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Titanium N-heterocyclic carbene complexes incorporating an imidazolium-linked bis(phenol)†

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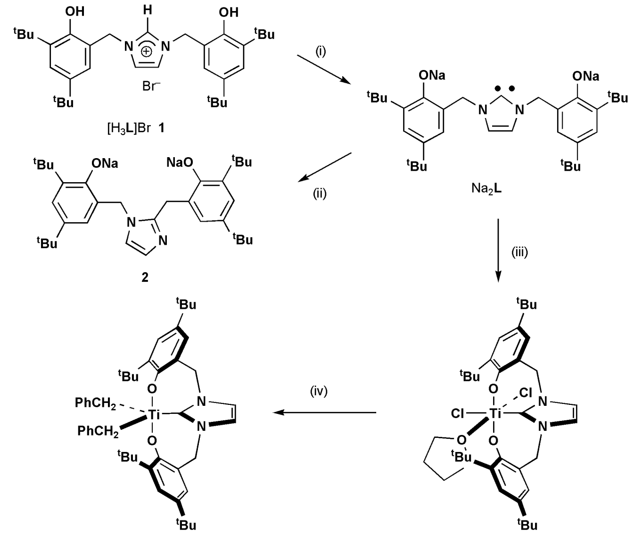
The synthesis and characterization of titanium complexes of the aryloxido-functionalized N-heterocyclic carbene ligand (L) is reported, in which the tridentate L ligand meridionally coordinates to the metal center.

The chemistry of N-heterocyclic carbenes (NHC) constitutes an active area of research because their metal complexes are highly active and very stable catalysts for various organic reactions.[1] The vast majority of NHC systems contain late transition metals, while NHC complexes of early transition metals are considerably less developed despite the great potential of this class of molecule.[2–4] This is due to the lack of NHC derivatives suitable for studies of early transition metal chemistry. In our ongoing program aimed at developing new ancillary ligands to support reactive metal centers, we are interested in the addition of a NHC function to multidentate aryloxido ligands.[5] The aryloxido group acts as an anchor and reduces the tendency for NHC dissociation. This enables us to explore the effect of NHC on the properties of early transition metal complexes. Here we describe the synthesis of titanium compounds with the aryloxide-NHC hybrid ligand. Recently, related alkoxy-functionalized NHC complexes of copper and silver have been reported.[6]

The proligand, 1,3-bis(4,6-di-*tert*-butyl-2-hydroxybenzyl)imidazolium bromide [H_3**L**]Br **1**, was prepared in 60% yield through step-wise alkylation on the nitrogen atoms of imidazole using 2-bromomethyl-4,6-di-*tert*-butylphenol. The ^{1}H and ^{13}C{^{1}H} NMR spectra of **1** are consistent with its formula. The most notable features are the resonances for imidazolium protons at 9.51 ppm and the corresponding imidazolium carbon at 139.1 ppm.

We sought to prepare the Na derivative of the ligand for use in subsequent salt metathesis reactions with metal halides. Treatment of [H_3**L**]Br with 3 equiv. of $NaN(SiMe_3)_2$ in THF at −78 °C resulted in the formation of Na_2**L**. However, the Na species Na_2**L** was thermolabile, readily decomposing at rt to the 2-alkylated imidazole derivative **2** *via* the 1,2-benzyl migration (Scheme 1). It is well known that 1,2-migration is a common reaction for singlet carbenes.[7] In a separate experiment, a freshly prepared [H_3L]Br–$NaN(SiMe_3)_2$ mixture was transferred into a THF solution of $TiCl_4(THF)_2$ at −78 °C to give a red solution, from which Ti(**L**)Cl_2(THF) **3** was isolated as a red powder in 74% yield.† In contrast to the sodium derivative Na_2**L**, the titanium complex **3** is thermally stable, as $CDCl_3$ samples stored at 60 °C for 24 h showed no signs of decomposition.

A crystal structure determination of **3** (Fig. 1) confirms the monomeric nature of the complex, where the tridentate **L** ligand meridionally coordinates to the metal center.‡ The pseudo-octahedral Ti is completed by one THF molecule and two mutually *cis* chlorine atoms. The Ti–C(carbene) distance of 2.200(9) Å falls within the range observed previously for Ti–NHC complexes [2.19–2.29 Å].[4] The dihedral angle between $TiCN_2$ and TiCO(1)O(2) planes is 31.5 °, and this twist in the ligand is necessary for meridional coordination. There is a significant difference (0.044 Å) between two Ti–Cl bond distances, the Ti–Cl(2) bond *trans* to the THF molecule being shorter. This may be attributed to the strong σ-donor properties of the NHC functional group.



