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Chemistry of Group 4 metals supported by carbazole ligation

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A series of new derivatives of titanium and zirconium containing carbazole ligation have been isolated and studied. Treatment of $[Zr(NMe_2)_4]$ with carbazole (cbH) leads to the adduct $[Zr(cb)_2(NMe_2)_2(NHMe_2)]$. Structural studies (trigonal bipyramidal with axial cb and NMe_2) show the Zr–N(carbazole) distances to be 0.15 Å longer than the Zr–NMe_2 distances. This is consistent with almost negligible nitrogen-p to metal-d π-bonding from the carbazole ligands. Treatment of $[M(CH_2Ph)_4]$ (M = Ti or Zr) with cbH leads to the derivatives $[Zr(cb)_4]$ and $[Ti(cb)_2(CH_2Ph)_2]$. The latter reacts with 2,6-dimethylphenyl isocyanide (xyNC) to generate the corresponding bis(iminoacyl) derivative, the iminoacyl carbon chemical shift of δ 246.9 in the ^{13}C NMR of which indicates η^2-C,N binding. The reaction of the more bulky alkyl substrate $[Ti(CH_2SiMe_3)_4]$ with cbH at 100 °C the reaction produces a sparingly soluble, red crystalline product identified as the alkylidene bridged dimer $[(cb)_2Ti(\mu\text{-}CHSiMe_3)_2Ti(cb)_2]$ which was structurally characterized. Treatment of it with xyNC (>3 equivalents) produces a single organometallic species [(cb)Ti(μ-cb)-(μ-xyNCCSiMe$_3$){μ-xyNCC(SiMe$_3$)CHNxy)Ti(cb)] and one equivalent of free carbazole. The molecular structure could only be elucidated by a solid state structure that shows it to be dinuclear, containing a total of three equivalents of isocyanide within two distinct bridging units. Two terminal and one non-symmetrically bridged carbazole ligand are also present. The reaction of $[TiCpCl_3]$ with potassium carbazolate (Kcb) leads to formation of $[TiCp(cb)Cl_2]$ (structurally characterized) which can readily be converted into the dimethyl $[TiCp(cb)Me_2]$.

Introduction

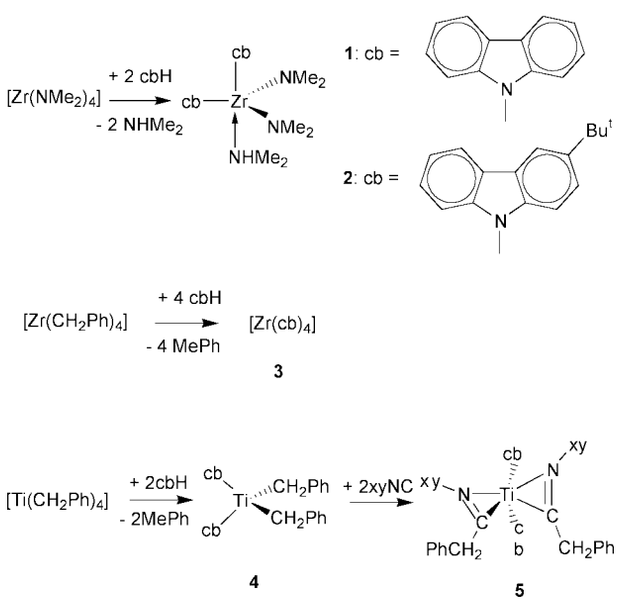
Complexes with ancillary cyclopentadienyl groups, a class of ligands pioneered by Wilkinson and Birmingham,[1] have dominated many of the developments in the area of early d-block metal chemistry. The search for new ligand systems to replace the cyclopentadienyl ligand has been a major area of recent research in inorganic and organometallic chemistry. Specifically, there has been considerable interest in the organometallic chemistry of the Group 4–6 metals associated with "hard" donor ligation.[2–4] Within this context the search for new types of amido ligation is also a rapidly expanding area of chemistry with chelating, tripodal and hybrid metallocene–amide ligands all being developed to support novel organometallic and inorganic chemistry at early transition metal centers.[5–12]

In the context of this background we have been exploring the inorganic and in particular organometallic chemistry of ligands derived from the carbazole (cbH) nucleus. This is a class of ligands that have so far been underutilized.[13,14] The choice of the carbazole ligand was stimulated by an expectation that the presence of the two co-planar aryl rings would decrease nitrogen-p to metal-d π donation, possibly leading to derivatives that exhibit different chemistry than found with more strongly π-donating dialkylamido ligation. We have previously studied niobium and tantalum derivatives supported by carbazole ligation and have isolated many interesting complexes including a ditantalum hexahydride compound and "1,3-dimetallabenzenes".[15] In this paper we report the synthesis of a mixed carbazole–amide zirconium complex and of organotitanium derivatives supported by carbazole ligation. Some aspects of this work have been communicated.[16]

Results and discussion

Synthesis and spectroscopic characterization of compounds

The tetra-amido zirconium compound $[Zr(NMe_2)_4]$ has been shown to undergo transamination reactions with amines resulting in the displacement of the more volatile dimethylamine group.[17] The addition of two equivalents of carbazole to a toluene solution of $[Zr(NMe_2)_4]$[18] at 100 °C produces the disubstituted compound $[Zr(cb)_2(NMe_2)_2(NHMe_2)]$ **1** (Scheme 1).



