

A structurally characterised, naked sp^3 -hybridised carbanion in the zwitterionic imido complex $[\text{Ti}(\text{NBu}^t)\{\text{C}(\text{Me}_2\text{pz})_3\}\text{Cl}(\text{THF})]$ ($\text{HMe}_2\text{pz} = 3,5\text{-dimethylpyrazole}$)[†]

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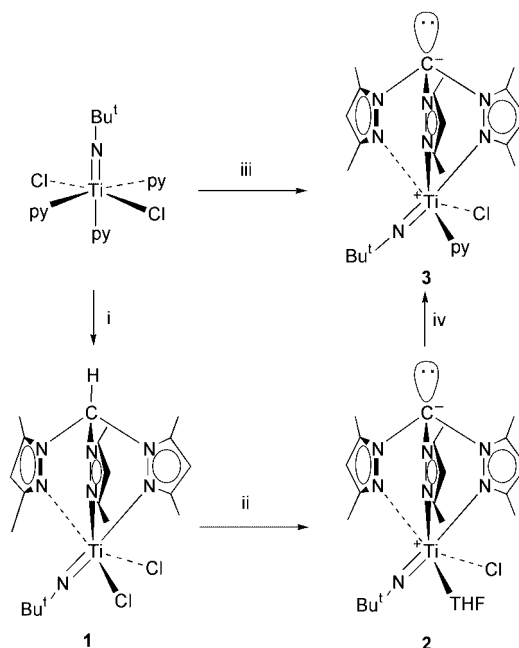
Reaction of the tris(3,5-dimethylpyrazolyl)methane complex $[\text{Ti}(\text{NBu}^t)\{\text{HC}(\text{Me}_2\text{pz})_3\}\text{Cl}_2]$ with MeLi or LiNPr_2 in tetrahydrofuran (THF) gives the zwitterionic titanium imido derivative $[\text{Ti}(\text{NBu}^t)\{\text{C}(\text{Me}_2\text{pz})_3\}\text{Cl}(\text{THF})]$ **2** which contains the first structurally authenticated, naked sp^3 -hybridised carbanion; the molecular and electronic structures of **2** are described.

The tris(pyrazolyl)hydroborate ligands are important face-capping, anionic, six-electron donor ligands in inorganic and organometallic coordination chemistry.¹ Their neutral analogues, the tris(pyrazolyl)methanes are considerably less well developed.² We are interested in the use of tris(pyrazolyl)methanes in our ongoing program in early transition metal imido chemistry.³ Target complexes of the type $[\text{Ti}(\text{NR})\{\text{tris}(\text{pyrazolyl})\text{methane}\}\text{Cl}_2]$ are isolobal analogues of the group metallocenes $[\text{M}(\eta\text{-C}_5\text{R}_5)_2\text{Cl}_2]$ ($\text{M} = \text{Ti}, \text{Zr}$) which are in turn a very important class of single-site olefin polymerisation catalysts;⁴ no tris(pyrazolyl)methane-supported imido complexes have been described previously. As part of these studies we found a unique example of a stabilised, naked sp^3 -hybridised carbanion as described below.

Reaction of $[\text{Ti}(\text{NBu}^t)\text{Cl}_2(\text{py})_3]$ ⁵ with $\text{HC}(\text{Me}_2\text{pz})_3$ ($\text{HMe}_2\text{pz} = 3,5\text{-dimethylpyrazole}$) in CH_2Cl_2 afforded the tris(3,5-dimethylpyrazolyl)methane complex $[\text{Ti}(\text{NBu}^t)\{\text{HC}(\text{Me}_2\text{pz})_3\}\text{Cl}_2]$ **1** in 80% yield after the addition of hexane (Scheme 1).[‡] Reaction of **1** with one equivalent of MeLi (initially in a failed attempt to alkylate titanium) or $\text{LiN}(\text{Pr})_2$ in THF leads to smooth removal of the apical proton of $\text{HC}(\text{Me}_2\text{pz})_3$ and formation of the diamagnetic compound $[\text{Ti}(\text{NBu}^t)\{\text{C}(\text{Me}_2\text{pz})_3\}\text{Cl}(\text{THF})]$ **2** in ca. 60% yield. Reaction of **2** in benzene with HCl (1 equivalent) reforms **1**; the corresponding reaction of **2** with DCl forms $[\text{Ti}(\text{NBu}^t)\{\text{DC}(\text{Me}_2\text{pz})_3\}\text{Cl}_2]$ **1-d** with deuterium enrichment occurring exclusively at the apical carbon of the tridentate ligand.

