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Short communication

Synthesis and structure of an amidoimido titanium cage complex $[(Me_2N)_6Ti_4(\mu\text{-}NPh)_5]^{\dagger}$

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The combination of $PhNH_2$ and $(Me_2N)_4Ti$ in toluene at 23 °C leads to the formation of a red–orange crystalline compound that displays unexpectedly complex ^1H and ^{13}C NMR spectra. Subsequent single crystal X-ray diffraction analysis reveals that the compound is not an anticipated mononuclear transamination product $(Me_2N)_3Ti[N(H)Ph]$, but instead it is a bicyclic cage compound with a (Ti_4N_5) core with bridging phenylimido groups and terminal dimethylamino groups. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: titanium; amides; imides; cage; X-ray structure

INTRODUCTION

The reaction chemistry between transition metal fragments and organoamine compounds is rich and continues to reveal new structural and bonding features.[1,2] One particularly useful reaction class involves transamination chemistry of metal amides, and our group has used this reaction to introduce transition metal fragments into aminoborazine oligomers and poly(borazinylamines).[3] In initial studies it appeared that the resulting metallated polymers serve as precursors for metal nitride–boron nitride composites.[3] During the course of these studies, we have also explored model reactions of several metal amides, $(R_2N)_3M$ and $(R_2N)_4M$, with aminoborazine monomers and sterically related organoamines with the intent of learning how steric features in the reactants influence the reactivity of the metal amides with poly(borazinylamines). In the course of these studies, several unexpected transamination products have been discovered.[4] Here, we report on the reaction of $(Me_2N)_4Ti$ with aniline ($PhNH_2$) in a 1 : 1 ratio that forms a novel cluster molecule instead of the anticipated mononuclear transamination product, $(Me_2N)_3Ti[N(H)Ph]$.

RESULTS AND DISCUSSION

In 1963, Bradley and Torrible[5] reported that the combination of $(Me_2N)_4Ti$ with excess $PhNH_2$ gave a black, relatively insoluble, unreactive polymeric solid that was only characterized by elemental analysis and proposed to be $(PhN)_2Ti$. As far as we are aware, this compound has not been defined further. In the present study, we initially examined the 1 : 1 combination of $(Me_2N)_4Ti$ with $PhNH_2$ in hexane. This results in the formation of an insoluble transamination product, as evidenced by the release of Me_2NH. However, when the 1 : 1 reaction is performed in toluene, a soluble red compound **1** forms, which is isolated as a moisture-sensitive red–orange, crystalline solid in 77% yield. Interestingly, ^1H and $^{13}C\{^1H\}$ NMR spectra recorded from C_6D_6 solutions show three resonances that could be assigned to inequivalent dimethylamido groups Me_2N. Although such spectra might be expected for a mononuclear transamination product $(Me_2N)_3Ti(PhNH)$ if hindered rotation about the Ti–N bonds existed, the elemental analysis and mass spectral data suggest that **1** is a more complex product. In particular, fast atom bombardment (FAB) mass spectrometry (MS) shows several ions with *m*/*z* between 300 and 912 amu.

In order to determine the true nature of **1**, the molecular structure was determined by single crystal X-ray diffraction, and selected crystal data are summarized in Table 1. A view of the molecular unit is shown in Fig. 1, excluding hydrogen atoms, and a view of the $N_6Ti_4N_5$ core is depicted in Fig. 2. The structure contains four titanium(IV) atoms

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†Dedicated to Professor Thomas P. Fehlner on the occasion of his 65th birthday, in recognition of his outstanding contributions to organometallic and inorganic chemistry.

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Table 1. Crystal data, data collection and structure refinement information for $(Me_2N)_6Ti_4(\mu\text{-}NPh)_5]$ (1)

Empirical formula	$C_{42}H_{61}N_{11}Ti_4$
Formula weight	911.6
Color	Red–orange
Crystal size (mm^3)	0.28 × 0.48 × 0.55
Crystal system	Orthorhombic
Space group	*Pbca*
Unit-cell dimensions	
a (Å)	12.608(3)
b (Å)	20.279(4)
c (Å)	36.902(7)
Volume ($Å^3$)	9435(3)
Z	8
Density (calc.) ($Mg\ m^{-3}$)	1.283
μ (Mo Kα) (mm^{-1})	0.693
F(000)	3824
Radiation	Mo Kα ($\lambda = 0.71073$ Å)
Temperature (K)	293
Scan type	ω
2θ range (deg)	3.0–45.0
Scan speed ($deg\ min^{-1}$)	8–32, variable
No. of measured reflections	6851
No. of independent reflections	6166
No. of observed reflections	3434 ($F > 1.1\sigma(F)$)
Absorption correction	Semi-empirical
Min/max transmission	0.839/0.884
Data to parameter ratio	6.7 : 1
$R(F)^a$	0.0522
$wR(F)^a$	0.0187
R(*F*) (all data)	0.109
wR(*F*) (all data)	0.0226
Goodness of fit	0.75
Residual density ($e^-\ Å^{-3}$)	+0.29; −0.32