Scheme 1

The reaction was performed under an N_2 atmosphere and the evolved $NHMe_2$ allowed to escape *via* the mercury bubbler of a Schlenk vacuum system. Compound **1** was obtained as a pale white crystalline material, which was only sparingly soluble in aromatic solvents. The 3-*tert*-butylcarbazole derivative $[Zr(cb\text{-}3Bu^t)_2Zr(NMe_2)_2(NHMe_2)]$ **2** was found to be significantly more soluble in hydrocarbon solvents and saturated C_6D_6

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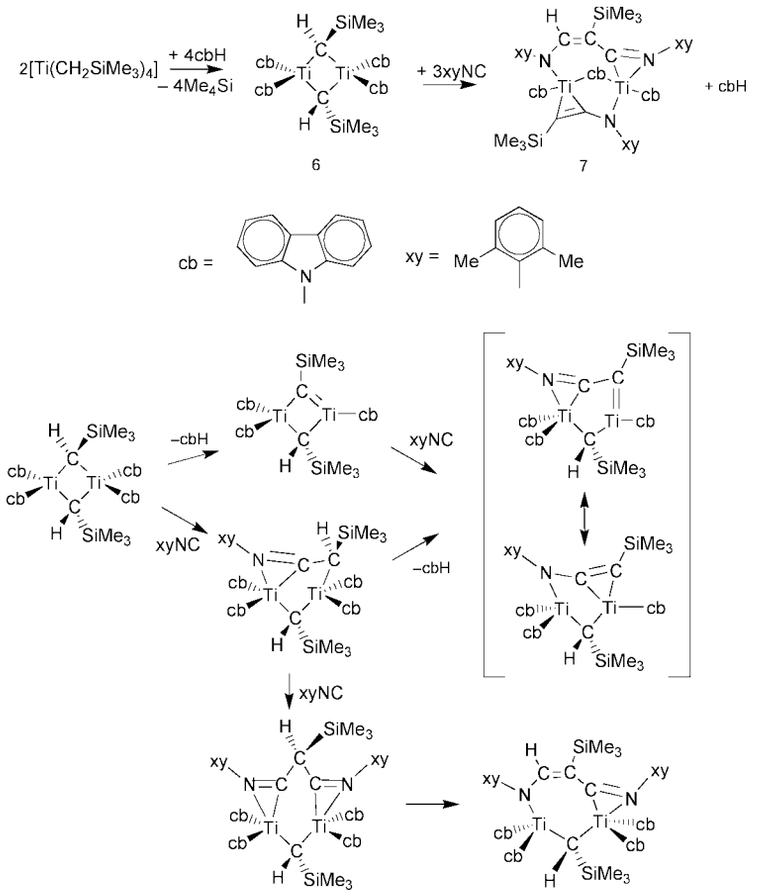


Scheme 2

solutions were sufficiently concentrated to detect the NMe_2 and *t*-butyl carbons by ^{13}C NMR spectroscopy.

The reaction of the zirconium tertra-benzyl $[Zr(CH_2Ph)_4]$[19] with an excess of carbazole in benzene at 105 °C produces the tetra-substituted derivative $[Zr(cb)_4]$ **3** (Scheme 1) and four equivalents of toluene. Compound **3** is obtained as a yellow crystalline material, which has very limited solubility in hydrocarbon solvents. Unfortunately, the crystals obtained were not satisfactory for an X-ray diffraction study. However, the ^1H NMR spectrum does show the expected carbazole resonances. Although monitoring the reaction in C_6D_6 solvent by ^1H NMR spectroscopy showed the formation of intermediate substitution products it was not possible to isolate them as pure materials. Presumably, carbazole does not possess the steric bulk necessary to selectively produce either the mono, bis or tris substitution products.

In contrast to the above zirconium chemistry the addition of carbazole (2 equivalents) to hydrocarbon solutions of $[Ti(CH_2Ph)_4]$ led to the bis(benzyl) compound $[Ti(cb)_2(CH_2Ph)_2]$ **4** in moderate yield (Scheme 1). The spectroscopic data on **4** indicate that the benzyl ligands are η^1 bound.[20] Solutions of **4** react with two equivalents of 2,6-dimethylphenyl isocyanide (xyNC) to produce the bis(η^2-iminoacyl) complex **5** (Scheme 1). The iminoacyl carbon chemical shift of δ 246.9 in the ^{13}C NMR spectrum indicates η^2-C,N binding, and is within the range of δ 215–263 found for Group 4 metal η^2-iminoacyl compounds.[21]

The reaction of the more bulky alkyl substrate $[Ti(CH_2SiMe_3)_4]$[22] with carbazole is slow (as monitored by ^1H NMR) at ambient temperatures. At 100 °C it produces a sparingly soluble, red crystalline product identified as the alkylidene bridged dimer $[(cb)_2Ti(\mu\text{-}CHSiMe_3)_2Ti(cb)_2]$ **6** (Scheme 2). In the ^1H NMR spectrum of **6** a singlet at δ 14.75 can be assigned to the alkylidene proton. The terminal alkylidene complex $[Ti(C_5H_5)_2(=CHCMe_3)(PMe_3)]$ has its Ti=C*H* resonance at δ 12.32, not quite as far downfield as the signals of dimeric **6**.[23] The insolubility of **6** precluded its analysis by ^{13}C NMR spectroscopy.