Scheme 1 *Reagent and conditions*: (i) Na[N($SiMe_3$)$_2$], THF, −78 °C; (ii) THF, rt; (iii) $TiCl_4(THF)_2$, THF, −78 °C; (iv) $PhCH_2MgCl$, toluene, −78 °C.

The ^{1}H NMR spectrum of **3** in $CDCl_3$ at −50 °C is consistent with the solid-state structure. The *tert*-butyl groups appear as four individual singlets, while the methylene group protons appears as four broad peaks. On warming an NMR sample from −50 to 25 °C the four *tert*-butyl group singlets broaden and give rise to two singlets, and the four signals for the methylene protons coalesce. A solution of **3** in the presence of excess amount of THF show only one set of resonances for the THF protons, indicating a rapid exchange between free and coordinated THF molecules. A likely mechanism involving the

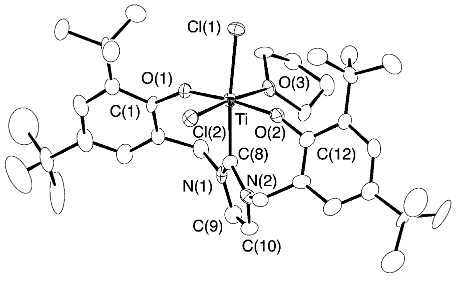


Fig. 1 The molecular structure of **3**. Selected bond distances (Å) and angles (°): Ti–Cl(1) 2.367(3), Ti–Cl(2) 2.323(3), Ti–O(1) 1.845(6), Ti–O(2) 1.850(6), Ti–O(3) 2.176(6), Ti–C(8) 2.200(9), N(1)–C(8) 1.360(11), N(2)–C(8) 1.362(11), C(9)–C(10) 1.33(1), O(1)–Ti–O(2) 170.6(3), Cl(1)–Ti–C(8) 168.3(2), Cl(2)–Ti–O(3) 174.9(2), Ti–O(1)–C(1) 151.7(6), Ti–O(2)–C(12) 160.5(6), N(1)–C(8)–N(2) 102.8(7).

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† Electronic supplementary information (ESI) available: full experimental, NMR and analytical data. See http://www.rsc.org/suppdata/cc/b3/b305745c/

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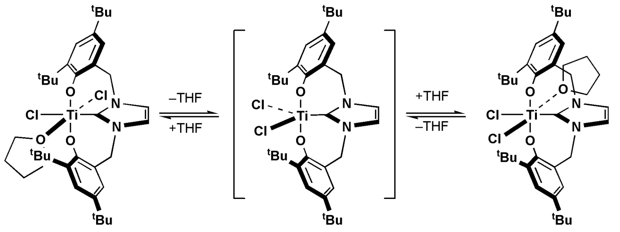
dissociation of THF, so equilibrating the *tert*-butyl protons, is described in Scheme 2. The $^{13}C\{^1H\}$ NMR signal of the carbene moiety is observed at 164 ppm, which is essentially invariant even at elevated temperatures. Thus the carbene moiety would remain bound to the metal center during this process.



Scheme 2

The chloro ligands in **3** can be substituted using 2 equiv. of $PhCH_2MgCl$ in Et_2O, forming the benzyl complex Ti(**L**)$(CH_2Ph)_2$ **4** as light yellow crystals in 30% isolated yield.† Analytical and ^1H and $^{13}C\{^1H\}$ NMR spectroscopic data are consistent with the formulation of **4**. In solution, **4** shows average C_2-symmetry at rt, with four signals being observed for the diasterotopic $N–CH_2$ and $Ti–CH_2$ protons. We have studied the dynamic behaviour of **4** by variable-temperature ^1H NMR line shape analysis for the exchange $N–CH_2$ and $Ti–CH_2$ resonances, giving the following activation parameters: $\Delta H^{\ddagger}$ = 64.8 kJ mol^{-1}; $\Delta S^{\ddagger} = -6.2$ J $mol^{-1}K^{-1}$. The activation parameters favor a nondissociative rearrangement and are comparable to those observed for $TiBr_2$(linked-bisphenoxido)[8] and PdBr(bis-carbene pincer).[9] The carbene signal of **4** appears at 188 ppm in its $^{13}C\{^1H\}$ NMR spectrum. This resonance is shifted to a lower field than that of **3**.