[a] Definitions of *R* values: $R(F) = (\sum ||F_o| - |F_c|| / \sum |F_o|)$; $wR = [\sum (w||F_o| - |F_c||)^2 / \sum (w|F_o|^2]^{1/2}$.

that are bridge-bonded by five phenylimino-group nitrogen atoms, and the nine atoms form a bicyclic cage. Two of the titanium atoms, Ti(1) and Ti(2), are connected through a single bridgehead PhN group and each of these titanium atoms is also bonded to an *exo* Me_2N group. The remaining two titanium atoms, Ti(3) and Ti(4), are each bonded to two *exo* Me_2N groups. All of the nitrogen atoms are planar, although N(4) has a bond angle sum of 367.8°. The average Ti–NPh bond length, 1.942 Å (range 1.89(4)–1.994(4) Å), in the bicyclic cage is comparable to distances in the upper end of the range associated with titanium–imido complexes, 1.86–1.94 Å.[6–9] As expected, the average *exo* Ti–NMe_2 bond length, 1.877 Å (range 1.866(5)–1.882(4) Å), is shorter than the bridging Ti–NPh distances, and the average Ti–NMe_2 distance is comparable to distances in other titanium alkylamido complexes, including the average distance of 1.870(4) Å in $(Me_2N)_2Ti(NPh_2)_2$.[4]

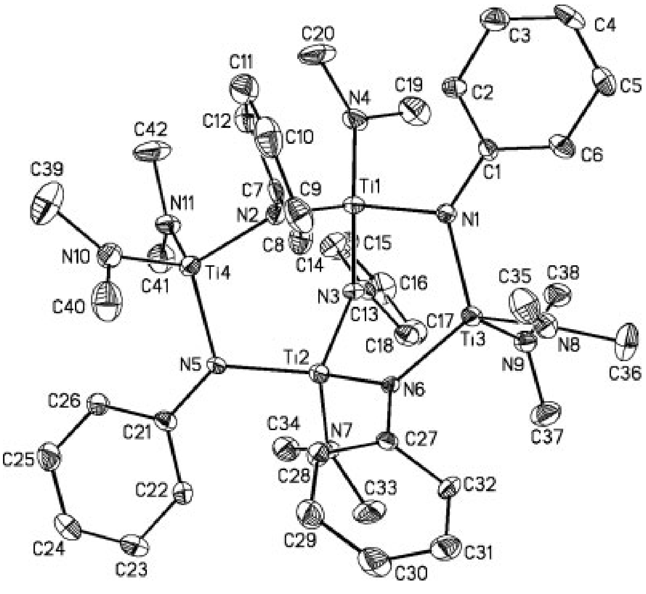

Figure 1. Molecular structure and atom labeling scheme for $(Me_2N)_6Ti(\mu\text{-}NPh)_5$ (**1**) with hydrogen atoms omitted (thermal ellipsoids set at 40% probability). Selected bond lengths (Å) and angles (°) are: Ti(1)—N(1) 1.912(4), Ti(1)—N(2) 1.898(4), Ti(1)—N(3), 1.958(4), Ti(1)—N(4) 1.881(4), Ti(2)—N(3) 1.938(4), Ti(2)—N(5) 1.968(4), Ti(2)—N(6) 1.905(4), Ti(2)—N(7) 1.866(5), Ti(3)—N(1) 1.945(4), Ti(3)—N(6) 1.994(4), Ti(3)—N(8) 1.881(4), Ti(3)—N(9) 1.882(4), Ti(4)—N(2) 1.968(4), Ti(4)—N(5) 1.931(4), Ti(4)—N(10) 1.874(5), Ti(4)—N(11) 1.879(5); N(1)—T(1)—N(2) 110.6(2), N(1)—Ti(1)—N(3) 99.5(2), N(2)—Ti(1)—N(3) 105.6(2), N(1)—Ti(1)—N(4) 106.5(2), N(3)—Ti(1)—N(4) 119.1(2), N(5)—Ti(2)—N(6) 120.5(2), N(5)—Ti(2)—N(3) 111.9(2), N(6)—Ti—N(3) 101.0(2), N(5)—Ti(2)—N(7) 106.6(2), N(6)—Ti—N(7) 106.6(2), N(1)—Ti(3)—N(6) 114.8(2), N(2)—Ti(4)—N(5) 111.3(2).