The formation of the alkylidene-bridged dimer **6** occurs by a still undetermined pathway. The reaction mixture has yet to produce the anticipated product $[Ti(cb)_2(CH_2SiMe_3)_2]$. Attempts to trap this compound by conducting the reaction in the presence of donor ligands such as pyridine or phosphines have failed. One possible pathway for the formation of **6** is an α-hydrogen abstraction within $[Ti(cb)_2(CH_2SiMe_3)_2]$ and finally dimerization. A less likely alternative is formation of $[Ti(cb)_3(CH_2SiMe_3)]$ followed by elimination of free carbazole.

Treatment of compound **6** with xyNC (>3 equivalents) slowly (^1H NMR) produces a single organometallic species $[(cb)Ti(\mu\text{-}cb)(\mu\text{-}xyNCCSiMe_3)\{\mu\text{-}xyNCC(SiMe_3)CHNxy)Ti(cb)]$ **7** (Scheme 2) and one equivalent of free carbazole. The molecular structure of **7** could only be elucidated by a solid state structure that shows it to be dinuclear, containing a total of three equivalents of isocyanide 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 resonance picture for **7** shown in Scheme 2. In the ^1H NMR spectrum of **7** six well resolved signals are observed for the *ortho*-methyl groups indicating slow rotation of the three xylyl groups on the NMR timescale.

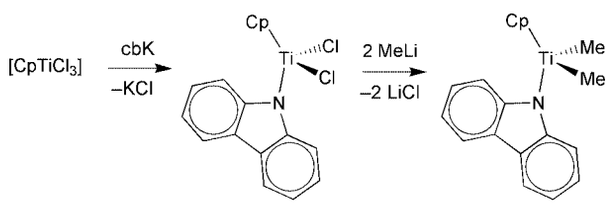
Although the exact sequence of events leading to compound **7** is presently unknown, reasonable elementary steps for its formation can be proposed (Scheme 2). Shown are possible pathways for the formation of the two bridging units in **7**. Based upon the structural studies (see below) one of the bridging units in **7** is best described as an amido-alkyne ligand. 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

Table 1 Selected bond distances (Å) and angles (°) for $[Zr(cb)_2(NMe_2)_2(NHMe_2)]$ **1**

Zr–N(11)	2.213(3)	Zr–N(4)	2.034(4)
Zr–N(21)	2.196(3)	Zr–N(5)	2.439(4)
Zr–N(3)	2.022(4)		
N(3)–Zr–N(4)	112.5(1)	N(3)–Zr–N(21)	129.0(1)
N(3)–Zr–N(11)	90.2(1)	N(4)–Zr–N(21)	117.1(1)
N(4)–Zr–N(11)	102.8(1)	N(21)–Zr–N(11)	90.0(1)
N(3)–Zr–N(5)	84.6(1)	N(4)–Zr–N(5)	90.1(1)
N(11)–Zr–N(5)	167.0(1)	N(21)–Zr–N(5)	84.1(1)

hydrogen abstraction takes place by a carbazole ligand. The other bridging unit corresponds to the insertion of two equivalents of isocyanide into an alkylidene bridge combined with a 1,2-hydrogen shift. The transfer of adjacent hydrogen to iminoacyl carbon atoms has precedence.[21] What is not known is which of the two bridging units is formed first. Mechanistic studies of the reaction pathway are hindered by the low solubility of **6**, *i.e.* during the reaction it is essentially swamped by a large excess of xyNC throughout the reaction.

All of the above reactions involve introduction of the carbazole ligand by protonation of suitable leaving groups by parent carbazole. However, an alternative approach makes use of the reagent potassium carbazolate (Kcb) which can readily be prepared from KOH and carbazole. Hence the reaction of $[TiCpCl_3]$ with Kcb leads to formation of $[TiCp(cb)Cl_2]$ **8** (Scheme 3). This compound is easily isolated in high yield as a



8 **9**

Scheme 3

red-purple crystalline solid. The solution NMR spectroscopic properties are as expected with single C_5H_5 and cb resonances. In the ^{1}H NMR spectrum the C_5H_5 protons resonate at δ 5.79 which compares well with the range of δ 5.6–5.8 for Cp protons found in $[TiCp(OAr)Cl_2]$ derivatives isolated previously in our laboratory.[24]

