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Titanium complexes incorporating bicyclic guanidinate ligands. Structure of a novel titanium–aluminium complex

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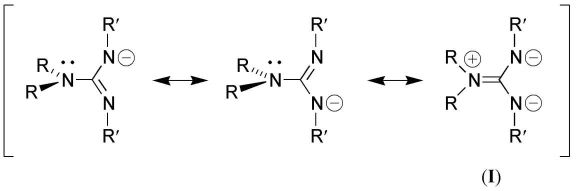
Synthetic routes to titanium complexes incorporating the bicyclic guanidinate, 1,3,4,6,7,8-hexahydro-2*H*-pyrimido-[1,2-*a*]pyrimidinate, [hpp]$^-$, are described; the first example of a chelating coordination mode for the [hpp]$^-$ anion and the trimetallic complex [$Me_2Al(hpp)_2TiCl_2{\cdot}AlMe_3$] containing [hpp]$^-$ ligands that chelate to titanium and, in addition, bridge to an $AlMe_2$ unit *via* nitrogen are reported.

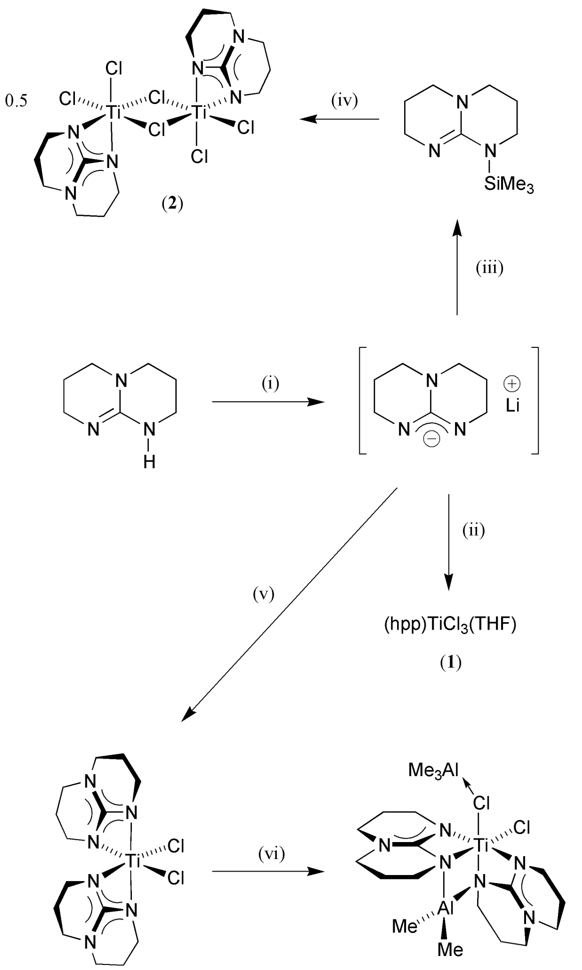
The search for new ancillary ligand sets to replace the bis-cyclopentadienyl framework in Group 4, α-olefin polymerisation procatalysts is an area of intense study.[1] Within this context, the amidinate ligands [$PhC(NSiMe_3)_2$]$^-$ and [RC-(NR′)$_2$]$^-$ have previously received attention.[2,3] Replacement of the carbon substituent with an amide group affords the related guanidinate anions [$R_2NC(NR')_2$]$^-$ which have successfully been used as ligands in main group,[4] transition metal,[5] and lanthanide chemistry.[6] Delocalisation of the lone pair from the non-coordinated nitrogen into the π-system generates an additional resonance structure [$R_2N^{(+)}{=}C(NR')^{(-)}{}_2$] (**I**, Scheme 1), not possible in amidinate ligands, able to contribute to the stabilisation of electron deficient metal centres through enhanced electron donation.[4a,5i] We anticipated that the guanidinate ligand derived from 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine (hpp-H) would promote contribution from resonance form **I** by constraining the R_2N and NCN components into a coplanar conformation, affording the correct orbital alignment for delocalisation throughout the CN_3 core of the ligand. We therefore initiated a study of the [hpp]$^-$ anion as a suitable ligand for early transition metals, focusing on Group 4 complexes as potential α-olefin polymerisation procatalysts.



