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Titanium indenyldimethylamido complexes: synthesis, characterisation and theoretical calculations. Crystal structure of [Ti(η^5-Ind)(NMe_2)Cl_2]

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Reactions of Ti(Ind)Cl_3, **1**, with $LiNMe_2$ afforded the corresponding titanium indenyldimethylamido complexes Ti(Ind)(NMe_2)Cl_2, **2**, Ti(Ind)$(NMe_2)_2$Cl, **3**, and Ti(Ind)$(NMe_2)_3$, **4**, depending on the reaction conditions. Treatment of **2** and **3** with LiMe yielded Ti(Ind)(NMe_2)Me_2, **5**, and Ti(Ind)$(NMe_2)_2$Me, **6**, respectively. Chloride metathesis reactions of Ti(Ind)$(NMe_2)_2$Cl with Me_3SiCH_2MgCl, LiC≡CPh and LiC≡C$SiMe_3$ gave Ti(Ind)$(NMe_2)_2$(CH_2SiMe_3), **7**, Ti(Ind)$(NMe_2)_2$(C≡CPh), **8** and Ti(Ind)$(NMe_2)_2$(C≡C$SiMe_3$), **9**. The solid-state molecular structure of **2** was determined. ^1H and ^{13}C NMR data and DFT calculations (full geometry optimisations) showed that the indenyl ring remains approximately planar and exhibits an η^5 co-ordination mode in all the complexes. The amido groups have a preference for binding in the way that favours π bonding to the titanium. Even in the trisamido complex the indenyl remains η^5, π bonding to the ring being preferred to that from the amides.

Introduction

Group 4 tetrakisdialkylamido compounds have been known for a long time[1,2] and their reactions with acidic hydrogen atoms of hydrocarbons, alcohols, amines and thiols have been reported.[2,3] However, despite the fact that deprotonation of cyclopentadiene with amides has been known for 30 years, the chemistry of cyclopentadienyl-amido complexes remained unstudied until recently.

The catalytic activity of *ansa*-cyclopentadienyl-amido complexes of scandium and Group 4 metals in Ziegler–Natta olefin polymerisation[4] played a pivotal role in the increasing interest in this research area.[5] The replacement of a cyclopentadienyl moiety of a linked bis-cyclopentadienyl ligand by a 3-electron donating amido group led to complexes with higher Lewis acidity and increased reactivity towards α-olefins. The electronic and steric properties of the amido ligand in the stabilisation of an electrophilic metal centre were associated with this behaviour. As a result, studies of the synthesis, characterisation and reactivity of *ansa*-cyclopentadienyl-amido complexes have grown steadily.[6,7]

Group 4 unbridged cyclopentadienyl-amido complexes have also been reported,[8–11] and M(Ind)$(NMe_2)_3$ complexes (M = Ti or Zr; Ind = indenyl) are known, although poorly characterised. Based on the ^1H NMR spectrum, η^3 hapticity of the indenyl ligand was proposed for the titanium compound.[12]

Our study of titanium indenyl-amido complexes aims at the synthesis of several compounds and understanding of the parameters that determine both titanium–indenyl and –amido bonding modes. Owing to the unsaturated nature of the metal centre, both the indenyl ring and the amido ligands will compete for the empty metal orbitals in order to maximise π donation, as will be discussed.

Results and discussion

Chemical studies

Structures of the complexes synthesized in this study are shown in Scheme 1. Treatment of a cold (−80 °C) solution of Ti(Ind)Cl_3, **1**,[13] in toluene with 1 equivalent of $LiNMe_2$ followed by recrystallisation at −20 °C afforded orange crystals of Ti(Ind)(NMe_2)Cl_2, **2**. By a similar procedure, using 2 equivalents of $LiNMe_2$, Ti(Ind)$(NMe_2)_2$Cl, **3**, was synthesized in high yield. Both compounds may be prepared on a multigram scale and stored in the solid state under dry nitrogen at −20 °C without noticeable decomposition. In solution they tend to decompose slowly even at −30 °C. In contrast to the syntheses of **1** and **2**, the reaction of Ti(Ind)Cl_3 with 3 equivalents of $LiNMe_2$ gave a mixture of Ti(Ind)$(NMe_2)_3$, **4**, and Ti$(NMe_2)_4$ in a 3 : 1 ratio. In an effort to optimise the synthesis of **4**, we investigated the reaction of Ti$(NMe_2)_4$ with indene. The reaction was carried out in toluene at 80 °C under a continuous flow of argon to allow the dimethylamine co-product to escape through an oil bubbler. Under these conditions, Ti(Ind)$(NMe_2)_3$ was prepared in 94% yield based on Ti$(NMe_2)_4$.

Reactions of **4** with NMe_3·HCl were carried out to evaluate whether this is a suitable starting material for the synthesis of **2** and **3**. As previously reported by others[7,14,15] we found that amine elimination from titanium dialkylamido complexes is a tricky reaction. Addition of 1 equivalent of NMe_3·HCl to a toluene solution of **4** followed by reflux gave a mixture of Ti(Ind)$(NMe_2)_2$Cl and Ti(Ind)$(NMe_2)_3$ (**3** : **4** = 1 : 5) and a black residue insoluble in hydrocarbons. Under the same experimental conditions, the reaction with 2 equivalents of NMe_3·HCl led mainly to an insoluble black residue that was not further characterised.

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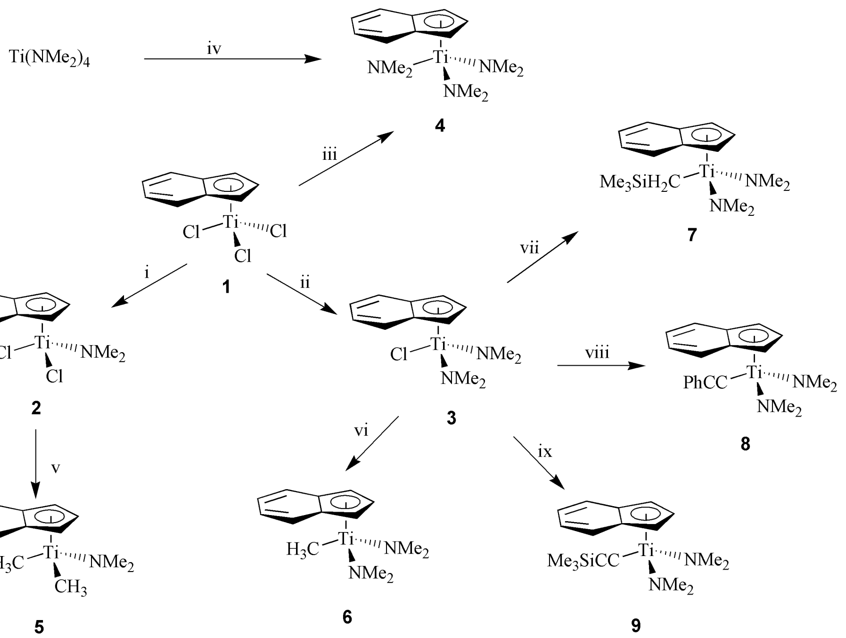
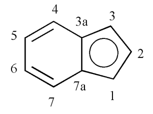