Treatment of $[TiCp(cb)Cl_2]$ **8** with 2 equivalents of MeLi leads to the corresponding dimethyl compound $[TiCp(cb)Me_2]$ **9** (Scheme 3) as a red solid in good yield. The solution NMR properties of **9** are as expected with single resonances for the C_5H_5 and methyl protons. Attempts to isolate single crystals for an X-ray diffraction study have thus far been unsuccessful. Additional alkylation reactions with other lithium reagents including PhLi, $LiCH_2CMe_3$ and $LiCH_2SiMe_3$ have failed to produce isolable products. The reaction of $[TiCp(cb)Cl_2]$ **8** with 2 equivalents of $PhMgCH_2Cl$ at −78.0 °C produced a complex mixture, within which was identified the known compound $[TiCp(CH_2Ph)_3]$. It appears that the carbazole ligand is labile to substitution.

Structural studies

The compounds **1**, **5**, **6**, **7** and **8** were all subjected to single-crystal X-ray diffraction analysis. The molecular structure of **1** is shown in Fig. 1, and selected structural parameters can be found in Table 1. The coordination geometry about the zirconium atom corresponds to a distorted trigonal bipyramid with an axial carbazole and dimethylamine ligand. The Zr–N(carbazole) distances are 2.213(3) and 2.196(3) Å respectively. The Zr–N(NMe_2) distances are 2.022(4) and 2.034(4) Å, typical

Table 2 Selected bond distances (Å) and angles (°) for $[Ti(cb)_2(\eta^2\text{-xyNCCH}_2Ph)_2]$ **5**

Ti–N(1)	2.017(2)	Ti–N(31)	2.008(2)
Ti–N(2)	2.150(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)		

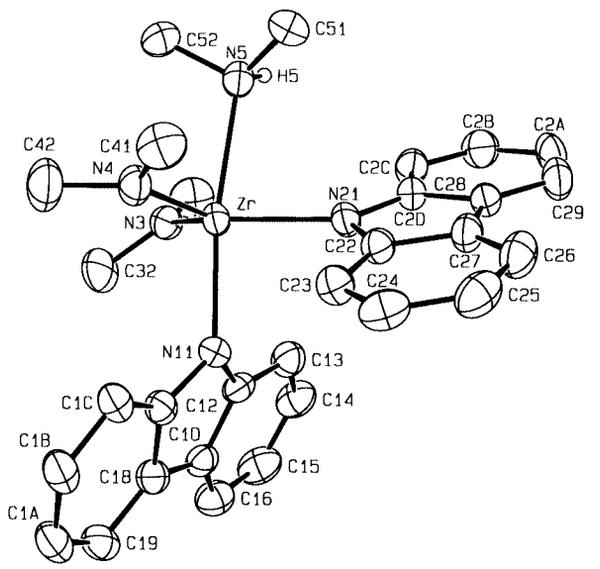


Fig. 1 Molecular structure of $[Zr(cb)_2(NMe_2)_2NHMe_2)]$ **1**.

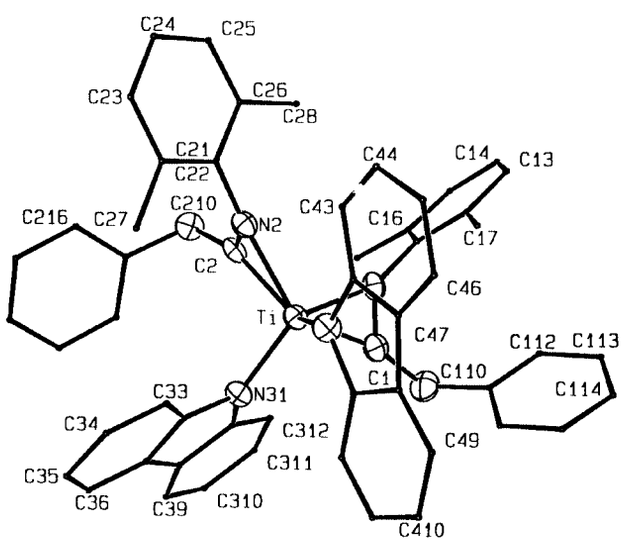


Fig. 2 Molecular structure of $[Ti(cb)_2(xyNCCH_2Ph)_2)]$ **5**.

of Zr–amide bonds and indicative of a significant degree of Me_2N-to-Zr π bonding.[25] The >0.15 Å difference is significant and bears out the expectation that carbazole is a weaker π donor than dialkylamido ligands. The even longer Zr–N(amine) distance of 2.439(4) Å is consistent with a Zr–N(sp^3) single bond and compares well with related Zr–N(neutral donor) distances reported.[12c]

The molecular structure of compound **5** is shown in Fig. 2 (Table 2). It is one of the few structurally characterized Group 4 metal complexes that contain two iminoacyl ligands.[26] The coordination geometry and iminoacyl parameters in **5** are similar to that found in other Group 4 metal bis(η^2-iminoacyl) compounds,[21,26] the only significant difference being the non-parallel orientation of the iminoacyl units in **5**.

