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Novel titanium complexes of a multidentate dicarbollide ligand. Synthesis and structural characterization of a constrained geometry complex†

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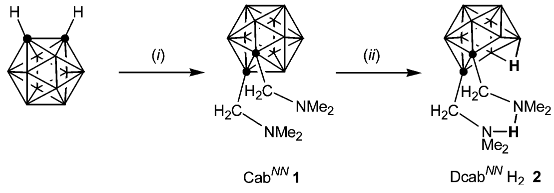
Received (in Cambridge, UK) 14th February 2003, Accepted 16th April 2003
First published as an Advance Article on the web 9th May 2003

The multidentate dicarbollide ligand *nido*-7,8-$(NMe_2CH_2)2$–7,8-$C_2B_9H_{11}$ has been prepared, structurally characterized, and employed in the preparation of the novel mono- and trimetallic titanium complexes {η^5:η^1-$(NMe_2CH_2)C_2B_9H_9CH_2NMe_2$}$Ti(NMe_2)_2$ and [η^5:η^1-{$(NMe_2CH_2)C_2B_9H_9CH_2NMe_2$}$Ti(NMe_2)$]2-$\mu^3$-O-$Ti(NMe_2)_2$.

The preparation of new types of constrained-geometry complexes comprising various donor groups is currently of interest because of remarkable activity for copolymerization of ethylene with α-olefins.[1] For example, the incorporation of the versatile dicarbollide ancillary ligand into a donor chelate array through the functionalization of the C_2B_3 unit with various pendant donors is an effective means of altering the coordination environment of the parent non-functionalized dicarbollyl compounds.[2] Recently, a chelating dicarbollide ligand with an aminoalkyl donor was investigated in the context of ligand design for homogeneous olefin polymerization catalysts.[3] In such a ligand system, the amine coordinates only weakly to group 4 metals and forms relatively labile complexes due to the lack of a π-donor capability. As a consequence, a hetero-bifunctional ligand containing two amine donors, one firmly bound to the metal center and another weakly bonded, which can temporarily block and protect a metal coordinate site, holds promise as a novel class of ligands for olefin polymerization. In this context, we report the synthesis and crystal structural characterization of the multidentate ligand *nido*-7,8-$(NMe_2CH_2)_2$-7,8-$C_2B_9H_{11}$ (**2**) and its use in the preparation of the monometallic diaminodicarbollyl derivative {η^5:η^1-$(NMe_2CH_2)C_2B_9H_9CH_2NMe_2$}$Ti(NMe_2)_2$ (**3**) and the trimetallic complex [η^5:η^1-{$(NMe_2CH_2)C_2B_9H_9CH_2NMe_2$}-$Ti(NMe_2)$]$_2$-$\mu^3$-O-$Ti(NMe_2)_2$ (**4**), obtained by reacting the ligand with $Ti(NMe_2)_4$ and $Ti(NMe_2)_4/O_2$, respectively.

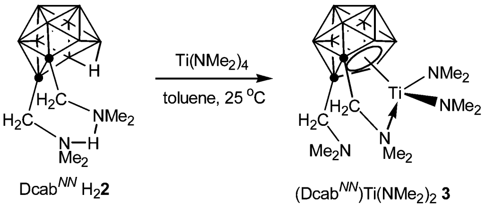
The new diaminoalkyl-*o*-carboranyl ligand **1** (Cab^{NN}) which contains two pendant amine donors was synthesized in excellent yield from commercially available starting materials (Scheme 1).

Thus, the one-pot generation of **1** was accomplished by *in situ* deprotonation of *o*-carborane with two equivalents of *n*-butyllithium and treatment with Eschenmoser's salt ($CH_2NMe_2^+I^-$). The straightforward and complete conversion of *closo*-diamino-*o*-carborane (**1**) into *nido*-dicarbollyl-diamino ligand **2** (Dcab*NN*H_2) was then achieved by heating in neat methanol.‡ An X-ray structural determination on crystals formed from the reaction revealed the formula of the salt to be the zwitterionic form of *nido*-(*N*,*N*′-μ-H)-7,8-$(NMe_2CH_2)_2$-7,8-$C_2B_9H_{10}$ with a dimethylamino unit linked to the dimethylammonium cation by a N–H···N hydrogen bond.[4]§†



Scheme 1 Synthesis of the diamido bridging ligands **1** and **2**. (*i*) (*a*) 2 *n*-BuLi, toluene, 25 °C; (*b*) 2 $CH_2NMe_2^+I^-$, toluene, 110 °C; (*ii*) CH_3OH, 65 °C.

The monometallic diaminodicarbollyl derivative (Dcab^{NN})-$Ti(NMe_2)_2$ (**3**) was prepared by treatment of **2** with $Ti(NMe_2)_4$ (eqn. 1).



