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Titanium(III) Alkoxy-N-heterocyclic Carbenes and a Safe, Low-Cost Route to $TiCl_3(THF)_3$

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Summary: A new, facile method for the synthesis of $[TiCl_3(THF)_3]$ *is reported; THF extraction from the commercially widely available and cheap compound* $3TiCl_3{\cdot}AlCl_3$ *affords aluminum-free* $[TiCl_3(THF)_3]$ *in excellent yield as a blue microcrystalline solid. Treatment of* $[TiCl_3(THF)_3]$ *with 3 equiv of the potassium alkoxy carbene KL* $[K\{OCMe_2CH_2(1\text{-}C[NCHCHNPr^i])\}]$ *affords the homoleptic, octahedral Ti(III) tris(carbene) complex* $[TiL_3]$ *in high yield, which is shown to form as the mer-isomer by a single-crystal X-ray diffraction study.*

1. Introduction

Increasingly, homogeneous catalyst systems that combine a Lewis acidic metal cation, such as titanium, and an NHC (N-heterocyclic carbene) are being described. A number of titanium bis(cyclopentadienyl) and halide adducts of symmetrical, *N,N′*-dialkyl NHCs have been reported, such as $[(C_5H_5)_2TiMe\{C(NPr^iCH)_2\}][BPh_4]$ and $[TiCl_4\{C(NPr^iCMe)_2\}]$, and many were shown to be active alkene polymerization precatalysts.[1−6] In recent years, the incorporation of additional donor or anionic functional groups into the NHC ligand has resulted in more elaborate complexes, e.g., adducts of “pincer” dicarbenes such as $[Ti\{NC_5H_3\text{-}2,6\text{-}(C[NCHN\{2,6\text{-}Pr^i_2C_6H_3\}CH])_2\}Cl_3(THF)_3]$ and of *N*-hydroxybenzyl-functionalized carbenes, 1-alkyl-(2-alkoxy-)carbenes, many of which are also active alkene, and D,L-lactide polymerization precatalysts.[7−12] The only Ti(III)−NHC complex reported to date is $[Ti\{C(N[\text{-}(CH_2)_2\text{-}9\text{-fluorenyl}]N[2,6\text{-}Pr^i_2C_6H_3]CH_2)_2\}(NMe_2)Cl]$, which was generated by an in situ redox reaction between the proligand and Ti(IV).[13] We have been studying the suitability of heterobidentate alkoxy-functionalized NHCs for electropositive metals in lower oxidation states.

Arguably, the most useful starting material for Ti(III) chemistry is $[TiCl_3(THF)_3]$, since commercial, anhydrous $TiCl_3$ is prohibitively expensive for exploratory synthetic chemistry. Commercial $[TiCl_3(THF)_3]$ is available, but is quite expensive for exploratory applications. Currently, a variety of complicated experiments exist for producing pure $TiCl_3$ by $TiCl_4$ reduction on a laboratory synthetic scale: (i) reduction with hydrogen gas at high (650 °C) temperatures, with careful removal of the evolved HCl, to avoid reoxidation;[14] (ii) reduction with sodium metal in DME or dispersed on alumina;[15,16] (iii) synthesis of $[TiCl_4(THF)_2]$ followed by in situ reduction with aluminum, titanium, magnesium, or aluminum trialkyls;[17−21] (iv) reduction with hexamethyldisilane (which affords chlorotrimethylsilane as a byproduct).[22] In general, the reduction with other metals leads to contamination of the product,[23−25] and these reactions require careful anaerobic containment, measures to control the corrosive, volatile byproducts, and control over the exothermic reactions that are involved.

Herein, we report a straightforward procedure for isolating pure $[TiCl_3(THF)_3]$ from commercially available $3TiCl_3{\cdot}AlCl_3$ in excellent yield and demonstrate its synthetic efficacy in the synthesis of a new organometallic Ti(III) complex, the homoleptic alkoxy-N-heterocyclic carbene adduct $[Ti\{OCMe_2CH_2\text{-}(1\text{-}C[NCHCHNPr^i])\}_3]$.