Table 3 Selected bond distances (Å) and angles (°) for $[(cb)_2Ti(\mu\text{-}CHSiMe_3)_2Ti(cb)_2]$ **6**

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)	N(29)–Ti–C(30)	114.20(8)

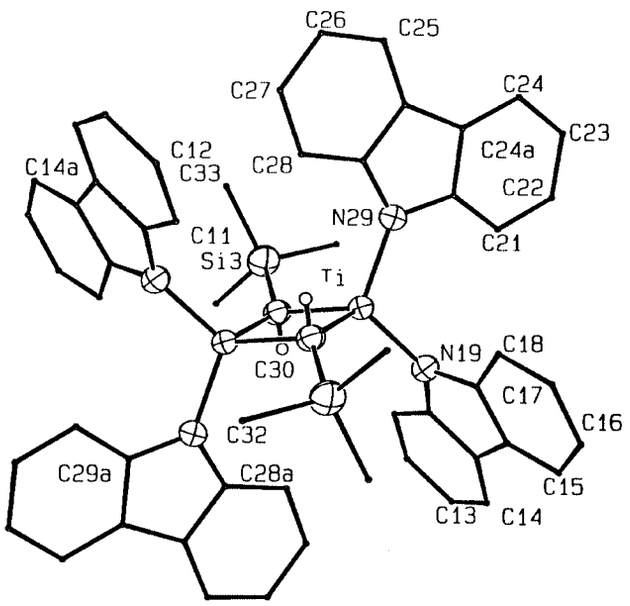


Fig. 3 Molecular structure of $[(cb)_2Ti(\mu\text{-}CHSiMe_3)_2Ti(cb)_2]$ **6**.

Fig. 3 (Table 3) shows the molecular structure for compound **6**. The molecule is dimeric and consists of a crystallographically imposed center of inversion. The coordination geometry around each titanium atom is distorted tetrahedral. The structural parameters for the 1,3-dimetallacyclobutane unit in **6** are similar to those found in related molecules and in particular the methylidene bridged $[(Cy_2N)_2Ti(\mu\text{-}CH_2)_2Ti(NCy_2)_2]$.[3] For example the Ti–C(30) distances of 2.026(2) and 2.035(2) (Å) in **6** compare well with the Ti–CH_2 distances of 2.020(5) and 2.016(5) Å in Gamboratta's complex.

The molecular structure of compound **7** is shown in Fig. 4 (Table 4). The first non-symmetrically bridging carbazole ligand with distances of 2.018(7) and 2.321(7)Å to the titanium metal centers is observed. An interesting feature of the molecular structure of **7** 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).[21] This value combined with the long C(4)–N(5) distance are consistent with the much debated amido-carbene resonance picture.[27] The second nitrogen atom within this bridging unit possess an amido type interaction [Ti(1)–N(1) 2.064(7)Å]. The other bridging unit within this molecule can be described as an amido-alkyne ligand (with some contribution from an iminoacyl ligand). This group is bound to Ti(2) *via* the amido nitrogen atom while the alkyne unit is strongly η^2 bound to Ti(1) resulting in a metallacyclopropene ring. Identical ligands have been formed by addition of xyNC to trimethylsilylmethylidyne bridges in 1,3-dimetallacyclobutadiene derivatives of Nb, Ta.[15b]

The solid state structure (Fig. 5) of compound **8** revealed a pseudo-tetrahedral coordination environment around the titanium metal center. The Ti-N(11) distance of 1.969(3)Å (Table 5) is similar to the titanium–carbazole distance found in other compounds isolated in this series. This distance is slightly longer (*ca.* 0.05 Å) than the Ti–N values of 1.912(9) and 1.923(14) Å reported for the related compound

Table 4 Selected bond distances (Å) and angles (°) for [(cb)Ti(μ-cb)-(μ-xyNCCSiMe$_3$){μ-xyNCC(SiMe$_3$)CHNxy)Ti(cb)] **7**

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)	2.16(1)	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)		
N(11)–Ti(1)–N(1)	101.2(3)	N(21)–Ti(2)–N(6)	96.9(3)
N(11)–Ti(1)–N(31)	87.0(3)	N(21)–Ti(2)–N(31)	106.4(3)
N(11)–Ti(1)–C(8)	106.4(3)	N(6)–Ti(2)–N(5)	117.3(3)
N(31)–Ti(1)–N(1)	143.3(3)	N(5)–Ti(2)–N(21)	104.0(3)
N(1)–Ti(1)–C(8)	99.3(3)	N(6)–Ti(2)–N(31)	116.8(3)
Ti(1)–N(1)–C(2)	112.8(5)	Ti(2)–N(6)–C(7)	80.3(5)
Ti(1)–C(8)–C(7)	76.0(5)	Ti(2)–N(5)–C(4)	84.8(5)
Ti(1)–C(7)–Ti(2)	82.3(3)	N(5)–C(4)–C(3)	127.7(8)

