Bis(N-trimethylsilylamino)titanium Dichlorides Bearing Two Identical or Two Different Amino Groups

Bernd Wrackmeyer and Jürgen Weidinger

Laboratorium für Anorganische Chemie, Universität Bayreuth, D-95440 Bayreuth, Germany

Reprint requests to Prof. Dr. B. Wrackmeyer; Fax: (+49) 9 21/55-21 57;
e-mail: B. Wrack@uni-bayreuth.de; http://www.uni-bayreuth.de/departments/acil/

Z. Naturforsch. 54 b, 1391–1395 (1999); received August 17, 1999

Silylamines, Titanium, Plumbylenes, NMR Data

N-Trimethylsilylamino­titanium trichlorides, Me₃Si(R)N-TiCl₃ [R = 'Bu (2a), SiMe₃ (2b),
9-borabicyclo[3.3.1]nonyl (9-BBN) (2c)] react with the corresponding plumbylenes 1a - c or
with the lithium amides LiN(R)SiMe₃ to give the bis(amino)titanium dichlorides 3a - c, and
4 - 6. The titanium dichlorides 4 - 6 are the first examples, in which the titanium atom bears
two different amino groups. The compounds were characterised by a consistent set of ¹H, ¹³C,
¹⁴/¹⁵N and ²⁹Si NMR data.

Introduction

N-silyl substituted titanium halides are of considerable interest due to their suitability as cata­
lysts in olefin polymerisation [1]. However, their synthesis is not fully described in the literature,
and the proposed methods appear to be unreliable. In 1983 Andersen [2] reported the synthesis
of bis[bis(trimethylsilylamino)titanium dichloride (3b) from TiCl₄ and NaN(SiMe₃)₂. In the course
of our attempts to reproduce this method for preparing 3b, we found that there are impurities, and that one
of the impurities possesses the reported ¹H NMR data which were assigned to 3b [2]. Andersen de­
scribed 3b as a red oil or a waxy dark-red solid after distillation, while we could obtain it as a yellow, mi­
crocrystalline solid following another reaction pathway. This situation prompted us to optimise proce­
dures for the synthesis of bis(N-silylamino)titanium dichlorides, and a stepwise synthesis of these com­
pounds, as reported in this paper, turns out to be superior to direct transmetallation.

Recently, the facile synthesis of N-silylaminoti­tanium trichlorides 2 has been reported (eq. 1) [3],
and these compounds are ideal starting materials for the synthesis of bis(N-silylamino)titanium dichlo­
rides 3. Furthermore, starting with 2, attempt to ob­
tain derivatives with two different amino groups linked to titanium are promising. The compounds
2 are obtained in about 80% yield and in high purity and can be used for further synthesis without
purification.
compounds 3a,b,c as slightly air and moisture sensitive, hydrocarbon soluble, dark yellow (3b), orange (3c) or dark red (3a) microcrystalline solids in yields of 70 - 80 % in high purity. The formation of 3a,b,c is accompanied by precipitation of a highly insoluble yellowish solid which presumably is Me₃Si(R)NPbCl [3]. The mechanism of this reaction is not clear as yet. Insertion of the plumbylene into a Ti-Cl bond followed by transfer of one amino group from lead to titanium is a possible pathway. In agreement with this suggestion is the finding that an excess of 1 never leads to tris(amino)titanium chlorides. This indicates that the steric overcrowding at both the Ti and the Pb atom hampers the insertion as the first step of the reaction.

The titanium trichlorides 2 are also suitable reagents for further transmetallation (Scheme 1) with one equivalent of lithium amide to give the respective bis(amino) compounds in about 80 % yield. In some cases, further substitution of chlorine by a bulky amino group was possible by using two equivalents of lithium amide [6]. So far tetrakis(amino)titanium compounds were not observed due to the high steric demand of the silylamino groups.