Scheme 1 Reagents and conditions: (i) $LiNMe_2$ in toluene, 1 eq., −80 °C; (ii) $LiNMe_2$ in toluene, 2 eq., −80 °C; (iii) $LiNMe_2$ in toluene, −80 °C; (iv) C_9H_8 in toluene, 120 °C; (v) $LiCH_3$ in Et_2O, 2 eq., −78 °C; (vi) $LiCH_3$ in Et_2O, 1 eq., −80 °C; (vii) Me_3SiCH_2MgCl, 1.4 eq., r.t.; (viii) LiC≡CPh, 1 eq., r.t.; (ix) $LiC{\equiv}CSiMe_3$, r.t.



The NMR spectra of complexes **2** and **3** are consistent with η^5 co-ordination of the indenyl ligands.[14,16,17] Single crystal structure determination of complex **2** (see below) also confirmed this assignment. The ^1H NMR spectrum of **4** is slightly different from those of **2** and **3**, exhibiting a deshielded H^2 resonance (δ 6.27) relative to the $H^{1,3}$ doublet (δ 6.11). For mid to late transition metal complexes a low field shift of the H^2 proton is a characteristic feature of η^3 bonded indenyl ligands and may be correlated to the degree of folding of the ligand.[18] This effect, that reflects the *meso*-pseudo allylic character of the H^2 proton, was also reported for $[Ti(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_9H_7)(N^tBu)(NC_5H_5)]$ and taken as evidence of η^3-indenyl co-ordination.[19] The inversion of $H^{1,3}$ and H^2 chemical shifts in the proton NMR spectrum of $Ti(Ind)(NMe_3)_3$, **4**, was previously attributed to the H^4H^1 (or H^7H^3) coupling and associated with an η^3 co-ordination of the indenyl ligand.[12] However, a similar inversion was found for $Ti(Ind)_2(CO)_2$, for which X-ray analysis revealed two η^5-indenyl ligands.[20] In view of the small H^2 shift, much smaller than those reported for tri-hapto indenyl ligands, and the quaternary carbons chemical shift observed for complex **4** (in the range reported for η^5-indenyl ligands[21]), we wondered about the description of the titanium–indenyl co-ordination mode and performed DFT calculations on these complexes. Our results suggest a five-co-ordinated indenyl (see below) and therefore we attribute the resonance inversion of the C_5 ring protons to anisotropy associated with non-bonding electrons of the dimethylamido ligands.

The NMR spectrum of complex **4** in d^8-toluene is invariant with temperature, from 23 to −80 °C. As previously reported for similar complexes, the equivalence of the NMe_2 ligands denotes free rotation around the titanium–nitrogen bonds[10] and is in agreement with the fluxional behaviour suggested by our theoretical studies (see below). In this family of complexes the ^1H dimethylamido resonances are progressively shifted upfield with increasing degree of halide replacement, an expected result in view of the multiple bond character of the metal–nitrogen bonds that is presumed to diminish from **2** to **4**.

The reactions of $Ti(Ind)(NMe_2)Cl_2$ and $Ti(Ind)(NMe_2)_2Cl$ with LiMe led to the synthesis of $Ti(Ind)(NMe_2)Me_2$, **5**, and $Ti(Ind)(NMe_2)_2Me$, **6**, respectively. Both compounds were isolated as orange oils and the Ti–Me bonds were characterised by the ^1H and ^{13}C resonances at δ 0.14 and 52.1 for **5** and 0.04 and 39.5 for **6**. The shifts to higher field observed for the methyl resonances of complex **6** are a consequence of the presence of two NMe_2 ligands. $Ti(Ind)(NMe_2)Me_2$ is a very unsaturated d^0 complex, formally a 14 electron compound, where agostic hydrogen bonds might be possible.[22] Although partial isotopic labelling has not been carried out to test this hypothesis,[23] we ran NMR spectra at −90 °C and observed that $J_{C\text{-}H}$ (120.68 Hz) did not change with temperature. This result is in accordance with values measured for isoelectronic titanium dimethyl compounds[24] where strong agostic bonds are also absent and may be associated with the presence of good π donor ligands that compete for the metal acceptor orbitals[25] (see discussion below).

Table 1 Selected distances (Å) and angles (°) for complex **2**

Ti(1)–C(1)	2.418(11)	Ti(1)–C(5)	2.404(11)
Ti(1)–C(2)	2.339(11)	Ti(1)–Cl(1)	2.283(3)
Ti(1)–C(3)	2.336(10)	Ti(1)–Cl(2)	2.270(4)
Ti(1)–C(4)	2.320(10)	Ti(1)–N(1)	1.864(9)
N(1)–Ti(1)–Cl(1)	103.1(3)	Ti(1)–N(1)–C(10)	109.9(7)
N(1)–Ti(1)–Cl(2)	105.6(3)	Ti(1)–N(1)–C(11)	139.9(8)
Cl(2)–Ti(1)–Cl(1)	101.75(14)	C(10)–N(1)–C(11)	110.2(10)

Chloride metathesis of $Ti(Ind)(NMe_2)_2Cl$ with Me_3SiCH_2MgCl led to synthesis of $Ti(Ind)(NMe_2)_2(CH_2SiMe_3)$, **7**, and with LiC≡CR (R = Ph or $SiMe_3$) gave $Ti(Ind)(NMe_2)_2(C{\equiv}CPh)$, **8**, and $Ti(Ind)(NMe_2)_2(C{\equiv}CSiMe_3)$, **9**. The indenyl and NMe_2 NMR resonances of **7**, **8** and **9** are similar to those of the starting material and the signals corresponding to the CH_2SiMe_3,[26] C≡CPh[27] and $C{\equiv}CSiMe_3$[28] ligands show similar chemical shifts and multiplicities to those reported for other Group 4 d^0 compounds.