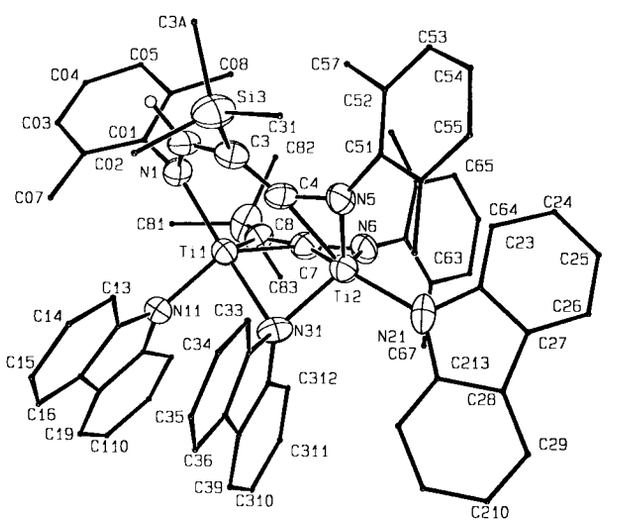


Fig. 4 Molecular structure of [(cb)Tu(μ-cb)(μ-xyNCCSiMe$_3$){μ-xy-NCC(SiMe$_3$)CHNxy)Ti(cb)] **7**.

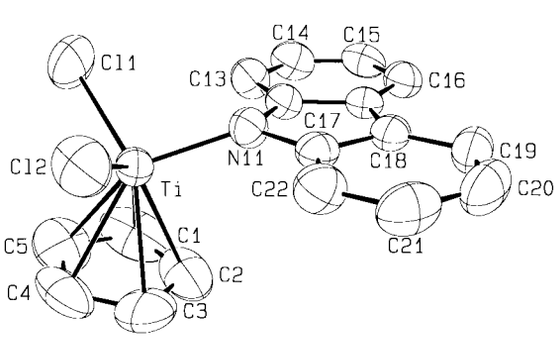


Fig. 5 Molecular structure of $[TiCp(cb)Cl_2]$ **8**.

$[TiCp^*(NMe_2)_3]$,[28] once again indicative of a less π-donating carbazole ligand.

Experimental

All operations were carried out under a dry nitrogen atmosphere or *in vacuo* either in a Vacuum Atmosphere Dri-Lab or by standard Schlenk techniques. Hydrocarbon solvents were dried by distillation from sodium–benzophenone and stored under dry nitrogen. The compounds 3-*tert*-butylcarbazole,[29] Kcb,[30] $[Zr(NMe_2)_4]$,[18] $[Zr(CH_2Ph)_4]$,[19] $[Ti(CH_2Ph)_4]$,[19] $[Ti(CH_2SiMe_3)_4]$,[22] and $[TiCpCl_3]$[31] were prepared by literature methods. 9H-Carbazole was purchased from Aldrich Chemical Company, 2,6-dimethylphenyl isocyanide from Fluka Chemical

Table 5 Selected bond distances (Å) and angles (°) for [TiCp(cb)Cl_2] **8**

Ti–N(11)	1.969(3)	Ti–C(2)	2.311(5)
Ti–Cl(1)	2.236(2)	Ti–C(3)	2.329(5)
Ti–Cl(2)	2.239(1)	Ti–C(4)	2.351(5)
Ti–C(1)	2.300(5)	Ti–C(5)	2.341(5)
N(11)–Ti–Cl(1)	102.3(1)	N(11)–Ti–Cl(2)	106.2(1)
Cl(1)–Ti–Cl(1)	101.53(6)	Cp–Ti–N(11)	115.2(2)
Cp–Ti–Cl(1)	116.3(3)	Cp–Ti–Cl(2)	113.8(2)

Company. The ^{1}H and ^{13}C NMR spectra were recorded on Varian Associates Gemini 200 and General Electric QE-300 spectrometers and referenced to protio impurities of commercial benzene-d_6. Microanalyses were obtained in-house at Purdue University.

Syntheses

[Zr(cb)$_2$(NMe$_2$)$_2$(NHMe$_2$)] 1. To a toluene solution (20 mL) of [Zr(NMe$_2$)$_4$] (1.00 g, 3.74 mmol) was added carbazole (1.31 g, 7.83 mmol). The light yellow solution was heated at 100 °C for 24 h under N_2, while allowing the evolving $NHMe_2$ to escape *via* a mercury bubbler. Upon cooling a light white solid precipitated. The solid was washed with hexane (25 mL) and dried *in vacuo*. Yield: 1.57 g (75%). Calc. for $C_{30}H_{35}N_5Zr$: C, 64.71; H, 6.34; N, 12.58. Found: C, 64.46; H, 6.05; N, 11.87%. ^{1}H NMR (C_6D_6, 30 °C): δ 2.92 (s, NMe_2, 6 H), 1.40 (br, HN*Me*$_2$, 6 H) and 7.21–8.16 (m, aromatics, 16 H).

