119 ($I > 2\sigma(I)$), wR_2 = 0.301 (all data). Crystals were not single. For the sample measured (Rigaku MSC R-Axis IIc image plate diffractometer), data for the major crystal were selected, and diffraction from the seondary crystal(s) were ignored. Also, there was site disorder in one of the CF_3 groups. CCDC reference number 225816. See http://www.rsc.org/suppdata/dt/b3/b315711c/ for crystallographic data in CIF or other electronic format.

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