Crystallography

Crystals of $Ti(Ind)(NMe_2)Cl_2$ suitable for single crystal X-ray analysis were grown by cooling a toluene solution to −20 °C. The molecular structure together with the atomic labelling is shown in Fig. 1. Selected bond lengths and angles are given in Table 1.

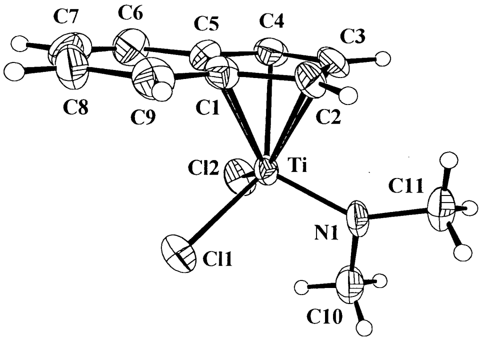


Fig. 1 Molecular structure of Ti(Ind)(NMe$_2$)Cl$_2$, **2**, with the atom numbering scheme (40% probability ellipsoids).

Ti(Ind)(NMe$_2$)Cl$_2$ is monomeric and crystallises in the orthorhombic $P2_12_12_1$ space group. In the solid state complex **2** adopts a distorted pseudo tetrahedral arrangement. The angles between the dimethylamido and the two chloride ligands are 103.1(3) (Cl(1)–Ti–N(1)) and 105.6(3)° (Cl(2)–Ti–N(1)), slightly larger than the angle between the two chloride ligands (Cl(1)–Ti–Cl(2) 101.8(1)°). This asymmetry was also reported for Ti(Ind)Cl$_3$ and Ti(Ind*)Cl$_3$,[13,16] (Ind* = C$_9$Me$_7$) but is not present in Ti(Ind)(OMe)Cl$_2$, which has a crystallographic mirror plane.[17] The indenyl ligand is typically η^5 bonded (coplanar to within *ca.* 0.03 Å) and the Ti–C bond lengths range between 2.32(1) and 2.42(1) Å, falling in three groups characteristic of this co-ordination mode.[29] The Ti–N bond length (1.864(9) Å) is comparable to others reported for titanium(IV)–amido complexes (1.871(5) and 1.879(3) Å in Ti(C$_5$H$_4$R)Cl$_2${N(H)^{t}Bu} (R = CH$_3$ or H);[11] 1.906(4), 1.924(5) and 1.972(4) Å in Ti(C$_5$H$_4$SiMe$_2$N^{t}Bu)(NMe$_2$)$_2$;[7] 1.8711(2), 1.8732(7) Å in Ti(NMe$_2$)$_2$[N(SO$_2$C$_6$H$_4$CF$_3$)CHPhCHPhN-(SO$_2$C$_6$H$_4$CF$_3$)][30]). The multiple Ti–N bond is revealed by the planar nitrogen atom and the vertical position adopted by the NMe$_2$ ligand that results in the best overlap between donor and acceptor orbitals (see below).

Molecular orbital calculations

As described above, NMR evidence is not always conclusive in determining the hapticity of indenyl ligands and theoretical calculations can be very helpful. We therefore performed DFT calculations[31] (ADF program[32]) on the four types of complexes described above, in order to optimise their geometries. We used the data from X-ray analysis available for two of the complexes and some of their Cp* analogues as a calibration of our results. Although the M–amide bond has been the subject of previous theoretical works,[33] the species studied contained the ligands in rather different environments, and bear no direct relation to the ones addressed here. The simplest model compound studied was Ti(Ind)Cl$_3$, and there are two structures known, namely Ti(η^5-C$_9$Me$_7$)Cl$_3$[16] and Ti(η^5-C$_9$H$_7$)Cl$_3$.[13] The last one is not available from the Cambridge Data Base[34] and the printed communication does not provide enough information to understand the relative orientation of the ligands. In the methyl analogue the five Ti–C distances range from 2.352 to 2.400 Å, and in Ti(η^5-C$_9$H$_7$)Cl$_3$ from 2.309 to 2.433 Å, two of them being slightly longer, in agreement with the typical co-ordination of an η^5-indenyl.[29,35] The relative orientation of the ring to the other ligands in Ti(η^5-C$_9$Me$_7$)Cl$_3$ is such that one chlorine lies under the benzene ring and there is no symmetry. In our calculations we fully optimised the geometry without any symmetry constraints. The two limiting conformations, differing by a 180° rotation of the indenyl ligand, are practically isoenergetic (Δ = 0.5 kJ mol^{-1}). We show below the structure of Ti(η^5-C$_9$Me$_7$)Cl$_3$ (left) and our model with the lowest energy (right; Ti–Cl and Ti–N distances are given in italics). The Ti–C distances vary from 2.338 to 2.517 Å, in good agreement with available structural information (the complex is not exactly the same). The experimental geometry is between our two calculated models, suggesting fluxional behaviour of the complex, a fact that is further supported by the negligible energy difference calculated.

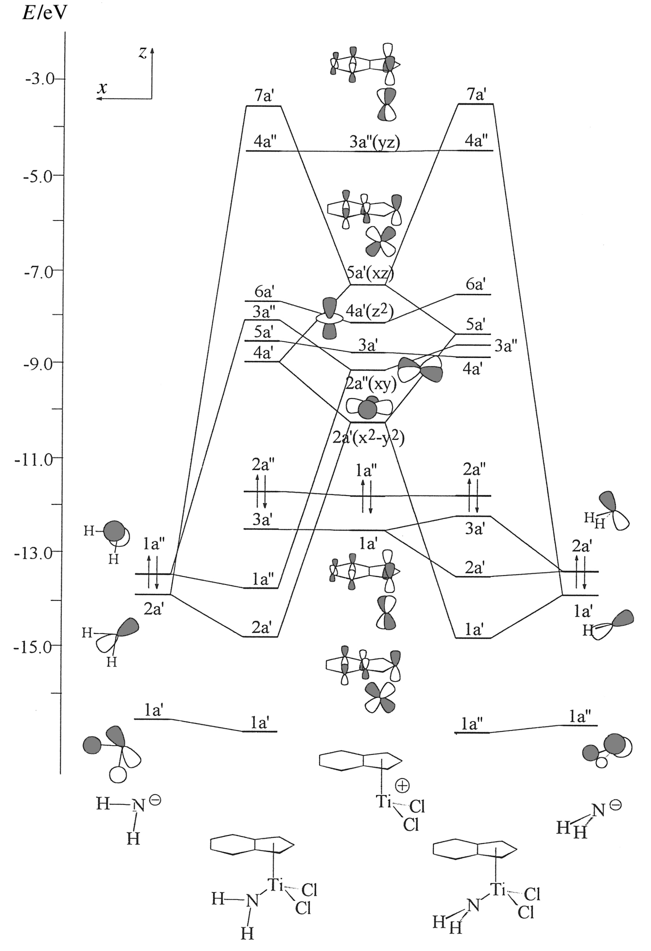
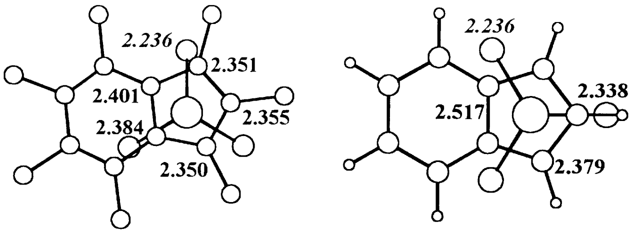