Crystallization of **2** from toluene at 5 °C gave diffraction-quality crystals.[§] The molecular structure of **2** is shown in Fig. 1 together with selected bond lengths and angles. Fourier difference syntheses revealed the positions of all hydrogen atoms of the $\{\text{C}(\text{Me}_2\text{pz})_3\}^-$ ligand; none was located for the apical carbon C(24). A formal negative charge is assigned to this atom as illustrated in Scheme 1; the Ti centre thus has a formal charge of +4 in line with the observed diamagnetism. The N–C–N angles subtended at C(24) lie in the range 108.3(3)–109.6(3)°, consistent with this atom being formally sp^3 hybridised. In general, the distances and angles for **2** are comparable with those of previously reported titanium imido and tris(pyrazolyl)methane complexes.^{2,3,6} The solution ¹H and ¹³C NMR data for **2** support the solid state structure.

The $\{\text{C}(\text{Me}_2\text{pz})_3\}^-$ ligand in $[\text{Ti}(\text{NBu}^t)\{\text{C}(\text{Me}_2\text{pz})_3\}\text{Cl}(\text{THF})]$ **2** is analogous to the hydroborate relative $\{\text{HB}(\text{Me}_2\text{pz})_3\}^-$. We have previously reported a series of titanium imido complexes with tris(pyrazolyl)hydroborate li-



Scheme 1 Reagents and conditions: i $\text{HC}(\text{Me}_2\text{pz})_3$, CH_2Cl_2 , rt, 1 h, 80%; ii MeLi or $\text{LiN}(\text{Pr})_2$, THF, -80°C to rt, 2–4 h, 60–62%; iii $\text{LiC}(\text{Me}_2\text{pz})_3$, THF, -80°C to rt, 16 h, 50%; iv pyridine (1 equiv.), C_6D_6 , rt, 20 min, >95%.

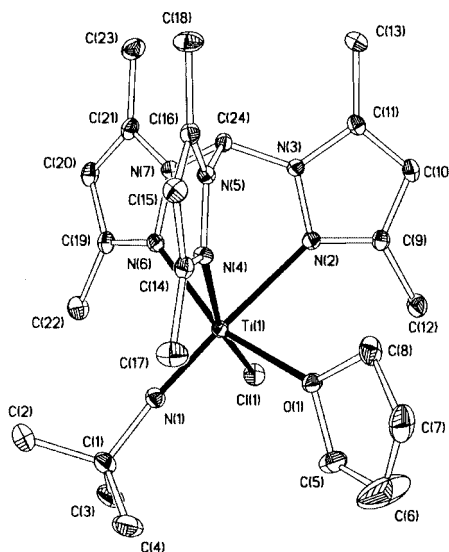


Fig. 1 Displacement ellipsoid (20%) plot of $[\text{Ti}(\text{NBu}^t)\{\text{C}(\text{Me}_2\text{pz})_3\}\text{Cl}(\text{THF})]$ **2**. Hydrogen atoms and toluene of crystallization are omitted for clarity. For selected bond lengths see Table 1.

[†] Electronic supplementary information (ESI) available: isosurface for the HOMO of **2a**. See <http://www.rsc.org/suppdata/cc/b1/b1003151/>

Table 1 Comparison of selected bond distances (Å) for [Ti(NH){HC(pz)₃}Cl₂] **1a**, [Ti(NpBu^t){C(Me₂pz)₃}Cl(THF)] **2**, [Ti(NH){C(pz)₃}Cl(OH₂)] **2a** and [Ti(NH){HB(pz)₃}Cl(OH₂)] **4**. For the Ti–N_{pyrazole} distances 'A', 'B' and 'C' refer to the nitrogens *trans* to imide, Cl and O (or Cl for **1a**), respectively

	1a	2	2a	4
Ti=N _{imide}	1.711	1.713(3)	1.71	1.70
Ti–O	—	2.152(3)	2.15	2.08
Ti–Cl	2.40	2.394(1)	2.41	2.37
Ti–N _{pyrazole(A)}	2.44	2.358(3)	2.36	2.30
Ti–N _{pyrazole(B)}	2.28	2.191(4)	2.22	2.17
Ti–N _{pyrazole(C)}	2.28	2.169(3)	2.16	2.11

gands. The Ti=N_{imide}, Ti–Cl and Ti–N_{pyrazolyl} distances in **2** are comparable to those of tris(pyrazolyl)hydroborate analogues.

DFT (density functional theory) calculations⁸ were used to optimise the geometry of [Ti(NH){C(pz)₃}Cl(OH₂)] **2a** as a model for [Ti(NBu^t){C(Me₂pz)₃}Cl(THF)] **2**, and to determine its electronic structure.¶ Comparative calculations were also carried out for the tris(pyrazolyl)hydroborate species [Ti(NH){HB(pz)₃}Cl(OH₂)] **4** and for C_s symmetric [Ti(NH){HC(pz)₃}Cl₂] **1a** (as a model for [Ti(NBu^t){HC(Me₂pz)₃}Cl₂] **1**). Table 1 compares selected bond distances for **1a**, **2**, **2a** and **4**. There is very good agreement between those of the real compound **2** and of its model **2a**. The N–C_{apical}–N angles in **1a** (110–111°) are comparable to those of **2a** (108–109°) in line with the sp³ hybridisation of the apical carbon; in **4** the N–B–N angles lie in the range 107–109°.