2. Results and Discussion

As discussed above, commercially available anhydrous $TiCl_3$ and $[TiCl_3(THF)_3]$ are expensive reagents for exploratory synthetic chemistry. However, the aluminum-reduced material, $3TiCl_3{\cdot}AlCl_3$, is available for 1/50 the price of anhydrous $TiCl_3$[26] and is easily manipulated as a mildly air-sensitive powder. The similarities in physiochemical properties of Ti(III) and Al(III) have generally been accepted as a barrier to the use of this compound in coordination chemistry; however, we find that a simple extraction protocol generates aluminum-free $[TiCl_3(THF)_3]$ in high yield. This method utilizes a cheap, com-

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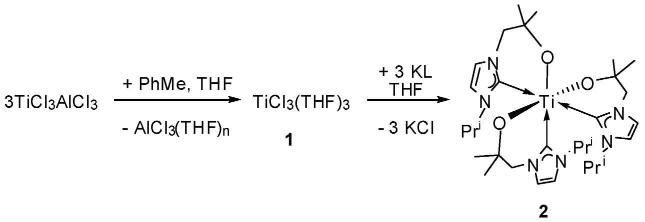
10.1021/om060486d CCC: $37.00

Scheme 1



mercially available reagent, avoids the evolution of volatile, corrosive byproducts, and obviates the necessity to handle corrosive $TiCl_4$, to carefully solvate $TiCl_4$ with THF, or to use reagents, some of which are pyrophoric, to carry out in situ reductions. An ampule was charged under a dinitrogen atmosphere with a 20 g portion of $3TiCl_3{\cdot}AlCl_3$, slurried in 10 mL of toluene, and a stirrer bar. The flask was then cooled to −50 °C, while 200 mL of THF was added. The toluene functions as a heat sink and prevents hot spots forming during the THF addition; otherwise the reaction is too exothermic. The blackish-blue mixture was then refluxed for 14 h, during which time a pale blue crystalline solid formed. Once the mixture was allowed to cool to room temperature, the crystalline powder was isolated by filtration and washed with portions of hexanes, then dried in vacuo to yield pale blue $[TiCl_3(THF)_3]$ (**1**) in 82% isolated yield. Elemental analysis confirms the constitution of **1**. At these concentrations, the aluminum trichloride remains in solution during the workup, so the titanium trichloride solvate that is isolated contains no aluminum, according to atomic absorption spectrometry. Upon standing in air, a powdered pale blue sample of **1** reverts to the characteristic violet color of titanium trichloride (which is hygroscopic), since titanium trichloride is only slowly attacked by atmospheric oxygen.[23]

The purity of this isolated titanium(III) solvate is underlined by the clean further reactivity it displays. We chose a tris(NHC) complex as a simple, but potentially interesting air-sensitive organometallic target to exemplify the purity and synthetic utility of $[TiCl_3(THF)_3]$ prepared by this route.

Treatment of a sample of $[TiCl_3(THF)_3]$ with 3 equiv of $[K\{OCMe_2CH_2(1\text{-}C[NCHCHNPr^i])\}]$, [KL], in THF affords a red mixture. Drying under reduced pressure, followed by extraction with hexanes, affords a red solution, from which a vermillion-colored solid, characterized as $[TiL_3]$ (**2**), can be isolated. Analysis of the crude material **2** suggests that the reaction is essentially quantitative, but the solubility (in addition to the air-sensitive nature) of the complex in organic solvents results in an isolated yield of 72%. This is the first group 4 complex with three NHC ligands, and the first homoleptic Ti(III)−NHC complex, to the best of our knowledge. Complex **2** sublimes very well under mass spectrometric conditions; the parent ion^{2+} is clearly and consistently seen as the highest peak in the EI mass spectrum.

Red blocks of **2** were grown from hexanes and studied by single-crystal X-ray diffraction. The molecular structure of the complex is shown in Figure 1.

The Ti(III) center is approximately octahedral. There are two molecules of **2** in the asymmetric unit, which are the two configurational isomers (Δ-*mer* and Λ-*mer*) of the tris(chelate); the Λ-*mer* isomer is that shown in the figure. In these the average Ti−$C_{carbene}$ bond length in **2** is 2.279 Å, with a range of 2.252(4) to 2.300(5) Å. All the Ti−C distances here are significantly longer than the Ti−$C_{carbene}$ bond length in the other Ti(III) NHC complex, $[Ti\{C(N[-(CH_2)_2\text{-9-fluorenyl}]N[2,6\text{-}Pr^i{}_2C_6H_3]CH_2)_2\}(NMe_2)Cl]$, in which it is 2.221(2) Å.[13] The average Ti(IV)−$C_{carbene}$ distance for complexes in the literature