Scheme 1 Principal resonance structures for the guanidinate anion [$R_2NC(NR')_2$]$^-$.

Accordingly, deprotonation of hpp-H with ^{n}BuLi followed by *in situ* reaction with $TiCl_4(THF)_2$ (1 equiv.) affords the red crystalline product, (hpp)$TiCl_3$(THF) (**1**, Scheme 2).† To generate the base free complex, hpp-$SiMe_3$[7] was reacted with $TiCl_4$ in CH_2Cl_2 to afford dimeric [(hpp)$TiCl_3$]$_2$ (**2**, Scheme 2).[8]† The reaction between the *in situ* generated lithium salt with 0.5 equiv. of $TiCl_4(THF)_2$ affords the bis-ligand complex (hpp)$_2$-$TiCl_2$ (**3**, Scheme 2).†

NMR data for **3** are consistent with the base-free complex and the mass spectrum shows a molecular ion peak at *m*/*z* 394 (36%) corresponding to monomeric (hpp)$_2TiCl_2$. It has been previously shown however that the [hpp]$^-$ ligand has a propensity to bridge between metal centres due to the parallel projection of the N-donor orbitals.[4a,9] It was therefore of interest to investigate the bonding mode of the [hpp]$^-$ ligand in **3**.



Scheme 2 (i) ^{n}BuLi, 0 °C, THF; (ii) $TiCl_4(THF)_2$, THF; (iii) Me_3SiCl; (iv) $TiCl_4$, CH_2Cl_2; (v) 0.5 $TiCl_4(THF)_2$, THF; (vi) 2 $AlMe_3$, toluene.

The molecular structure of **3**, which crystallises from toluene as the mono-solvate, is presented in Fig. 1.‡ The titanium is distorted octahedral, with the main distortion imposed by the small bite angles of the [hpp]$^-$ ligands [65.04(11)° and 65.06(10)°]. Complex **3** is the first reported example of a chelating coordination mode for the [hpp]$^-$ ligand. The dihedral angle between the C(1)–N(1)–N(2)–N(3) and N(3)–C(1)–C(4)–C(5) planes is 3.8° (corresponding angle in the other ligand = 2.9°), significantly less than that observed in the acyclic guanidinate derivative {$Et_2NC(NPh)_2$}$_2TiCl_2$ (30.4°).[5i] Accordingly, the intra-ligand C–N distances [1.338(4)–1.347(4) Å] are indicative of π-delocalisation from the amide nitrogen. The remaining carbon atoms of the ligand are situated in a staggered arrangement ‘above’ [C(7), C(3) and C(13), C(9)] and

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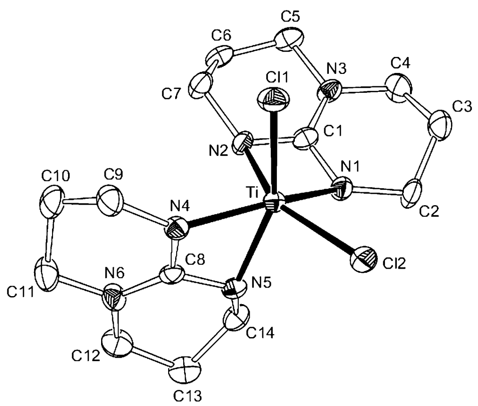
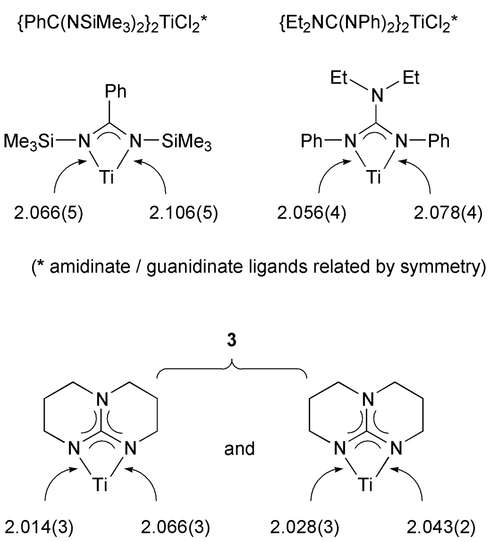