Fig. 2 Interaction diagram between Ti(η^5-Ind)Cl$_2$$^+$ and NH$_2$ perpendicular (left) or parallel (right).

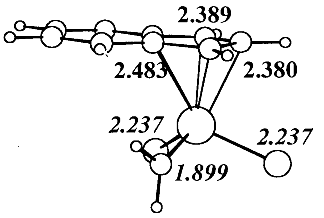


The next model complex is [Ti(η^5-Ind)Cl$_2$(NH$_2$)], NH$_2$ replacing NMe$_2$ in the calculations (crystal structure in previous section). The new ligand can orient in different ways relative to the N–Ti bond and the formation of π bonds can therefore be tuned. The arrangement found in the crystal structure will be called perpendicular and the other, obtained by rotating the H–N–H plane by 90°, parallel. The perpendicular conformation is preferred owing to the possibility of π donation from the amide to the metal in this orientation, as can be seen in a qualitative molecular orbital diagram (Fig. 2), based on extended Hückel calculations.

The π lone pair of the amide is represented by the orbital 1a″ (left, perpendicular) or 2a′ (right, parallel). In the perpendicular arrangement the two electrons in 1a″ are donated to the empty 2a″ of the metal (centre) and an occupied bonding molecular orbital results. Conversely, for the parallel conformation, the π lone pair, 2a′, participates in a four-electron destabilising interaction with the metal 1a′ orbital and there is a net destabilisation owing to this π interaction. There is a well defined preference for the perpendicular arrangement and, as will be seen later, it tends to be achieved whenever possible.

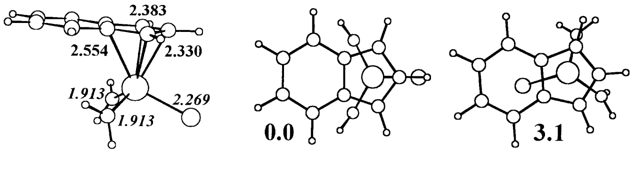
A geometry optimisation (ADF) was performed with a model having the N atom in a mirror plane, constraining the amide to be parallel or perpendicular. The perpendicular form was lower in energy by 1.5 kJ mol^{-1}. An ADF bond decomposition analysis gave for the perpendicular form a higher Pauli repulsion (102.6 kJ mol^{-1}), which was compensated both by a more favourable electrostatic interaction (−41.1 kJ mol^{-1}) and a stronger covalent interaction (−63.1 kJ mol^{-1}). This result confirms the EH qualitative result that the perpendicular conformation favours bonding, but also leads to more relevant repulsions.

The structure of the complex was partially optimised fixing the amido ligand in the two limiting conformations but allowing the indenyl to amido relative rotation, and the energy of the perpendicular form was found to be lower by 17.3 kJ mol^{-1}. A full optimisation of the structure with a perpendicular amide was performed and a η^5 co-ordination mode of the indenyl ligand was found, as shown below. The five Ti–C bonds are typical of η^5-indenyl, and very close to the experimental ones (from 2.380 to 2.483 Å, *vs.* 2.32 to 2.42 Å for [Ti(η^5-Ind)Cl$_2$(NMe$_2$)]) and the ligand is planar. The Ti–N distance was calculated as 1.899 Å, very close to the experimental 1.864 Å. The Cl–Ti–Cl angle of 100.3° (exp. 101.8°) is smaller than the Cl–Ti–N angles, calculated as 103.4° (exp. 103.1 and 105.6°). As the calculations were done without symmetry constraints (there is no symmetry in the molecule) and equivalent Ti–Cl and Ti–C distances were obtained, it appears that the asymmetry found in the crystal structure is caused by crystal packing and not by the presence of an amido ligand in the co-ordination sphere of Ti.

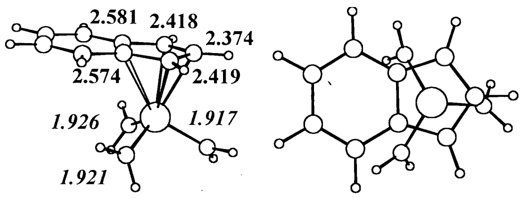


Although these results favour the perpendicular amido ligand, the energy difference encountered is small and compatible with the fluxionality observed in solution for all half-sandwich transition metal amido complexes. In the solid state the perpendicular form was reported for all the complexes characterised by X-ray diffraction except for TiCp*(NMe$_2$)(CH$_2$Ph)$_2$ where stereochemical factors become dominant.[9]

In the bisamido compound, Ti(η^5-Ind)(NH$_2$)$_2$Cl, the number of structural arrangements is larger, as each amide has two limiting conformations, perpendicular and parallel, as well as several orientations relative to the indenyl. The most stable arrangement occurs when both are perpendicular. Full geometry optimisations were performed for two limiting conformations of the indenyl relative to the amide, the optimised structures being depicted below (left and centre, most stable form; right, top view of less stable form; the numbers give the energy difference in kJ mol^{-1}). The preferred arrangement allows the amides to remain perpendicular and maximise π bonding. The two top views also show clearly that steric repulsion is minimised in this geometry as, at the right, the amides are not totally perpendicular. In the optimised geometry the Ti–C distances are typical of η^5-indenyl co-ordination, and very symmetric (the calculations were performed without symmetry constraints), as well as the two Ti–N distances (1.913 Å). On the other hand, for the less stable form, the Ti–C distances are less symmetric (2.375 and 2.382, 2.425 and 2.520, and 2.558 Å), as may be expected from the structure, since one amide eclipses a C–H bond of the indenyl. Although there is no available structure to compare, the good agreement found in the previous examples suggests that this should be a good prediction.