By using a lithium amide or a plumbylene bearing different amino substituents than the substrate one obtains a novel type of bis(N-silylamino)titanium dichlorides with two different silylamino groups as in 4, 5 and 6 (Schemes 2 and 3). These reactions are straightforward except when 2c is used as a substrate: In this case, the reactions with lithium amides such as (Me₃Si)NLi or 'Bu(Me₃Si)NLi do not lead to the desired titanium dichlorides 5 or 6. Instead, slow decomposition of the compounds in the reaction mixture takes place. Compounds 5 and 6 nevertheless are accessible via salt elimination starting from 2a and 2b (Scheme 2). In comparison, 2c reacts with 1a or 1b straightforwardly to give also 5 and 6, respectively. As in the synthesis of aminotitanium trichlorides [3], the plumbylenes prove to be ideal reagents for amide metatheses under mild conditions.
Table I. $^{13}$C, $^{14}$N and $^{29}$Si NMR chemical shift data\textsuperscript{[a]} of aminotitanium dichlorides 3-6 and trichlorides 2.

<table>
<thead>
<tr>
<th></th>
<th>$\delta^{13}$C (SiMe$_3$)</th>
<th>$\delta^{13}$C (other)</th>
<th>$\delta^{14}$N/$^{15}$N</th>
<th>$\delta^{29}$Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>5.3</td>
<td>33.1, 69.8</td>
<td>61 (140)</td>
<td>8.3</td>
</tr>
<tr>
<td>2b</td>
<td>4.2</td>
<td></td>
<td>22 (60)/23.8</td>
<td>11.4</td>
</tr>
<tr>
<td>2c\textsuperscript{[b]}</td>
<td>2.9</td>
<td>22.3, 30.0 (br), 32.7</td>
<td>18 (80)</td>
<td>16.4</td>
</tr>
<tr>
<td>3a</td>
<td>6.2</td>
<td>34.3, 65.0</td>
<td>-18 (350)</td>
<td>0.6</td>
</tr>
<tr>
<td>3b</td>
<td>5.1</td>
<td></td>
<td>-54 (120)</td>
<td>4.1</td>
</tr>
<tr>
<td>3c\textsuperscript{[c]}</td>
<td>3.8</td>
<td>23.0, 30.5 (br), 32.0</td>
<td>-41 (75)</td>
<td>5.1</td>
</tr>
<tr>
<td>4</td>
<td>5.2</td>
<td>34.4, 64.5</td>
<td>-7.4</td>
<td>4.1</td>
</tr>
<tr>
<td>5\textsuperscript{[d]}</td>
<td>6.0</td>
<td>32.7, 65.3</td>
<td>-45 (100)</td>
<td>6.5</td>
</tr>
<tr>
<td>6\textsuperscript{[e]}</td>
<td>4.9</td>
<td>22.6, 29.4 (br)</td>
<td>-46 (120)</td>
<td>4.6</td>
</tr>
</tbody>
</table>

\textsuperscript{[a]} All measurements in C$_6$D$_6$ solutions at 298 K, br = broad; full line width at half height in Hz for the $^{14}$N NMR signals is given in brackets; \textsuperscript{[b]} $\delta^{11}$B = 54; \textsuperscript{[c]} $\delta^{11}$B = 53; \textsuperscript{[d]} $\delta^{11}$B = 53; \textsuperscript{[e]} $\delta^{11}$B = 53.

Fig. 1. Nitrogen chemical shift ranges of N-silylamino substituted titanium chlorides; within the respective range, specific substitution patterns can be distinguished.

