Alkyl and alkylidene derivatives of titanium supported by carbazole ligation

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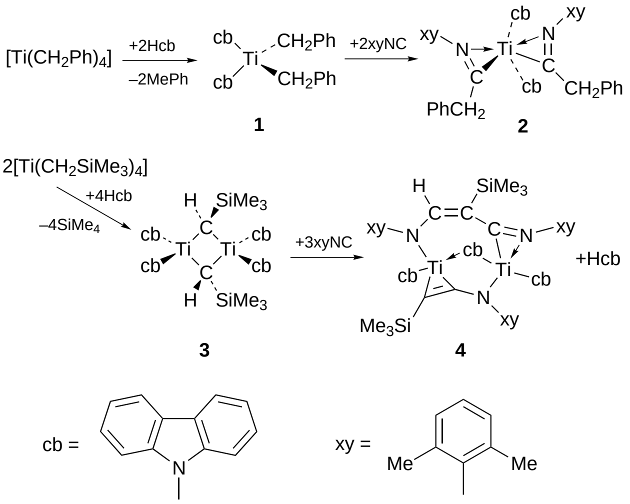
The bis(benzyl) [(cb)$_2$Ti(CH$_2$Ph)$_2$] 1 and alkylidene bridged dimer [(cb)$_2$Ti(μ-CHSiMe$_3$)$_2$Ti(cb)$_2$] 3 are formed by adding carbazole (Hcb) to the tetraalkyls [TiR$_4$] (R = CH$_2$Ph, CH$_2$SiMe$_3$); the reaction of 1 and 3 with 2,6-dimethylphenyl isocyanide leads to organometallic products containing new carbon–carbon bonds.

There has recently been considerable research interest in the organometallic chemistry of the group 4 metals associated with amido ligation.[1–3] In this context we communicate here our studies of some organotitanium chemistry of the carbazole ligand, an amido group predicted to be a weaker π donor than dialkylamido ligands.[4]

The addition of carbazole (2 equiv.) to hydrocarbon solutions of [Ti(CH$_2$Ph)$_4$][5] lead to the bis(benzyl) compound **1** in moderate yield (Scheme 1). The spectroscopic data† on **1** indicate that the benzyl ligands are η^1-bound.[6] Solutions of **1** react with 2 equiv. of 2,6-dimethylphenyl isocyanide (xyNC) to produce the bis(η^2-iminoacyl) complex **2**. The iminoacyl carbon chemical shift of δ 246.9 in the ^{13}C NMR spectrum indicates η^2-C,N binding and this is confirmed by the solid-state molecular structure of **2** (Fig. 1).[7] The coordination geometry and iminoacyl parameters in **2** are similar to those found in other group 4 metal bis(η^2-iminoacyl) compounds,[7,8] the only significant difference being the non-parallel orientation of the iminoacyl units in **2**.

The reaction of the more bulky alkyl substrate [Ti(CH$_2$SiMe$_3$)$_4$][9] with carbazole is slow (as monitored by ^{1}H NMR) at ambient temperatures. At 100 °C the reaction produces a sparingly soluble product identified (Fig. 2) as the alkylidene bridged dimer [(cb)$_2$Ti(μ-CHSiMe$_3$)$_2$Ti(cb)$_2$] **3**. In the ^{1}H NMR spectrum of **3** a singlet at δ 14.75 can be assigned to the alkylidene proton. The structural parameters for the 1,3-dimetallacyclobutane unit in **3** are similar to those found in related molecules and in particular the methylidene bridged [{(C$_6$H$_{11}$)$_2$N}$_2$Ti(μ-CH$_2$)$_2$Ti{N(C$_6$H$_{11}$)$_2$}$_2$].[2] Treatment of **3** with xyNC (> 3 equiv.) slowly (^{1}H NMR) produces a single organometallic species **4** and 1 equiv. of free carbazole. The molecular structure of **4** (Fig. 3) shows it to be dinuclear, containing a total of three isocyanides within two distinct bridging units. Two terminal and one non-symmetrically bridged carbazole ligand are also present. The structural parameters lead us to propose the structure for **4** shown in Scheme 1. Although the exact sequence of events leading to **4** is presently unknown, reasonable elementary steps for its formation can be proposed. One of the bridging units in **4** [N(6)–C(7)–C(8)] is best described as an amidoalkyne ligand. Identical