[Zr(cb-3Bu^t)$_2$(NMe$_2$)$_2$(NHMe$_2$)] 2. To a toluene solution (20 mL) of [Zr(NMe$_2$)$_4$] (1.00 g, 3.74 mmol) was added 3-*tert*-butylcarbazole (1.75 g, 7.84 mmol). The light yellow solution was heated at 100 °C for 24 h under N_2, while allowing the evolving $NHMe_2$ to escape *via* a mercury bubbler. Upon cooling a white solid precipitated. The solid was washed with hexane (25 mL) and dried *in vacuo*. Yield: 1.98 g (85%). ^{1}H NMR (C_6D_6, 30 °C): δ 2.96 (s, NMe_2, 6 H), 1.10 (br, HN*Me*$_2$), 1.42 (s, CMe_3, 9H) and 7.20–8.14 (m, aromatics, 16 H). ^{13}C NMR (C_6D_6, 30 °C): δ 32.4 (C*Me*$_3$), 34.9 (*C*Me$_3$) and 43.0 (NMe_2).

[Zr(cb)$_4$] 3. To a benzene (15 mL) solution of [Zr(CH_2Ph)$_4$] (0.35 g, 0.77 mmol) was added an excess of carbazole (0.54 g, 3.2 mmol). The brown solution was heated at 105 °C for 18 h, removed and allowed to cool slowly during which time yellow crystals precipitated. They were washed with hexane (25 mL) and dried *in vacuo*. Yield: 0.32 g (55%). Calc. for $C_{48}H_{32}N_4Zr$: C, 76.26; H, 4.27; N, 7.41. Found: C, 76.28; H, 3.98; N, 7.19%. ^{1}H NMR (C_6D_6, 30 °C): δ 7.73 (d, cb *ortho*) and 6.8–7.4 (m, aromatics).

[Ti(cb)$_2$(CH$_2$Ph$_2$)$_2$] 4. To a solution of $PhCH_2MgCl$ (15.52 g, 0.103 mol) in diethyl ether (200 mL) cooled to −55 °C was slowly added $TiCl_4$ (4.65 g, 0.025 mol) in hexane (30 mL). The resulting red mixture was stirred for 0.5 h at −40 °C before carbazole (8.18 g, 0.05 mol) was added rapidly. Toluene (200 mL) was added to aid stirring and the red solution stirred for 18 h at 25 °C. The solvent was removed *in vacuo* to yield a dark brown-red solid. Extraction of the solid with benzene and filtration gave a red solution. Removal of benzene *in vacuo* produced a red solid that was washed with hexane (25 mL) to yield the product. Yield: 3.80 g (28%). ^{1}H NMR (C_6D_6, 30 °C): δ 3.24 (s, C*H*$_2$Ph) and 6.58–7.91 (m, aromatics). ^{13}C NMR (C_6D_6, 30 °C): δ 98.3 (s, *C*H$_2$Ph).

[Ti(cb)$_2$(xyNCCH$_2$Ph)$_2$] 5. To a toluene (10 mL) solution of [Ti(cb)$_2$(CH_2Ph)$_2$] (0.18 g, 0.32 mmol) was added 2.0 equivalents of 2,6-dimethylphenyl isocyanide (0.08 g, 0.64 mmol). The red mixture was stirred for 24 h then cooled to −15 °C affording a red solid. The solid was washed with hexane (25 mL) and dried *in vacuo*. Calc. for $C_{56}H_{48}N_4Ti$: C, 81.54; H, 5.87; N, 6.79. Found: C, 78.65; H, 5.77; N, 6.00%. ^{1}H NMR (C_6D_6, 30 °C): δ 1.46 (s, *Me*C_6H_3), 3.69 (s, C*H*$_2$Ph) and 6.39–8.02 (m, aromatics). ^{13}C NMR (C_6D_6, 30 °C): δ 18.46 (*Me*C_6H_3), 43.49 (*C*H$_2$Ph) and 246.9 (xyN*C*).

[(cb)$_2$Ti(μ-CHSiMe$_3$)$_2$Ti(cb)$_2$] 6. To a benzene (15 mL) solution of [Ti(CH_2SiMe_3)$_4$] (1.00 g, 2.25 mmol) was added 2.4 equivalents of carbazole (0.93 g, 5.56 mmol). The brown solution was heated at 100 °C for 5 days during which time red crystals precipitated. They were washed with hexane (10 mL) and dried *in vacuo*. Yield: 0.74 g (71%). Calc. for $C_{56}H_{52}N_4Si_2Ti_2$: C, 72.09; H, 5.62; N, 6.01. Found: C, 71.76; H, 5.55; N, 5.94%. ^{1}H NMR (C_6D_6, 30 °C): δ −0.50 (s, μ-CHSi*Me*$_3$), 14.75 (s, μ-C*H*$SiMe_3$) and 6.6–7.8 (m, aromatics).