Fig. 1 Molecular structure of **3** (H-atoms omitted for clarity) with selected bond distances (Å) and angles (°); Ti–N(1) 2.014(3), Ti–N(2) 2.066(3), Ti–N(4) 2.028(3), Ti–N(5) 2.043(2), Ti–Cl(1) 2.3455(9), Ti–Cl(2) 2.3414(10), C(1)–N(1) 1.347(4), C(1)–N(2) 1.340(4), C(1)–N(3) 1.340(4), C(8)–N(4) 1.344(4), C(8)–N(5) 1.338(4), C(8)–N(6) 1.339(4); N(1)–Ti–N(2) 65.04(11), N(4)–Ti–N(5) 65.06(10).

'below' [C(2), C(6)and C(10), C(14)] the approximate C_3N_3 plane.

The Ti–N bond distances in **3** are on average shorter than those in corresponding benzamidinate and acyclic-guanidinate complexes (Scheme 3).[10,5i] This is consistent with greater electron donation from [hpp]$^-$ due to an increased contribution from the zwitterionic resonance form (**I**) (*vide supra*), although it is recognised that the reduced steric demand of the [hpp]$^-$ ligands will result in an analogous trend in bond lengths.



Scheme 3 Comparison of ligand bond lengths (Å) in {PhC-$(NSiMe_3)_2\}_2TiCl_2$,[10] $\{Et_2NC(NPh)_2\}_2TiCl_2$,[5i] and **3**.

Preliminary studies of the catalytic properties of **1**, **2** and **3** in ethylene polymerisation have been conducted. Solutions of **1** and **2** (0.03 mmol) in toluene (200 mL) in the presence of excess MAO (Al/Ti = 1000) show low[1] polymerisation activities at room temperature (7.5 bar, activity = 7.4 (**1**) and 7.1 (**2**) g mmol^{-1} h^{-1} bar^{-1}). The low activity may be due in part to the titanium procatalyst retaining THF (**1**) or adopting a dimeric structure (**2**),[8] thus hindering activation by MAO and/or approach of an incoming monomer to the active catalyst species. Surprisingly, lower activity (2.2 g mmol^{-1} h^{-1} bar^{-1}) was observed with the monomeric, base-free complex **3** under identical reaction conditions, suggesting that a facile deactivation pathway is present in these systems.

To investigate possible explanations for the observed low activity and to gain insight into the stability of the [hpp]$^-$ ligands with respect to the alkyl aluminium component of MAO, the stoichiometric reaction between **3** and $AlMe_3$ was probed. Addition of a solution of $AlMe_3$ (2 equiv.) to **3** gave an immediate colour change from red/orange to green/red. Upon work-up, pale green crystals (**4**) were isolated. The ^1H NMR spectrum indicated the presence of paramagnetic species, confirmed by the presence of an ESR signal at $g_{iso} = 1.9617$. The mass spectrum indicated a peak at *m*/*z* 180 (100%) corresponding to $[(hpp)AlMe]^+$, and the elemental analysis was consistent with the formula $\mathbf{3}\cdot Al_2Me_5$.† To ascertain the nature of complex **4**, the molecular structure was solved.‡

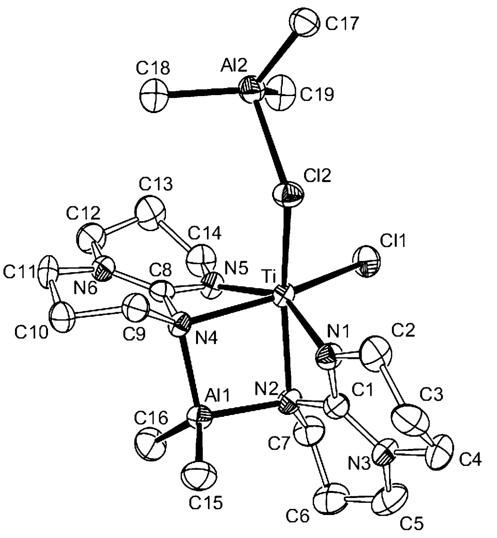


Fig. 2 Molecular structure of **4** (H-atoms omitted for clarity) with selected bond distances (Å) and angles (°); Ti–N(1) 2.069(2), Ti–N(2) 2.227(2), Ti–N(4) 2.250(3), Ti–N(5) 2.055(3), Ti–Cl(1) 2.350(1), Ti–Cl(2) 2.460(1), N(2)–Al(1) 1.957(3), N(4)–Al(1) 1.959(2), Cl(2)–Al(2) 2.382(1), C(1)–N(1) 1.326(4), C(1)–N(2) 1.379(4), C(1)–N(3) 1.339(4), C(8)–N(4) 1.389(4), C(8)–N(5) 1.328(4), C(8)–N(6) 1.320(4); N(1)–Ti–N(2) 62.34(9), N(4)–Ti–N(5) 62.22(9).