The final system we studied, [Ti(η^5-Ind)(NH$_2$)$_3$], contains three amido groups and the structure of the complex has not been determined. As in the previous case, there is a conflict in determining the orientation of the amides. They prefer to be perpendicular but this introduces steric repulsion, as three NH$_2$ groups are present. As before, the structure was fully optimised after searching for the best arrangement of ligands relative to the indenyl. The final geometry is shown below (side and top view). The interesting features of this structure include Ti–C bond lengths ranging from 2.374 to 2.419, 2.418 and 2.581, 2.574 Å, more asymmetric than before, in an essentially planar ring. The three amido groups are between perpendicular and parallel, owing to the balance between electronic and steric effects discussed above. Among the possible π donors, the indenyl ring keeps the η^5 co-ordination mode, although the Ti–C bonds are slightly longer than for the previous structures, and the amides try to form π bonds by adopting a perpendicular geometry, being limited by steric inter ligand repulsions.



This calculated structure can be compared with that of the related zirconium complex, *meso*-[{Zr(NMe$_2$)$_3$}$_2${μ-η^5:η^5-[Me$_2$Si(1-C$_9$H$_7$)$_2$]}],[15] which also exhibits this co-ordination mode. The arrangement of the NR$_2$ groups is very similar, all of them exhibiting a conformation between parallel and perpendicular.

For the mononuclear molybdenum analogue of the model titanium complex, a η^5-Ind co-ordination mode has also been postulated.[36] It is interesting to compare the hapticity of the indenyl ring in these two species, as molybdenum has two extra electrons and the same arrangement as shown above would lead to an 18 electron count, rather than the 16 electrons obtained for titanium and zirconium. The geometry of [Mo(η^5-Ind)(NH$_2$)$_3$] was also optimised and the result is not significantly different from that of the titanium complex. The three types of Mo–C distances to the indenyl are 2.241, 2.355, and 2.775 Å, the folding angle being 9.5°. One of the amides is parallel and the other two are perpendicular. The indenyl is slightly folded and more slipped than for Ti. The pattern of Mo–C distances and the folding is very similar to that calculated for the 19-electron complex [Mo(η-Ind)Cp{P(OMe)$_3$}$_2$]$^+$.[37] For this last complex, and also for the formally 20-electron compound [Ni(η-Ind)$_2$],[29] an intermediate co-ordination of the indenyl ligand was postulated. Indeed, in the nickel complex each indenyl can be considered as having accepted one extra electron.

A full geometry optimisation was also performed for a model of [Ti(Ind)(NMe$_2$)Me$_2$], **5**, where agostic interactions might in principle be expected, due to the 14 electron count on the metal. The optimised structure exhibits two undistorted methyl groups, a perpendicular NH$_2$ group and a co-ordinated η^5-Ind ring. These features indicate that the metal prefers to achieve a higher electron count by making stronger bonds to indenyl and the amido group, rather than by engaging in an agostic interaction. Among other factors, this interaction implies distortion of the methyl groups, an energetic requirement not needed in π-bond formation.

Conclusion

The optimised syntheses of several titanium indenyldimethylamido derivatives are described. Owing to the oily nature of most of the complexes their structural characterisation was carried out by NMR and DFT calculations. Titanium indenyldimethylamido complexes containing a variable number of amido ligands have a marked preference for an η^5 co-ordination of the indenyl ligands, the amido ligands orienting in such a way as to provide effective π bonding with the metal, minimising steric repulsion. As the number of amido ligands increase, a compromise between the two effects must be achieved, and in the trisamido complex all the groups exhibit an arrangement between parallel and perpendicular. The energy differences between the several amido and indenyl conformations are small and it is most probable that the real amido groups, with more bulky ligands than NH_2, may have conformational preferences mostly dictated by steric hindrance. Nevertheless, the rise in the rotational barriers should be small, as implied by the fluxional behaviour observed in solution. The molybdenum analogue has two more electrons, and less metal–ligand bonds are required. The way this is achieved, according to our calculations, is by weakening the Mo–indenyl bond in such a way that this ligand starts to become η^3.

Experimental

General methods and instrumentation

All manipulations were carried out under an atmosphere of argon using either Schlenk-line or dry-box techniques. Solvents were pre-dried over activated 4 Å molecular sieves and refluxed over sodium or calcium hydride under argon and collected by distillation. The NMR samples were prepared in Wilmad 505-PS tubes fitted with a J. Young NMR/5 valve. $LiNMe_2$ and 1.6 M LiMe solution in diethyl ether (Aldrich) were used as received, $TiCl_4$ (Aldrich) was distilled before use under reduced pressure and $Ti(Ind)Cl_3$ was prepared according to the literature.[13]

Proton and ^{13}C NMR spectra were recorded on a Varian Unity 300 spectrometer. When necessary the assignments were confirmed by NOE difference spectra and one bond ^1H–^{13}C HETCOR. Long-range ^1H–^{13}C correlations were obtained using the gradient version of the HMBC (heteronuclear multiple bond correlation) experiment, recorded with a Varian Inova 300 spectrometer. The spectra were referenced internally to the residual protio-solvent (^1H) or solvent (^{13}C) resonances and reported relative to tetramethylsilane (δ 0) at ambient probe temperature. Chemical shifts are quoted in δ (ppm). Elemental analyses were carried out by the analytical laboratory of I.S.T. The mass spectra (FAB and EI) were recorded on a TRIO 2000, VG micromass quadrupole spectrometer.