[(cb)Ti(μ-cb)(μ-xyNCCSiMe$_3$){μ-xyNCC(SiMe$_3$)CHNxy)-Ti(cb)] 7. To a toluene (5 mL) solution of [Ti(cb)$_2$(μ-CHSiMe_3)$_2$Ti(cb)$_2$] (0.10 g, 0.11 mmol) was added 3.0 equivalents of 2,6-dimethylphenyl isocyanide (0.04 g, 0.33 mmol). The brown solution was heated at 100 °C for 12 h, removed and allowed to cool slowly during which time red crystals precipitated. They were washed with hexane (10 mL) and dried *in vacuo*. Calc. for $C_{71}H_{74}N_6Si_2Ti_2$: C, 73.69; H, 5.92; N, 7.26. Found: C, 73.52; H, 6.04; N, 7.14%. ^{1}H NMR (C_6D_6, 30 °C): δ −0.14, −0.03 (s, $CSiMe_3$); 1.17, 1.64, 1.66, 2.45, 2.47, 2.55 (s, *Me*C_6H_3).

[TiCp(cb)Cl$_2$] 8. To a benzene (50 mL) solution of [$TiCpCl_3$] (2.00 g, 9.12 mmol) was added 1.1 equivalents of 9-potassiocarbazole (2.06 g, 10.03 mmol) over 15 min. The green solution became red and was stirred for 3.5 h, filtered, concentrated *in vacuo*, and layered with hexane (1 : 1). The red crystals that precipitated were washed with hexane (25 mL) and dried *in vacuo*. Yield: 2.38 g (70%). Calc. for $C_{19}H_{13}Cl_2NTi$: C, 61.00; H, 3.50; Cl, 18.95; N, 3.74. Found: C, 61.01; H, 3.64; Cl, 18.84; N, 4.08%. ^{1}H NMR (C_6D_6, 30 °C): δ 5.79 (s, C_5H_5) and 6.6–7.8 (m, aromatics).

[TiCp(cb)Me$_2$] 9. To a toluene (50 mL) solution of [TiCp(cb)Cl_2] (1.35 g, 3.61 mmol) at −78 °C was added a 1.4 M diethyl ether solution of MeLi (4.15 g, 7.94 mmol) dropwise over 15 min. The red solution turned darker red after the addition was complete. It was allowed to warm to room temperature and stirred for 6 h. The solution was filtered, the solvent removed *in vacuo* and the red solid recrystallized from pentane. Yield: 0.68 g (61%). ^{1}H NMR (C_6D_6, 30 °C): δ 1.47 (s, Ti(CH_3)$_2$, 6 H); 5.74 (s, C_5H_5, 10 H) and 7.04–8.08 (m, aromatics, 16 H). ^{13}C NMR (C_6D_6, 30 °C): δ 72.0 (CH_3) and 115.3 (C_5H_5).

X-Ray data collection and reduction

Crystal data and data collection parameters are contained in Table 6. A suitable crystal was mounted on a glass fiber in a random orientation under a cold stream of dry nitrogen. Preliminary examination and final data collection were performed with Mo-Kα radiation (λ = 0.71073 Å) on a Nonius KappaCCD diffractometer. Lorentz and polarization corrections were applied[32] and an empirical absorption correction using SCALEPACK.[33] Intensities of equivalent reflections were averaged. The structure was solved using the program PATTY in DIRDIF 92.[34] The remaining atoms were located in succeeding Fourier difference syntheses. Hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bonded. The structure was refined by full-matrix least squares where the function minimized was $\Sigma w(|F_o|^2 - |F_c|^2)^2$. Scattering factors were taken from ref. 35. Refinement

Table 6 Crystal data and data collection parameters for complexes **1** and **5**–**8**

	1	**5**·$\frac{1}{2}C_6H_6$	**6**	**7**	**8**
Formula	$C_{30}H_{35}N_5Zr$	$C_{59}H_{51}N_4Ti$	$C_{56}H_{52}N_4Si_2Ti_2$	$Ti_2C_{71}H_{68}N_6Si_2$	$TiC_{17}H_{13}NCl_2$
Formula weight	556.87	863.99	933.04	1157.35	350.11
Space group	$P2_1/n$ (no. 14)	$C2/c$ (no. 15)	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)	$R\bar{3}$ (no. 148)
a/Å	12.0969(8)	37.221(10)	10.0663(17)	12.7883(17)	33.5339(12)
b/Å	16.3502(13)	12.153(3)	10.481(2)	33.329(5)	33.5339(12)
c/Å	14.6666(6)	21.069(9)	13.170(3)	14.616(3)	33.5339(12)
α/°			109.165(15)		
β/°	110.339(4)	104.23(3)	104.984(15)	96.755(13)	
γ/°			93.619(15)		
V/Å^3	2720.0(6)	9237(10)	1251.1(10)	6186(3)	7018(8)
Z	4	8	1	4	18
T/K	203	203	296	233	296
R	0.063	0.045	0.036	0.074	0.069
R_W	0.162	0.112	0.041	0.184	0.150

was performed on a AlphaServer 2100 using SHELXS 97.[36] Crystallographic drawings were done using ORTEP.[37]

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