Complex **4** consists of a distorted octahedral titanium centre with two chelating [hpp]$^-$ ligands and *cis*-chlorides (Fig. 2). A single nitrogen of each [hpp]$^-$ ligand also coordinates to an $AlMe_2$ group, and the structure is completed by one equivalent of $AlMe_3$ bonded to the titanium *via* a chloride bridge.

Inspection of the bond lengths and angles in **4** indicate that a redistribution of the π-electron density has occurred. The N(1) and N(5) atoms retain a planar sp^2 hybridisation, with distances to titanium slightly longer than in **3** [2.069(2) and 2.055(3) Å, respectively]. The N(2) and N(4) atoms have however undergone rehybridisation, with corresponding increased Ti–N bond distances of 2.227(2) and 2.250(3) Å, respectively. In addition, the π-system is no longer equally distributed throughout the CN_3 core of the ligand, with C(1)–N(2) and C(8)–N(4) bond lengths [1.379(4) and 1.389(4) Å, respectively] longer than the remaining C–N distances [1.320–1.339 Å]. Complex **4** may therefore represent an intermediate in a ligand abstraction process, analogous to that proposed to occur during the polymerisation of propylene by a zirconium benzamidinate/MAO system.[11] The Ti–(μ-Cl) distance [2.460(1) Å] is slightly longer than the terminal titanium chloride distance [2.350(1) Å] consistent with bridging between titanium and aluminium.[12]

In summary, the first examples of complexes containing chelating [hpp]$^-$ ligands have been synthesised, with bond distances to titanium consistent with increased electron donation when compared with acyclic amidinates and guanidinates. Selected compounds were found to exhibit ethylene polymerisation activity upon activation with MAO, with a possible explanation for the low activity being reduction to inactive Ti(III) species. Extension of this work to include other transition metal complexes and further polymerisation studies employing metal–alkyl derivatives are in progress.

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University of North London. C. Dadswell is acknowledged for the ESR measurement and Dr D. J. Wilson and Professor F. G. N. Cloke are thanked for help with the polymerisation experiments.