Preparations

[Ti(Ind)(NMe$_2$)Cl$_2$], 2. To a stirred suspension of $Ti(Ind)Cl_3$ (1.61 g, 5.98 mmol) in 120 ml of toluene at −80 °C was added dropwise a suspension of $LiNMe_2$ (0.30 g, 5.98 mmol) in toluene (80 ml). The mixture was allowed to warm to room temperature and stirred overnight. After evaporation of the solvents to dryness the dark orange residue was washed with hexane and extracted with toluene. Cooling to −20 °C yielded complex **2** as an orange crystalline solid. Yield: 2.01 g (93%). Electron-impact mass spectrum: *m*/*z* 277 (M^+), 242 ($M^+ - Cl$), 233 ($M^+ - NMe_2$), 163 (TiC_9H_7) and 115 (C_9H_7), with correct isotopic distributions [Found (Calc. for $C_{11}H_{13}Cl_2NTi$): C, 47.36 (47.52); H, 4.87 (4.71); N, 4.96 (5.04)%]. NMR (C_6D_6): ^1H (300 MHz), δ 7.32 (2 H, m, $^3J_{H7H6} = 6.0$, $^4J_{H7H5} = 3.0$, $H^{4,7}$), 6.95 (2 H, m, $^3J_{H6H7} = 6.0$, $^4J_{H5H7} = 3.0$, $H^{5,6}$), 6.32 (2 H, d, $^3J_{H2H1} = 3.0$, $H^{1,3}$), 6.08 (1 H, t, $^3J_{H1H2} = 3.0$ Hz, H^2) and 3.17 (6 H, s, $N(CH_3)_2$); ^{13}C-{^1H} (75.43 MHz), δ 128.8 ($C^{3a,7a}$), 127.9 ($C^{5,6}$), 125.9 ($C^{4,7}$), 118.7 (C^2), 110.1 ($C^{1,3}$) and 51.2 ($N(CH_3)_2$).

[Ti(Ind)(NMe$_2$)$_2$Cl], 3. A suspension of $LiNMe_2$ (0.26 g, 5.18 mmol) in toluene (40 ml) was added dropwise to a stirred solution of $Ti(Ind)Cl_3$ (0.70 g, 2.59 mmol) in 60 ml of toluene at −80 °C. The mixture was allowed to react overnight. The solvent was then evaporated to dryness and the dark red residue extracted with hexane and concentrated. Cooling to −20 °C yielded complex **3** as an orange crystalline solid. Yield: 0.45 g (61%). Electron-impact mass spectrum: *m*/*z* 286 (M^+), 251 ($M^+ - Cl$), 242 ($M^+ - NMe_2$), 198 ($M^+ - 2NMe_2$), 171 ($M^+ - C_9H_7$), 163 (TiC_9H_7) and 115 (C_9H_7) with correct isotopic distributions [Found (Calc. for $C_{13}H_{19}ClN_2Ti$): C, 53.61 (54.47); H, 6.87 (6.68); Cl, 11.92 (12.37); N, 9.01 (9.77)%]. NMR (C_6D_6): ^1H (300 MHz), δ 7.50 (2 H, m, $^3J_{H7H6} = 6.0$, $^4J_{H7H5} = 3.0$, $H^{4,7}$), 6.95 (2 H, m, $^3J_{H6H7} = 6.0$, $^4J_{H5H7} = 3.0$, $H^{5,6}$), 6.20 (2 H, d, $^3J_{H2H1} = 3.0$, $H^{1,3}$), 5.97 (1 H, t, $^3J_{H1H2} = 3.0$ Hz, H^2) and 2.96 (12 H, s, $N(CH_3)_2$); ^{13}C-{^1H} (75.43 MHz), δ 126.6 ($C^{3a,7a}$), 124.7 ($C^{5,6}$), 124.0 ($C^{4,7}$), 116.3 (C^2), 104.0 ($C^{1,3}$) and 48.1 ($N(CH_3)_2$).

[Ti(Ind)(NMe$_2$)$_3$], 4. *Method 1.* A solution of indene (0.43 ml; 3.66 mmol) and $Ti(NMe_2)_4$ (0.41 g, 1.83 mmol) was heated at 85 °C overnight under a steam of nitrogen. The volatiles were removed under vacuum and the resulting dark red oil was extracted in hexane. The solution was filtered and the solvent evaporated to dryness. Yield: 0.51 g (94%).

Method 2. To a stirred solution of $Ti(Ind)Cl_3$ (0.54 g, 2.00 mmol) in 60 ml of toluene at −80 °C was added dropwise a suspension of $LiNMe_2$ (0.31 g, 6.00 mmol) in toluene (40 ml). The mixture was allowed to warm slowly to room temperature and stirred overnight. Evaporation to dryness gave an oily residue that was extracted in hexane and filtered. Evaporation of the solvent to dryness gave an orange oil which was analysed by NMR as a 3 : 1 mixture of **4** and $Ti(NMe_2)_4$. FAB mass spectrum: *m*/*z* 295 (M^+), 251 ($M^+ - NMe_2$), 207 ($M^+ - 2NMe_2$), 180 ($M^+ - C_9H_7$), 163 (Ti(Ind)) and 115 (Ind) with correct isotopic distributions. NMR (C_6D_6): ^1H (300 MHz), δ 7.48 (2 H, m, $^3J_{H7H6} = 6.6$, $^4J_{H7H5} = 3.0$, $H^{4,7}$), 6.91 (2 H, m, $^3J_{H6H7} = 6.6$, $^4J_{H7H5} = 3.0$, $H^{5,6}$), 6.27 (1 H, t, $^3J_{H2H1} = 3.6$, H^2), 6.11 (2 H, d, $^3J_{H1H2} = 3.6$ Hz, $H^{1,3}$) and 2.92 (18 H, s, $N(CH_3)_2$); ^{13}C-{^1H} (75.43 MHz), δ 126.7 ($C^{3a,7a}$), 123.3 ($C^{4,7}$), 122.8 ($C^{5,6}$), 117.1 (C^2), 98.6 ($C^{1,3}$) and 48.9 ($N(CH_3)_2$).