Scheme 1

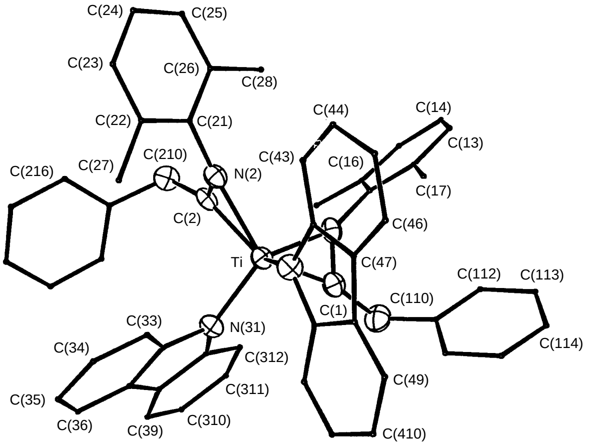


Fig. 1 Molecular structure of **2** showing the atomic numbering scheme. Selected interatomic distances (Å) and angles (°): Ti–N(1) 2.017(2), Ti–N(2) 2.150(2), Ti–N(31) 2.008(2), Ti–N(41) 2.030(2), Ti–C(1) 2.067(3), Ti–C(2) 2.065(3), C(1)–N(1) 1.268(4), C(2)–N(2) 1.281(4); N(1)–Ti–N(2) 100.54(9), N(31)–Ti–N(41) 108.5(1), C(1)–Ti–C(2) 119.0(1).

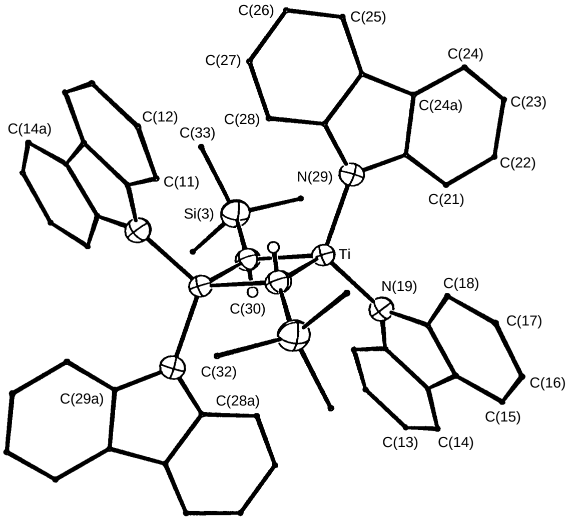


Fig. 2 Molecular structure of **3** showing the atomic numbering scheme. Selected interatomic distances (Å) and angles (°): Ti···Ti′ 2.9504(8), Ti–N(19) 1.950(2), Ti–N(29) 1.969(2), Ti–C(30) 2.026(2), Ti′–C(30) 2.035(2); N(19)–Ti–N(29) 113.29(7), C(30)–Ti–C(30)′ 86.83(9), Ti–C(30)–Ti′ 93.17(9).

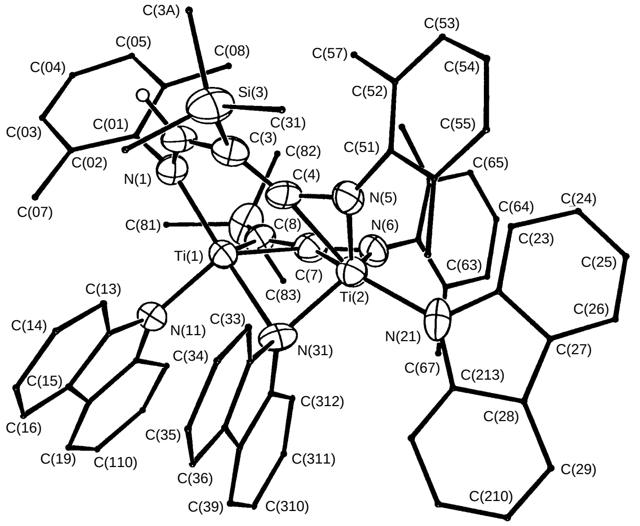


Fig. 3 Molecular structure of **4** showing the atomic numbering scheme. Selected interatomic distances (Å): Ti(1)···Ti(2) 2.804(2), Ti(1)–N(1) 2.064(7), Ti(1)–N(11) 2.006(7), Ti(1)–N(31) 2.321(7), Ti(1)–C(8) 1.970(8), Ti(1)–C(7) 2.097(9), Ti(2)–C(7) 2.16(1), Ti(2)–N(21) 2.013(8), Ti(2)–N(31) 2.018(7), Ti(2)–N(6) 1.936(7), Ti(2)–N(5) 1.950(8), Ti(2)–C(4) 2.250(9), Ti(2)–C(7) 2.163(10), C(7)–C(8) 1.34(1), C(7)–N(6) 1.34(1), C(4)–N(5) 1.31(1), C(3)–C(4) 1.44(1), C(2)–C(3) 1.38(1), N(1)–C(2) 1.37(1).