The complex displays a pseudo-trigonal-bipyramidal geometry in the solid-state (Fig. 2).‡ The **L** ligand is bound in a meridional fashion with the aryloxido donors occupying axial positions. The O(1)–Ti–O(2) angle of 166.91(9) ° deviates greatly from linearity. The phenyl groups of the two benzyl ligands are strongly bent toward the NHC moiety, because of the steric constraint caused by the two *tert*-butyl groups of the **L** ligand. The benzyl ligand in **4** has the open $Ti–C_{\alpha}–C_{ipso}$ angles of 109.3(2) and 113.9(2) °, which are normal for titanium-bound η^1-benzyl ligands.[10] The Ti–C(carbene) distance of 2.187(3) Å is shorter than that of **3** but is elongated relative to the Ti–C(benzyl) distances of 2.134(3) and 2.158(3) Å.

The bis(aryloxido) ligands with one additional donor have been shown to be a class of ancillary ligands whose Group 4 complexes exhibit the unique polymerization activity.[11] Therefore, a preliminary ethylene polymerization study was undertaken, and the new complexes are highly active[12] procatalysts for polymerization of ethylene. For example, ethylene was polymerized under MMAO activation of **3** (Al : Ti = 1000 : 1, 0.5 h, 1 L of toluene, 30 °C, 9 bar) with an activity of 290 kg mol_{Ti}^{-1} h^{-1} bar^{-1}. Analysis of this polymer by high temperature gel permeation chromatography showed $M_n = 3.98 \times 10^4$ (M_w/M_n = 4.65) and T_m = 135 °C.

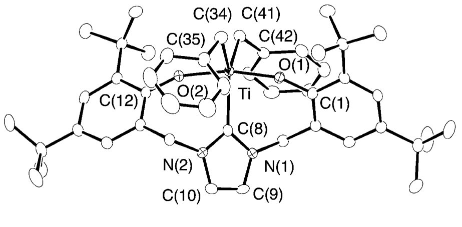


Fig. 2 The molecular structure of **4**. Selected bond distances (Å) and angles (°): Ti–O(1) 1.870(2), Ti–O(2) 1.874(2), Ti–C(8) 2.187(3), Ti–C(34) 2.134(3), Ti–C(41) 2.158(3), N(1)–C(8) 1.350(4), N(2)–C(8) 1.360(4), C(9)–C(10) 1.348(5), O(1)–Ti–O(2) 166.91(9), O(1)–Ti–C(8) 83.87(11), O(2)–Ti–C(8) 83.07(10), C(34)–Ti–C(41) 108.48(13), Ti–O(1)–C(1) 157.8(2), Ti–O(2)–C(12) 158.0(2), Ti–C(34)–C(35) 109.3(2), Ti–C(41)–C(42) 113.9(2), N(1)–C(8)–N(2) 104.5(3).

In summary, a new class of aryloxide-functionalized NHC complexes has been isolated and preliminary work on titanium derivatives has been reported. Further studies into these and related functionalized-NHC derivatives are in progress.

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Notes and references

‡ *Crystal data* for **3**: $C_{37}H_{54}N_2O_3Cl_2Ti \cdot 2.5C_4H_8O$, M = 873.92, monoclinic, space group $P2_1/c$, a = 16.501(10), b = 16.089(9), c = 18.504(10) Å, β = 100.243(9) °, V = 4834.5(49) Å^3, Z = 4, T = 173 K, μ(Mo–Kα) = 3.32 cm^{-1}, Rigaku Mercury CCD diffractometers, 38462 measured reflections, 11042 unique reflections. At convergence, $R1$ = 0.081, $wR2$ = 0.285, and GOF = 1.06 for 586 variables refined against 6301 reflections ($2\theta_{max}$ = 45°). For **4**: $C_{47}H_{60}N_2O_2Ti \cdot C_7H_8$, M = 852.04, monoclinic, space group $P2_1/n$, a = 9.858(4), b = 33.50(2), c = 14.289(6) Å, β = 93.045(6)°, V = 4711.8(35) Å^3, Z = 4, T = 173 K, μ(Mo–Kα) = 2.23 cm^{-1}, 37519 measured reflections. At convergence, $R1$ = 0.062, $wR2$ = 0.171, and GOF = 1.07 for 600 variables refined against all 10646 unique reflections ($2\theta_{max}$ = 55°). The structures were solved by Patterson methods for **3** and **4**, and refined on F^2 by full matrix least-squares procedures using the CrystalStructure package. For **3**, only unique reflections at $2\theta < 45°$ were used for refinement due to the low quality of crystals. See http://www.rsc.org/suppdata/cc/b3/b305745c/ for crystallographic data in .cif or other electronic format.

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