[Ti(Ind)(NMe$_2$)Me$_2$], 5. Dropwise addition of a 1.6 M solution of LiMe in Et_2O (3.35 ml, 5.9 mmol) to a solution of $[Ti(Ind)(NMe_2)Cl_2]$ (0.82 g, 2.95 mmol) in toluene (60 ml) at −78 °C gave, after warming to room temperature, an orange solution and a precipitate. The solvent was evaporated to dryness and the residue extracted with hexane and filtered. Evaporation of the solvent led to complex **5** as an orange oil. Yield: 0.49 g (70%). FAB mass spectrum: *m*/*z* 222 ($M^+ - Me$), 207 ($M^+ - 2Me$), 193 ($M^+ - NMe_2$), 163 (C_9H_7Ti) and 115 (C_9H_7) [Found (Calc. for $C_{13}H_{19}NTi$): C, 66.08 (65.83); H, 8.30 (8.07); N, 5.65 (5.90)%]. NMR (C_6D_6): ^1H (300 MHz), δ 7.34 (2 H, m, $^3J_{H7H6} = 6.6$, $^4J_{H7H5} = 3.0$, $H^{4,7}$), 6.99 (2 H, m, $^3J_{H6H7} = 6.6$, $^4J_{H6H4} = 3.0$, $H^{6,5}$), 6.09 (2 H, d, $^3J_{H2H1} = 3.6$, H^1), 5.66 (1 H, t, $^3J_{H1H2} = 3.6$ Hz, H^2), 3.19 (6 H, s, $N(CH_3)_2$) and 0.14 (6 H, s, CH_3); ^{13}C-{^1H} (75.43 MHz), δ 126.4 ($C^{3a,7a}$), 125.4 ($C^{4,7}$), 124.8 ($C^{5,6}$), 115.7 (C^2), 103.0 ($C^{1,3}$), 52.1 (CH_3) and 45.3 ($N(CH_3)_2$).

[Ti(Ind)(NMe$_2$)$_2$Me], 6. A 1.6 M solution of LiMe in Et_2O (0.57 ml, 0.907 mmol) was slowly added to a solution of

Ti(Ind)(NMe$_2$)$_2$Cl (0.24 g, 0.91 mmol) in 50 ml of toluene at −80 °C. The mixture was allowed to warm to room temperature and the solvent removed under vacuum. Extraction of the residue in hexane followed by filtration and evaporation of the solvent to dryness gave complex **6** as an orange oil. Yield: 0.20 g (84%). Electron-impact mass spectrum: *m*/*z* 251 (M$^+$ − Me), 222 (M$^+$ − NMe$_2$), 207 (TiC$_9$H$_7$NMe$_2$), 151 (M$^+$ − C$_9$H$_7$), 136 (Ti(NMe$_2$)$_2$), 115 (C$_9$H$_7$), 107 (Ti(NMe$_2$)Me), 63 (TiMe) and 44 (NMe$_2$) [Found (Calc. for $C_{14}H_{22}N_2Ti$): C, 61.96 (63.16); H, 7.85 (8.33); N, 9.95 (10.52)%]. NMR (C$_6$D$_6$): ^{1}H (300 MHz), δ 7.39 (2 H, m, $^3J_{H7H6} = 6.6$, $^4J_{H5H7} = 3.0$, H^{4,7}), 6.94 (2 H, m, $^3J_{H6H7} = 6.6$, $^4J_{H5H7} = 3.0$, H^{5,6}), 6.10 (2 H, d, $^3J_{H2H1} = 3.6$, H^{1,3}), 5.99 (1 H, t, $^3J_{H1H2} = 3.6$ Hz, H^2), 2.90 (12 H, s, N(CH$_3$)$_2$) and 0.04 (3 H, s, CH$_3$); ^{13}C-{^{1}H} (75.43 MHz), δ 125.6 (C^{3a,7a}), 124.2 (C^{4,7}), 123.8 (C^{5,6}), 114.9 (C^2), 101.6 (C^{1,3}), 46.2 (N(CH$_3$)$_2$) and 39.5 (CH$_3$).

[Ti(Ind)(NMe$_2$)$_2$(CH$_2$SiMe$_3$)], 7. A 1.0 M solution of Me$_3$SiCH$_2$MgCl in THF (4.03 ml, 3.73 mmol) was slowly added to a solution of Ti(Ind)(NMe$_2$)$_2$Cl (0.77 g, 2.69 mmol) in 20 ml of toluene. After 30 minutes the solvents were evaporated and the residue was extracted in hexane and filtered. Evaporation of the solvent gave the product as orange oil in 92% yield (0.84 g). [Found (Calc. for $C_{17}H_{30}N_2SiTi$): C, 59.37 (60.33); H, 7.24 (8.93); N, 8.61 (8.28%)]. NMR (C$_6$D$_6$): ^{1}H (300 MHz), δ 7.31 (2 H, m, $^3J_{H7H6} = 6.3$, $^4J_{H5H7} = 3.0$, H^{4,7}), 6.86 (2 H, m, $^3J_{H6H7} = 6.3$, $^4J_{H5H7} = 3.0$, H^{5,6}), 6.19 (2 H, d, $^3J_{H2H1} = 3.3$, H^{1,3}), 6.09 (1 H, t, $^3J_{H1H2} = 3.3$ Hz, H^2), 2.82 (12 H, s, N(CH$_3$)$_2$), 0.44 (2 H, s, C*H*$_2$SiMe$_3$) and 0.14 (9 H, s, Si(CH$_3$)$_3$); ^{13}C-{^{1}H} (75.43 MHz), δ 125.3 (C^{3a,7a}), 124.3 (C^{4,7}), 124.1 (C^{5,6}), 114.6 (C^2), 101.6 (C^{1,3}), 54.0 (*C*H$_2$SiMe$_3$), 47.1 (N(CH$_3$)$_2$) and 3.7 (CH$_2$Si(*C*H$_3$)$_3$).

[Ti(Ind)(NMe$_2$)$_2$(C≡CPh)], 8. A 1.0 M THF solution of LiC≡CPh (0.52 ml, 0.52 mmol) was added to a solution of Ti(Ind)(NMe$_2$)$_2$Cl (0.15 g, 0.52 mmol) in 10 ml of toluene at room temperature. The solvent was evaporated to dryness after 30 minutes and the residue extracted in hexane. Evaporation of the solvent gave 0.17 g of complex **8** as an oil (yield, 93%). Electron-impact mass spectrum: *m*/*z* 352 (M$^+$), 308 (M$^+$ − NMe$_2$), 264 (TiC$_9$H$_7$(C≡CPh)), 251 (M$^+$ − (C≡CPh)), 101 (C≡CPh)) and 44 (NMe$_2$) [Found (Calc. for $C_{21}H_{24}N_2Ti$): C, 70.03 (71.59); H, 6.61 (6.86); N, 7.26 (7.95)%]. NMR (C$_6$D$_6$): ^{1}H (300 MHz), δ 7.59 (2 H, dd, $^3J_{om} = 8.4$, $^4J_{op} = 1.5$, *o*-H of C$_6$H$_5$), 7.53 (2 H, m, $^3J_{H7H6} = 6.6$, $^4J_{H5H7} = 3.3$, H^{4,7}), 7.04 (2 H, m, $^3J_{mo} = 8.4$, $^3J_{mp} = 7.5$, *m*-H of C$_6$H$_5$), 6.95 (1 H, dt, $^3J_{pm} = 7.5$, $^4J_{po} = 1.5$, *p*-H of C$_6$H$_5$), 6.92 (2 H, m, $^3J_{H6H7} = 6.6$, $^4J_{H5H7} = 3.3$, H^{5,6}), 6.43 (2 H, d, $^3J_{H2H1} = 3.3$, H^{1,3}), 6.10 (1 H, t, $^3J_{H1H2} = 3.3$ Hz, H^2) and 2.96 (12 H, s, N(CH$_3$)$_2$); ^{13}C-{^{1}H} (75.43 MHz), δ 144.7 (*C*≡CPh), 131.9 (*ipso*- + *o*-C of C$_6$H$_5$), 128.0 (*m*-C of C$_6$H$_5$), 126.6 (*p*-C of C$_6$H$_5$), 125.9 (C^{3a,7a}), 124.5 (C^{4,7}), 124.4 (C^{5,6}), 115.5 (C^2), 110.1 (C≡*C*Ph), 103.2 (C^{1,3}) and 46.7 (N(CH$_3$)$_2$).