ligands have been formed by addition of xyNC to trimethylsilylmethylidyne bridges in 1,3-dimetallacyclobutadiene derivatives of Nb or Ta.[4] The unit may have originated *via* initial α-hydrogen abstraction to produce an alkylidyne intermediate or by hydrogen abstraction from an initially formed iminoacyl. In both cases the hydrogen abstraction takes place by a carbazole ligand. The other bridging unit corresponds to the insertion of 2 equiv. of isocyanide into an alkylidene bridge combined with a 1,2-hydrogen shift. The transfer of adjacent hydrogen to iminoacyl carbon atoms has precedence.[7]

An interesting feature of the molecular structure of **4** concerns the distances within the iminoacyl component. Specifically the Ti–N(5) and Ti–C(4) distances lead to a value of -0.3 Å for the parameter [d(Ti–N)$-d$(Ti–C)].[7] This value combined with the long C(4)–N(5) distance are consistent with the much debated amido-carbene resonance picture.[10]

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Footnotes

† *Selected spectroscopic data*: ^{1}H NMR (C_6D_6, 500 MHz, 30 °C): **1**, δ 6.58–7.91 (m, 18 H, aromatics), 3.24 (s, 4 H, TiCH_2Ph); **2**, δ 6.39–8.02 (m, 32 H, aromatics), 3.69 (s, 4 H, CH_2Ph), 1.46 (s, 12 H, $Me_2C_6H_3$); **3**, δ 14.75 (s, 2 H, μ-C*H*SiMe$_3$), -0.50 (s, 18H, μ-CHSi*Me*$_3$); **4**, δ 2.55 (s, 3 H), 2.47 (s, 3 H), 2.45 (s, 3 H), 1.66 (s, 3 H), 1.64 (s, 3 H), 1.17 (s, 3 H, *Me*C_6H_3). ^{13}C NMR (C_6D_6, 30 °C): **1**, δ 98.3 (CH_2Ph); **2**, δ 246.9 (xyN*C*), 43.5 (CH_2Ph), 18.5 (xy*Me*).

‡ *Crystal data*: for **2** at 203 K: $C_{59}H_{51}N_4Ti$, M = 863.99, monoclinic, space group $C2/c$ (no. 15), a = 37.22(1), b = 12.153(3), c = 21.069(9) Å, β = 104.23(3)°, U = 9237(10) Å^3, D_c = 1.242 g cm^{-3}, Z = 8. Of the 6154 unique reflections collected ($5.36 \leqslant 2\theta \leqslant 45.34°$) with Mo-K$\alpha$ radiation (λ = 0.710 73 Å), the 6154 with $F_o^2 > 2\sigma(F_o^2)$ were used in the final least-squares refinement to yield $R(F_o)$ = 0.045 and $R_W(F_o^2)$ = 0.112.

For **3** at 296 K: $C_{56}H_{52}N_4Si_2Ti_2$, M = 933.04, triclinic, space group $P\bar{1}$ (no. 2), a = 10.066(2), b = 10.481(2), c = 13.170(3) Å, α = 109.17(2), β = 104.98(2), γ = 93.62(2)°, U = 1251(1) Å^3, D_c = 1.238 g cm^{-3}, Z = 1. Of the 5056 unique reflections collected ($5.32 \leqslant 2\theta \leqslant 52.64°$) with Mo-K$\alpha$ radiation (λ = 0.710 73 Å), the 5056 with $I > 3\sigma(I)$ were used in the final least-squares refinement to yield R = 0.036 and R_W = 0.041.

For **4** at 233 K: $C_{71}H_{68}N_6Si_2Ti_2$, M = 1157.35, monoclinic, space group $P2_1/n$ (no. 14), a = 12.788(2), b = 33.329(5), c = 14.616(3) Å, β = 96.76(2)°, U = 6186(3) Å^3, D_c = 1.242 g cm^{-3}, Z = 4. Of the 8122 unique reflections collected ($5.26 \leqslant 2\theta \leqslant 113.70°$) with Cu-K$\alpha$ radiation (λ = 1.541 84 Å), the 8122 with $F_o^2 > 2\sigma(F_o^2)$ were used in the final least-squares refinement to yield $R(F_o)$ = 0.074 and $R_W(F_o^2)$ = 0.184. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/447.

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