Notes and references

† Preparation of **1**. A solution of hpp-H (0.50 g, 3.6 mmol) in THF was cooled to 0 °C and 1 equiv. of ^{n}BuLi (2.5 M solution in hexanes) was added. The solution was allowed to warm to room temperature and stirred for 1 h. The resulting mixture was added to a solution of $TiCl_4(THF)_2$ (1.20 g, 3.6 mmol) in THF at −78 °C. After stirring at ambient temperature for 15 h, the volatile components were removed and the product was extracted with CH_2Cl_2. Removal of the solvent afforded 1.11 g **1** (85%) as a red solid. Anal. calc. for $C_{11}H_{20}Cl_3N_3OTi$: C, 36.2; H, 5.5; N, 11.5. Found: C, 36.0; H, 5.7; N, 11.6%. NMR (C_6D_6, 298 K): ^{1}H (300.0 MHz), δ 3.75 (m, 8H, CH_2 + *THF*), 2.10 (br m, 4H, CH_2), 1.36 (br m, 4H, CH_2), 1.10 (m, 4H, *THF*); ^{13}C (75.5 MHz), δ 160.0 (CN_3), 70.3 (*THF*), 49.7 (CH_2), 45.4 (CH_2), 25.8 (*THF*), 21.7 (CH_2). Preparation of **2**. A solution of hpp-$SiMe_3$^{7} (1.43 g, 6.8 mmol) in CH_2Cl_2 was added dropwise to a solution of $TiCl_4$ (1.28 g, 6.8 mmol) in CH_2Cl_2 at room temperature. The reaction mixture was stirred for 15 h, during which time formation of a red precipitate was observed. Filtration and drying under vacuum afforded 1.22 g of **2** as a microcrystalline solid (62%). Anal. calc. for $C_7H_{12}Cl_3N_3Ti$: C, 28.8; H, 4.1; N, 14.4. Found: C, 28.7; H, 4.2; N, 14.5%. NMR (CD_2Cl_2, 298 K): ^{1}H (300.0 MHz), δ 4.04 (t, $^3J_{HH} = 5.8$, 4H, CH_2), 3.29 (t, $^3J_{HH} = 5.9$, 4H, CH_2), 1.97 (m, 4H, CH_2). ^{13}C (75.5 MHz), δ 160.3 (CN_3), 50.1 (CH_2), 46.2 (CH_2), 22.2 (CH_2). Preparation of **3**. This compound was prepared by the procedure outlined for **1**, using 1.00 g hpp-H (7.2 mmol) and 1.20 g $TiCl_4(THF)_2$ (3.6 mmol). Extraction with CH_2Cl_2 afforded 1.23 g of **3** (86%) as an orange solid. Crystals were obtained by the slow cooling of a warm (60 °C) toluene solution to 0 °C. Anal. calc. for $C_{14}H_{24}Cl_2N_6Ti$: C, 42.6; H, 6.1; N, 21.3. Found: C, 42.4; H, 6.2; N, 21.1%. NMR (C_6D_6, 298 K): ^{1}H (300.0 MHz), δ 3.86 (t, $^3J_{HH} = 5.7$, 8H, CH_2), 2.26 (t, $^3J_{HH} = 5.9$, 8H, CH_2), 1.34 (m, 8H, CH_2); ^{13}C (75.5 MHz), δ 160.2 (CN_3), 47.1 (CH_2), 45.7 (CH_2), 22.6 (CH_2). Preparation of **4**. A slurry of **3** (0.40 g, 1.0 mmol) in toluene was cooled to 0 °C, and 2 equivs. $AlMe_3$ (2.0 M solution in hexanes) were added. The mixture was allowed to warm to room temperature and stirred for 15 h. Removal of the volatiles and extraction with toluene afforded a green solution from which 0.15 g **4** (29%) precipitated. Anal. calc. for $C_{19}H_{39}Al_2Cl_2N_6Ti$: C, 43.5; H, 7.5; N, 16.0. Found: C, 43.5; H, 7.7; N, 15.8%. ESR (toluene, 298 K): $g_{iso} = 1.9617$ (width 8.3 G).

‡ Crystallographic data for **3** and **4**. **3**: $C_{14}H_{24}Cl_2N_6Ti(C_7H_8)$, $M = 487.33$, $T = 173(2)$ K, monoclinic, space group $P2_1/n$ (no. 14), $a = 12.4604(6)$, $b = 8.4351(6)$, $c = 22.9507(15)$ Å, $\beta = 104.261(4)$°, $U = 2337.9(3)$ Å^3, $Z = 4$, $D_c = 1.39$ Mg m^{-3}, μ(Mo-Kα) = 0.62 mm^{-1}, independent reflections = 3230 ($R_{int} = 0.070$), $R1$ [for 2567 reflections with $I > 2\sigma(I)$] = 0.041, $wR2$ (all data) = 0.091. **4**: $C_{19}H_{39}Al_2Cl_2N_6Ti$, $M = 524.32$, $T = 173(2)$ K, monoclinic, space group $C2/c$ (no. 15), $a = 32.1612(12)$, $b = 8.7247(6)$, $c = 22.3495(11)$ Å, $\beta = 120.135(3)$°, $U = 5423.6(5)$ Å^3, $Z = 8$, $D_c = 1.28$ Mg m^{-3}, μ(Mo-Kα) = 0.60 mm^{-1}, independent reflections = 4783 ($R_{int} = 0.060$), $R1$ [for 3406 reflections with $I > 2\sigma(I)$] = 0.046, $wR2$ (all data) = 0.106. One six membered ring is disordered with alternative positions for C(3). CCDC reference numbers 160792 and 160793. See http://www.rsc.org/suppdata/dt/b1/b102034j/ for crystallographic data in CIF or other electronic format.

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