[Ti(Ind)(NMe$_2$)$_2$(C≡CSiMe$_3$)], 9. A 0.5 M THF solution of LiC≡CSiMe$_3$ (7.52 ml, 4.05 mmol) was added to a solution of Ti(Ind)(NMe$_2$)$_2$Cl (0.77 g, 2.69 mmol) in 25 ml of toluene and the mixture allowed to react at room temperature during 1 h. The solvent was then evaporated to dryness and the residue extracted in hexane. Removal of the solvent gave 0.75 g of an orange oil that was identified as complex **9** (yield, 80%). Electron-impact mass spectrum: *m*/*z* 348 (M$^+$), 304 (M$^+$ − NMe$_2$), 251 (M$^+$ − (C≡C(SiMe$_3$)), 233 (M$^+$ − C$_9$H$_7$), 189 (Ti(NMe$_2$)(C≡CSiMe$_3$)), 145 (Ti(C≡CSiMe$_3$)) and 44 (NMe$_2$). NMR (C$_6$D$_6$): ^{1}H (300 MHz), δ 7.49 (2 H, m, $^3J_{H7H6} = 6.6$, $^4J_{H5H7} = 3.3$, H^{4,7}), 6.89 (2 H, m, $^3J_{H6H7} = 6.6$, $^4J_{H5H7} = 3.3$, H^{5,6}), 6.39 (2 H, d, $^3J_{H2H1} = 3.3$, H^{1,3}), 6.04 (1 H, t, $^3J_{H1H2} = 3.3$, H^2) (2 H, d, $^3J_{H2H1} = 3.3$ Hz, H^{1,3}), 2.88 (12 H, s, N(CH$_3$)$_2$) and 0.30 (9 H, s, SiCH$_3$); ^{13}C-{^{1}H} (75.43 MHz), δ 166.1 (*C*≡CSiMe$_3$), 125.7 (C^{3a,7a}), 124.5 (C^{4,7}), 124.3 (C^{5,6}), 115.6 (C^2), 114.0 (C≡*C*SiMe$_3$), 103.3 (C^{1,3}), 46.6 (N(CH$_3$)$_2$) and 1.2 (Si(CH$_3$)$_3$).

Crystallography

$C_{11}H_{13}Cl_2NTi$ **2**, $M = 278.02$, orthorhombic, space group $P2_12_12_1$, $a = 7.514(6)$, $b = 11.991(4)$, $c = 13.584(2)$ Å, $\mu = 1.101$ mm^{-1}, $V = 1223.9(11)$ Å^3, $U = 1224(1)$ Å^3, $Z = 4$, λ(Mo-Kα) = 0.71073 Å, $\mu = 11.01$ cm^{-1}, $T = 293$ K. 1009 Unique reflections (Nonius CAD4 automatic diffractometer) of which 688 had $I > 2.0\sigma(I)$, $R(\text{int}) = 0.0$. $R1 = 0.0497$, $wR2 = 0.1075$.

CCDC reference number 186/2221.

See http://www.rsc.org/suppdata/dt/b0/b006889f/ for crystallographic files in .cif format.

Molecular orbital calculations

Density functional calculations[31] were carried out on model compounds based on the structures of Ti(η^5-C$_7$Me$_9$)Cl$_3$[16] and of the complex described in this work, using the Amsterdam Density Functional (ADF) program[32] developed by Baerends and co-workers.[38] Full geometry optimisation, without symmetry constraints, of all compounds was done, except when mentioned in the text for specific purposes. Vosko, Wilk and Nusair's local exchange correlation potential was used[39] with Becke's non-local exchange[40] and Perdew's correlation corrections.[41] The geometry optimisation procedure was based on the method developed by Versluis and Ziegler,[42] using the non-local correction terms in the calculation of the gradients. The core orbitals were frozen for Ti ([1–3]s, [1–3]p) and C, N, O (1s). Triple-ζ Slater-type orbitals (STOs) were used for H 1s, C, N, O 2s and 2p, Ti 4s, 4p, and 3d. A set of polarisation functions was added: H (single ζ, 2p), C, N, O (single ζ, 3d).

The extended Hückel method[43] with modified H_{ij} values was used.[44] The basis set for the metal atoms consisted of *n*s, *n*p and (*n* − 1)d orbitals. The s and p orbitals were described by single Slater-type wavefunctions, and the d orbitals taken as contracted linear combinations of two Slater-type wavefunctions. Only s and p orbitals were considered for Cl. The parameters used for Ti were (H_{ii}/eV, ζ): 4s −8.97, 1.075; 4p −5.44, 0.675; 3d −10.81, 4.550, 1.400 (ζ_2), 0.4206 (C_1), 0.7839 (C_2). Standard parameters were used for other atoms. The calculations were performed on model complexes with idealised geometries and C_s symmetry, taken from the real structures quoted in the text. Methyl groups were replaced by hydrogen atoms, since the results were not qualitatively altered. Thus, Ti(Ind)(NH$_2$)Cl$_2$ complexes have a piano stool geometry with (Ind)–Ti–L angles of 115°. The bond distances (Å) were as follows: Ti–(C$_5$ ring centroid) 2.00, Ti–Cl 2.25, Ti–N 1.85, C–C 1.4, C–H 1.08, N–H 1.08.

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