The highest occupied molecular orbital (HOMO) for [Ti(NH){C(pz)₃}Cl(OH₂)] **2a** is based predominantly on the {C(pz)₃}[–] apical carbon and has a computed energy of –5.14 eV; the isosurface is shown in Fig. 2.† There is an energy separation of 2.00 eV between this MO and the lowest unoccupied molecular orbital (LUMO) which is Ti 3d in character. The calculations support our proposal that **2** and **3** are zwitterionic Ti(IV) complexes that contain naked, formally sp³-hybridised apical carbanions; an alternative interpretation of **2** and **3** as antiferromagnetically coupled Ti(III) complexes with an apical carbon-based radical can be discounted. There is a net atomic charge (calculated from the Voronoi Deformation Density⁸) of –0.13 e for the apical carbon in **2a** whereas the corresponding atomic charge in **1a** is 0.11 e; the atomic charges for Ti in **1a**, **2a** and **4** are 0.29, 0.32 and 0.29 e, respectively. The molecular and electronic structures for [Ti(NH){C(pz)₃}Cl(OH₂)] **2a** and [Ti(NH){HB(pz)₃}Cl(OH₂)] **4** confirm the analogy between {C(R₃pz)₃}[–] and {HB(R₃pz)₃}[–].

The apical carbon in [Ti(NBu^t){C(Me₂pz)₃}Cl(THF)] **2** is the first example of any naked, sp³-hybridised carbanion.⁶ Formally sp²-hybridised carbanions are very well-established in the literature and for such species the planar geometry around the

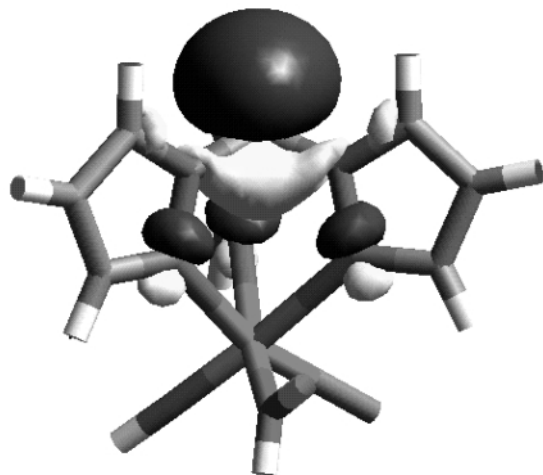


Fig. 2 Isosurface for the highest occupied molecular orbital of **2a**.

carbanion assists resonance stabilization.^{6,9} Previous reports have shown that the apical carbon of the free or complexed parent tris(pyrazolyl)methane can be deprotonated (and, in many instances, functionalised this way),¹⁰ but no carbanionic species have been structurally characterised.

The anionic {C(Me₂pz)₃}[–] is potentially a new ligand in transition metal chemistry, not least because of the improved, multi-gram synthesis now available for HC(Me₂pz)₃.^{2b} The methyl substituents in the 5-position of the pyrazolyl rings clearly offer significant protection of the carbanionic carbon in **2**. Moreover, it is possible to cleanly deprotonate HC(Me₂pz)₃ itself (*i.e.* without prior complexation to a metal centre) by reaction with MeLi in THF to form benzene-soluble LiC(Me₂pz)₃ **5** in quantitative isolated yield. The anionic apical carbon in **5** is confirmed by reaction with D₂O to generate DC(Me₂pz)₃ with deuterium enrichment exclusively in the apical position. We have established the potential use of LiC(Me₂pz)₃ **5** as a reagent (*via* salt-elimination type reactions) and source of anionic {C(Me₂pz)₃}[–]. Thus, reaction of [Ti(NBu^t)Cl₂(py)₃] with LiC(Me₂pz)₃ **5** in THF forms [Ti(NBu^t){C(Me₂pz)₃}Cl(py)] **3** in good yield (Scheme 1). A survey of the syntheses and chemistry of a range of zwitterionic complexes with the anionic {C(Me₂pz)₃}[–] ligand and its homologues is currently underway.

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Notes and references

† Satisfactory characterising data have been obtained for all the new compounds.

§ *Crystal data* for **2**: C₂₄H₃₈ClN₇O₇Ti·0.5C₇H₈, *M* = 570.04, monoclinic, *C*2/c, *a* = 23.894(2), *b* = 13.8900(9), *c* = 20.0340(9) Å, β = 114.882(3)°, *U* = 6031.85 Å³, *Z* = 8, *T* = 150 K, μ = 0.40 mm^{–1}, 5737 independent reflections (*R*_{merge} = 0.042), 3675 [*I* > 3σ(*I*)] used in refinement, final *R* indices: *R* = 0.0412, *R*_w = 0.0573.

CCDC 15549. See <http://www.rsc.org/suppdata/cc/b1/b100315l/> for crystallographic data in .cif or other electronic format.

¶ Calculations were performed using the density functional methods of the Amsterdam Density Functional (ADF) code Version 2000.02.⁸

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