2. NMR spectroscopic results

Selected NMR data for the reported compounds are given in Table I. As observed for the compounds 2 [3], the $^{14}$/15$^N$ NMR data of the bis(amine)titanium dichlorides 3 - 6 show strong deshielding of the $^{14}$N nuclei compared with the amines or the related tin compounds [5, 7]. However, the nitrogen shielding is higher than in the aminotitanium trichlorides 2 (Fig. 1). As in 2, the coupling constants $^1$J($^{29}$Si, $^{15}$N) are extremely small (< 1.5 Hz) when compared with other silylamines [8]. This could be an indication of Ti-N multiple bonding. For comparison, in (Me$_2$N)$_3$Ti-N(SiMe$_3$)$_2$ [9] a value of $^1$J($^{29}$Si, $^{15}$N) = 6.3 Hz [10] was measured. In this amide Ti-N multiple bonding should be reduced owing to the bonding of Ti to four amino nitrogen atoms. Our experiments have shown that $^{14}$N NMR is a most convenient method for studying N-silyl substituted titanium amides owing to relatively sharp $^{14}$N NMR signals (see Fig. 2 and line

In the cases of tert.-butylamino substituted titanium dichlorides the $^{14}$N NMR signals were found to be rather broad, and exact measurement of $\delta^{14}$N was not feasible. However, $^{15}$N NMR spectra are easily accessible by using an INEPT pulse sequence with polarization transfer from the tert.-butyl protons to $^{15}$N nuclei which allows to detect selectively such compounds in which the amino groups bear a tert.-butyl substituent (Fig. 3). The $^{11}$B chemical shifts in the range of $\delta = +53$ to +54 for 3c, 5 and 6 are close to those of other known 9-BBN substituted amines [11]. This means
that the TiCl₂N fragment is not a particularly strong \( \pi \) acceptor competing with the boron atom for the lone pair of electrons at the nitrogen atom. The \( ^{29}\text{Si} \) nuclei in 3-6 are significantly less deshielded than in the titanium trichlorides 2.

As in the case of the compounds 2, \(^{45/47}\text{Ti} \) NMR spectra could not be obtained. The reason must be fast \(^{45/47}\text{Ti} \) quadrupolar relaxation [12] due to unsymmetric charge distribution at the Ti atom.

### Experimental

All reactions were carried out in an inert gas atmosphere using the Schlenk technique. Glassware and solvents were dried carefully. Starting materials were commercially available (BuLi 1.6 M in hexane, (Me₃Si)₂NH, Me₃Si(Bu)NH, PbCl₂, TiCl₄) and used without further purification or were prepared according to literature procedures [1, 4, 5], [3], Me₃Si(9-BBN)NH [13] and Me₃Si(9-BBN)NLI [14]).

NMR spectra were recorded on Bruker ARX 250 or DRX 500 spectrometers, equipped with multinuclear units and accessories for measurements at variable temperature. Chemical shifts are given with respect to Me₃Si [\( \delta ^{1} \text{H} (\text{C}_{6} \text{D}_{5}/\text{C}_{6} \text{D}_{5} \text{H}) = 7.15, \delta ^{13} \text{C} (\text{C}_{6} \text{D}_{5}) = 128.0, \delta ^{29} \text{Si} = 0 \) for \( \Xi (^{29} \text{Si}) = 19.867184 \text{MHz} \), BF₃·OEt₂ [\( \delta ^{11} \text{B} = 0 \) for \( \Xi (^{11} \text{B}) = 32.083971 \text{MHz} \)], neat MeNO₂·[\( \delta ^{15} \text{N} = 0 \) for \( \Xi (^{15} \text{N}) = 10.136767 \text{MHz} \) and \( \delta ^{14} \text{N} = 0 \) for \( \Xi (^{14} \text{N}) = 7.226324 \text{MHz} \)].

### Synthesis of compounds 3-6 via amide metathesis

Two equivalents of the respective titanium trichloride 2 were dissolved in pentane (20 ml). Then one equivalent of the plumbylene 1 dissolved in pentane (20 ml) was added dropwise at 0°C. The mixture was stirred for 2 h at room temperature. Then pentane (100 ml) was added and the yellowish precipitate was filtered off. After removal of the solvent the desired compounds were obtained as microcrystalline solids (vide supra) in about 70 - 80 % yield.

### Acknowledgement

Support of this work by Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie is gratefully acknowledged.