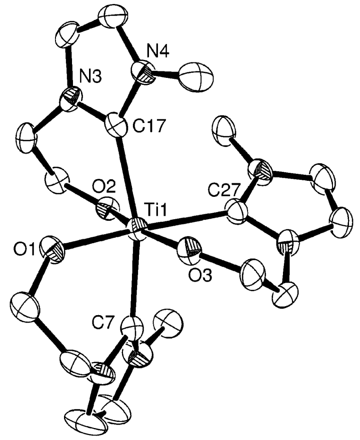


Figure 1. Displacement ellipsoid drawing of **2** (50% probability). Hydrogen atoms and methyl groups are omitted for clarity. Selected distances (Å) and angles (deg): Ti1−O1 1.994(3), Ti1−O2 1.948(3), Ti1−O3 1.958(3), Ti1−C7 2.263(5), Ti1−C17 2.252(4), Ti1−C27 2.299(4), N3−C17 1.351(5), N4−C17 1.368(5), N3−C17−N4 102.6(4), O2−Ti1−O1 98.33(12), C7−Ti1−C27 95.77(15).

is 2.242 Å (12 instances), although there is a wide range (2.194(7) to 2.313(5) Å).[1,3,4,7,8,27−29] Since the covalent radius of six-coordinate Ti(III) is 0.16 Å larger than for five-coordinate Ti(IV) (the approximate coordination number of the Ti(IV) carbene complexes reported to date), the ligands apparently fit well around this metal cation.

The average Ti−O bond length is 1.978 Å (range 1.945(3)−1.994(3) Å), longer than in other six-coordinate Ti(III) isopropoxide complexes, e.g., Ti−OPr^i = 1.824 Å in $[Ti\{N(CH_2\text{-3-}Bu^t\text{-5-Me}-C_6H_2O_2)_2(CH_2CH_2NMe_2)\}(OPr^i)_2{\cdot}Na(THF)_2]$.[30] The *mer*-conformation means that one alkoxide and one NHC ligand are mutually *trans* in each molecule; in both molecules, these bonds are the longest of the metal−atom distance range. The two *trans*-disposed NHC groups deviate the most significantly from octahedral, with a C17−Ti1−C7 angle of 162.36(17)°, rather than 180°, but the M−NHC moiety in each case is close to planarity at the sp^2-hybridized $C_{carbene}$ atom. While there are a number of structurally characterized Ti(III) aryloxide complexes,[31−34] simple Ti(III)-containing alkoxides are very rare.[35]

An EPR spectroscopic study of a solution of **2** in THF at room temperature was undertaken; the spectrum obtained is shown in Figure 2.

The experimental data are well simulated by modeling a system in which the electron resides in a metal-based orbital, with g_{iso}= 1.970, and coupling to titanium of A_{Ti} = 12.48 G. This simulation is also shown in Figure 2 (upper dashed trace).

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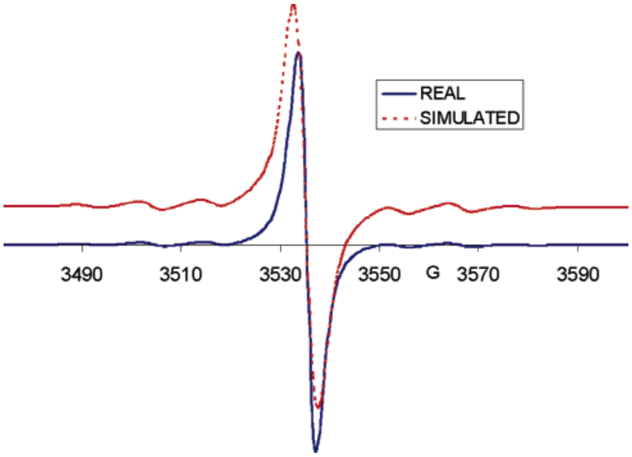

Figure 2. EPR spectrum (298 K, THF solution) of **2** upper (red, dashed), simulated; lower (blue), real.

3. Experimental Details

3.1. General Methods. All manipulations were carried out using standard Schlenk techniques, or an MBraun UniLab glovebox, under an atmosphere of dry dinitrogen. Hexane, toluene, THF, and diethyl ether were dried by passage through activated alumina towers and were degassed before use. Benzene was distilled from potassium under an atmosphere of dry dinitrogen. All solvents were stored over potassium mirrors (with the exception of THF, which was stored over activated 4 Å molecular sieves). Deuterated solvents were distilled from potassium, degassed by three freeze−pump−thaw cycles, and stored under dinitrogen. The reagent $3TiCl_3 \cdot AlCl_3$ was purchased from Aldrich and used without purification. The compound [KL] was prepared by a published literature procedure.[36]

^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker 300 spectrometer operating at 300.1 and 75.5 MHz, respectively; chemical shifts are quoted in ppm and are relative to $SiMe_4$. EPR spectra were recorded on a Bruker X-band ESP 300E spectrometer, with modulation amplitude 1.0 G, in fluid solution with external DPPH reference at 2.0036, and simulated using Bruker SimFonia version 1.25. Elemental microanalyses were carried out by Mr. Stephen Boyer at the Microanalysis Service, London Metropolitan University, UK. Atomic absorption analysis was carried out by Mr. Mark Guyler at the University of Nottingham using the flame method on a Perkin-Elmer 603 AA spectrometer.