(1)

The new multidentate dicarbollide titanium complex **3** was characterized by X-ray diffraction studies and NMR (^{1}H, ^{13}C, and ^{11}B) spectroscopy.[5]§† Several structural features were deduced from the spectral data of complex **3**. The deprotonation of the ligand **2** was evident from the disappearance of the bridge hydrogens of B–H–B and N–H–N (^{1}H NMR: δ −2.05 and 3.49). The coordination of one of the nitrogen atoms of the amine to the titanium was evident from the downfield shift of aminomethyl protons in the ^{1}H NMR spectrum. The C_1 symmetry of **3** was evident from the appearance of an AB pattern for the bridgehead methylene group and a broad singlet for the non-coordinated aminomethyl unit. The optimized geometry for compound **3** is in very good agreement with the X-ray structure obtained for **3** (Fig. 1).†

The non-coordinated amine tether in **3** had the potential to react with additional $Ti(NMe_2)_4$; therefore, the further treatment of **3** with $Ti(NMe_2)_4$ was investigated. The progress of the reaction of **3** with one equivalent of $Ti(NMe_2)_4$ in refluxing toluene-d_8 was monitored by ^{1}H NMR spectroscopy; this resulted in the disappearance of the aminomethyl peak of the

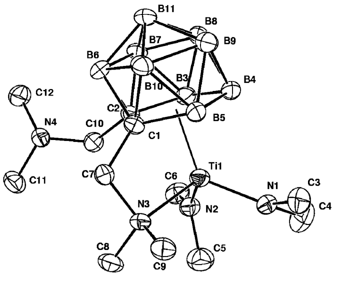


Fig. 1 Molecular structure of **3** with crystallographic labeling scheme (thermal ellipsoids with 40% probability). Selected distances (Å) and angles (°): Ti(1)–N(1) 1.889(4), Ti(1)–N(2) 1.901(4), Ti(1)–N(3) 2.240(3), Ti(1)–C(1) 2.406(4), Ti(1)–C(2) 2.534(4), Ti(1)–B(3) 2.458(5), Ti(1)–B(4) 2.418(5), Ti(1)–B(5) 2.344(5); N(1)–Ti(1)–N(2) 99.8(2), N(1)–Ti(1)–N(3) 107.6(2), N(2)–Ti(1)–N(3) 102.7(1).

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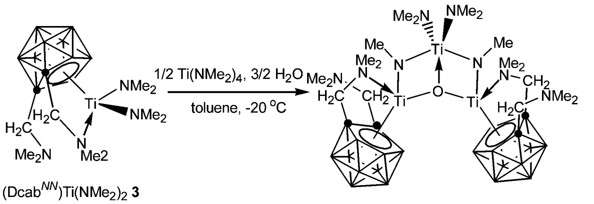
† Electronic supplementary information (ESI) available: experimental details and spectral data for **1–4** and crystal data for **2–4**. See http://www.rsc.org/suppdata/cc/b3/b301772a/

DOI: 10.1039/b301772a

non-coordinated amine tether and the formation of a new amidomethyl peak (δ 3.36) for the added $Ti(NMe_2)_4$. The mass spectrum of the product had a molecular ion at *m/z* 802. To our surprise, an X-ray study of **4** revealed it to be the oxygen insertion product of two dicarbollyl titanium units into the Ti–N bonds of the incoming $Ti(NMe_2)_4$ (eqn. 2).§



(2)

(Dcab^{NN})Ti(NMe$_2$)$_2$ **3**

(Dcab^{NN})$_2$(μ^3-O)(μ^2-NMe)Ti$_3$(NMe$_2$)$_2$ **4**

As shown in Fig. 2, the hydrolysis caused a dramatic change in the coordination environments, from a monometallic structure in **3** to trimetallic in **4**. At the core of the solid-state structure is a Ti_3N_2O ladder composed of two planar edge-fused (Ti_2NO) rings which incorporate the original one-armed tether of **3**. The imido nitrogen atoms in **4** bridge two titanium centers with nearly equal Ti–N distances. Both amido nitrogen atoms are coordinated to the Ti(1) atom with slightly shorter Ti–N distances than those of imido nitrogen–titanium bonds. The complex contains two types of titanium centers: the five-coordinate Ti(1) atom with one oxygen and four nitrogen atoms, and the four-coordinate Ti(2) and Ti(3) atoms with one dicarbollyl ligand, one oxygen, and two nitrogen atoms. The environment around the five-coordinate Ti(1) atom could be described as a distorted trigonal bipyramid in which N(1) and N(2) atoms occupy the axial positions.[6] The two remaining titanium atoms have approximately tetrahedral arrangements.