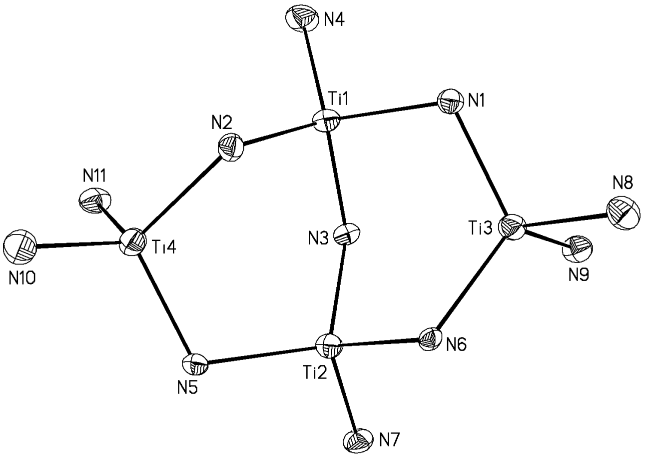

Figure 2. Core structure of $(Me_2N)_6Ti(\mu\text{-}NPh)_5$ (**1**) showing titanium and nitrogen atoms only.

In the light of the molecular structure determination, the inequivalence of the amido N–methyl groups, as indicated by the ^{1}H (three equal intensity methyl resonances) and ^{13}C{^{1}H} NMR spectra, can be better understood. The methyl groups on N(4) and N(7) give rise to one resonance, the methyl groups N(8) and N(10) (*anti* with respect to N(3)) give rise to a second resonance and the methyl groups on N(9) and N(11) give rise to the third resonance. The appearance of equivalency in the methyl group pairs on N(4), N(7) and on N(8), N(10) suggests that there is rotational averaging about Ti–NMe$_2$ bonds on the NMR time scale.

These results suggest that the transamination chemistry between $(R_2N)_4M$ reagents and primary amines still has novel aspects to be revealed; we will report separately on the related chemistry with borazinyl amines that provide access to the formation of nano-dispersed metal nitride–boron nitride composite materials.

EXPERIMENTAL

General comments

The reactants and product manipulations were performed under dry nitrogen atmosphere using anhydrous reagents and dry solvents. $(Me_2N)_4Ti$ was prepared as described in the literature.[10] Elemental analyses were performed by Galbraith Laboratories and the UNM microanalytical facility staff. NMR spectra were recorded on Bruker AC-250 and JEOL GSX-400 NMR spectrometers using flame-sealed samples dissolved in a deuterated lock solvent. The shift standard was Me$_4$Si (^{1}H and ^{13}C) and resonances downfield of the reference were assigned as positive shifts ($+\delta$). Mass spectra were obtained at the Midwest Center for Mass Spectrometry at the University of Nebraska.

$(Me_2N)_6Ti_4(\mu\text{-}NPh)_5$

A sample of PhNH$_2$ (0.62 g, 6.7 mmol) in toluene (20 ml) was added to a solution (0 °C) containing $(Me_2N)_4Ti$ (1.5 g, 6.7 mmol) in toluene (30 °C). The solution was stirred briefly at 0 °C and then warmed (23 °C) and stirred (1 day). The resulting solution was filtered to remove a small amount of insoluble material and the filtrate reduced in volume to about 15 ml by vacuum evaporation. The solution was allowed to stand undisturbed (1 day) and red–orange crystals of **1** deposited: yield, 1.2 g (77%). Anal. Found: C, 55.56; H, 6.96; N, 17.04. Calc. for $C_{42}H_{61}N_{11}Ti_4$ (911.628): C, 55.34; H, 6.74; N, 16.90%. ^{1}H NMR (C_6D_6): 2.68 (s, 12H), 2.87 (s, 12H), 3.36 (s, 12H), 6.70–7.16 (Ph). ^{13}C{^{1}H} NMR (C_6D_6): 44.15, 45.28, 45.55, 120.61, 121.35, 121.94, 122.62, 154.64, 157.10. MS (FAB) m/z (rel. inten.): 912 (10) [M$^+$], 338 (19), 318 (20), 275 (12), 274 (15), 261 (29), 231 (74), 230 (32), 227 (16), 183 (12), 78 (100).

Supplementary data

Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, deposition number CCDC 198365. Copies of this information may be obtained free of charge (e-mail: deposit@ccdc.cam.ac.uk; web: http://www.ccdc.cam.ac.uk).

Acknowledgements

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