3.2. Preparations. 3.2.1. Synthesis of [TiCl$_3$(THF)$_3$]. A Youngs tap-fitted glass ampule equipped with a stirrer bar was loaded with a portion of purple $3TiCl_3 \cdot AlCl_3$ (20 g, 100 mmol) under N_2 and slurried in 10 mL of toluene. The flask was then cooled to −50 °C, while 200 mL of THF was added via cannula transfer. The blackish-blue mixture was then heated to reflux (70 °C) for 14 hours, during which time a pale blue crystalline solid formed. Once the mixture had been allowed to cool to room temperature, the crystalline powder was isolated by filtration and washed with portions of hexanes, then dried at room temperature in vacuo to yield pale blue [TiCl$_3$(THF)$_3$] (**1**) in 82% isolated yield (30.82 g). This work is subject to a U.K. patent application.[37] Anal. Found: C, 38.55; H, 6.64. [TiCl$_3$(THF)$_3$] requires: C, 38.68; H, 6.50 (fw 370.5). Atomic absorption: found Al, 0.00%. The spectrometer can read a minimum of 2 mg per liter, so this sample contained less than 0.1% Al in total metal content.

3.2.2. Synthesis of [TiL$_3$], 2. To a cold, pale blue suspension of [TiCl$_3$(THF)$_3$] in THF (371 mg, 1 mmol, 10 mL, −50 °C) was added a cream-colored THF solution of [KL] (660 mg, 3 mmol, 10 mL) dropwise over 5 min, with stirring. The mixture was allowed to warm to room temperature over 48 h. After this time, the dark red gluey mixture was dried under reduced pressure and triturated with 10 mL of hexanes, to afford a bright orange solid. Extraction with hexanes (30 mL), followed by filtration and concentration of the dark orange solution, afforded vermillion crystalline **2** in 72% yield (424 mg).

NMR (C_6D_6 300 MHz, 300 K): ^1H, no visible resonances above baseline, + 50 to −50 ppm. MS (EI): m/z 591 ($[M]^+$, 100%), 533 ($[M - Pr^i - Me]^+$, 10%), 427 ($[TiL_2OH]^+$, 50%), 183 ($[H_2L]^+$, 65%). Anal. Found: C, 60.74; H, 8.57; N, 14.34. [TiL$_3$] requires: C, 60.85; H, 8.69; N, 14.20 (fw 591.6). EPR spectrum (295 K): g_{iso} 1.970. Simulated with A_{Ti} hyperfine (^{47}Ti abundance = 7.4%, $I = 5/2$, and ^{49}Ti abundance = 5.4%, $I = 3/2$) = 12.48 G and line broadening 4.5 G.

4. Crystal Experimental Details

Red blocks were examined on an Bruker AXS SMART Apex CCD area detector diffractometer, size 0.24 × 0.13 × 0.08 mm, $C_{30}H_{51}N_6O_3Ti$, M_r 591.67, triclinic, $P\bar{1}$, 150(2) K, a, b, c (Å) 10.706(2), 18.611(3), 19.692(3), α, β, γ (deg) 108.239(2), 103.011(3), 104.461(2), V 3406.6(15) Å^3, Z 4, D_x 1.154 Mg m^{-3}, Mo Kα μ 0.29 mm^{-1}, ω scans, multiscan absorption correction, T_{min} 0.93, T_{max} 0.98, no. of measured, independent, and observed reflections 21 200, 8789, 5525, criterion for observed reflections $I > 2\sigma(I)$, R_{int} 0.072, θ_{max} (deg) 22.5, $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S 0.058, 0.125, 0.95, 8789 reflections, 745 parameters, weighting $w = 1/[\sigma^2(F_o^2) + (0.0495P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$, $(\Delta/\sigma)_{max}$ 0.001, $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3}) 0.44, −0.28, Computer programs: Bruker SMART version 5.625 (Bruker, 2001); Bruker SAINT version 6.36a (Bruker, 2000); Bruker SHELXTL (Bruker, 2001); Bruker SHELXL97-2 (Sheldrick, 1998); PLATON (Spek, 2003).

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Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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