The formation of compound **4** raises the following question. What is the source of the oxygen atoms? A possible solution is that traces of water in the solvent entered the system, resulting in oxygen incorporation. To generate compound **4**, in an independent experiment, we carried out the controlled hydrolysis of a mixture of **3**, $Ti(NMe_2)_4$, and H_2O in 2 : 1 : 3 ratio in toluene at -20 °C. The ^1H and ^{13}C NMR analyses of the yellow powder that was produced were identical to those of **4**. A similar insertion of the oxo functionality into titanium has been observed in the early work of Lappert on the chemoselective addition of protic compound to the Ti–NMe$_2$ group.[7]

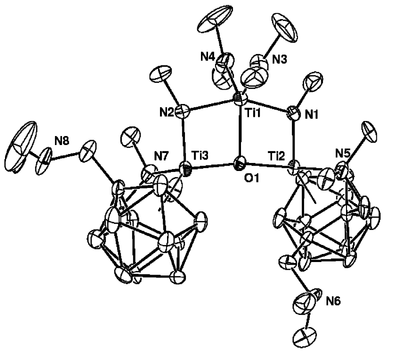


Fig. 2 Molecular structure of **4** with crystallographic labeling scheme (thermal ellipsoids with 25% probability). Selected distances (Å) and angles (°): Ti(1)–N(1) 2.071(9), Ti(1)–N(2) 2.11(1), Ti(1)–N(3) 1.85(1), Ti(1)–N(4) 1.87(1), Ti(1)–O(1) 2.057(8), Ti(2)–N(1) 1.77(1), Ti(2)–N(5) 2.24(1), Ti(2)–O(1) 1.937(7), Ti(3)–N(2) 1.81(1), Ti(3)–N(7) 2.20(1), Ti(3)–O(1) 1.897(7); N(3)–Ti(1)–N(4) 108.9(8), N(3)–Ti(1)–O(1) 122.6(6), N(4)–Ti(1)–O(1) 128.5(6), N(1)–Ti(1)–N(2) 155.5(4), N(1)–Ti(2)–O(1) 87.9(4), Ti(3)–O(1)–Ti(2) 170.8(4), Ti(2)–O(1)–Ti(1) 94.4(3).

This work was supported by Grant No. R03–2001-00030 from the Basic Research Program of the Korean Science and Engineering Foundation.

Notes and references

‡ *Synthesis* of **2**: compound **1** (1.03 g, 4.0 mmol) was dissolved in degassed MeOH (100 mL), and the reaction mixture was heated at reflux for 12 h. The resulting precipitate was collected by filtration and washed several times with degassed MeOH. The crude product was purified by recrystallization from acetone–diethyl ether to yield **2** (0.95 g, 3.8 mmol) as a colorless crystalline solid in 96% yield.

§ *Crystal data* for **2**: $C_8B_9H_{27}N_2$, M_r = 248.61, monoclinic, space group $P2_1/n$, a = 8.3868(5), b = 17.6878(8), c = 10.6643(9) Å, β = 99.485(6)°, V = 1560.4(2) Å^3, T = 293 K, Z = 4, D_c = 1.058 g cm^{-3}, μ(Mo-Ka) = 0.053 mm^{-1}, 3308 reflections measured, 3061 unique (R_{int} = 0.0375). F^2 refinement, R_1 = 0.0663 ($I > 2\sigma(I)$), wR_2 = 0.2070 (all data). CCDC 193018

Crystal data for **3**: $C_{12}B_9H_{37}N_4Ti$, M_r = 382.65, monoclinic, space group $P2_1/n$, a = 9.203(1), b = 15.714(2), c = 14.790(2) Å, β = 92.438(3)°, V = 2137.0(5) Å^3, T = 223 K, Z = 4, D_c = 1.189 g cm^{-3}, μ(Mo-Ka) = 0.404 mm^{-1}, 11211 reflections measured, 3982 unique (R_{int} = 0.1002). F^2 refinement, R_1 = 0.0740 ($I > 2\sigma(I)$), wR_2 = 0.1710 (all data). CCDC 193019.

Crystal data for **4**: $C_{22}B_{18}H_{68}N_8OTi_3\cdot2.5C_7H_8$, M_r = 1029.40, triclinic, space group Pi, a = 12.596(1), b = 13.048(1), c = 18.368(1) Å, a = 80.984(7), β = 82.147(7), γ = 80.152(9)°, V = 2918.8(5) Å^3, T = 293 K, Z = 2, D_c = 1.148 g cm^{-3}, μ(Mo-Ka) = 0.438 mm^{-1}, 11997 reflections measured, 11443 unique (R_{int} = 0.1673). F^2 refinement, R_1 = 0.1168 ($I > 2\sigma(I)$), wR_2 = 0.3165 (all data). CCDC 193020. See http://www.rsc.org/suppdata/cc/b3/b301772a/ for crystallographic data in .cif or other electronic format.

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