University of Groningen

New Amido- and Imido-titanium Complexes

Vroegop, Christina T.; Teuben, Jan H.; Bolhuis, Fré van; Linden, Johannes G.M. van der

Published in:
Journal of the Chemical Society%2C Chemical Communications

DOI:
[10.1039/c39830000550](https://doi.org/10.1039/c39830000550)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
1983

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):
Vroegop, C. T., Teuben, J. H., Bolhuis, F. V., & Linden, J. G. M. V. D. (1983). New Amido- and Imido-titanium Complexes. *Journal of the Chemical Society%2C Chemical Communications*, 260(10).
<https://doi.org/10.1039/c39830000550>

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

New Amido- and Imido-titanium Complexes

Christina T. Vroegop,^a Jan H. Teuben,^{*a} Fré van Bolhuis,^b and Johannes G. M. van der Linden^c

^a *Laboratorium voor Anorganische Chemie, Rijksuniversiteit Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands*

^b *Laboratorium voor Chemische Fysica, Rijksuniversiteit Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands*

^c *Laboratorium voor Anorganische Chemie, Katholieke Universiteit van Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands*

cpTiCl_3 ($\text{cp} = \eta^5\text{-C}_5\text{H}_5$) in reaction with $\text{Me}_3\text{SiN(H)R}$ ($\text{R} = \text{Et}, \text{Pr}^i, \text{Bu}^t, \text{or Ph}$) yields the amido complexes $\text{cpTi}(\text{Cl})_2\text{N(H)R}$, which react further by HCl abstraction to give the corresponding centrosymmetric binuclear imido complexes $[\text{cp}(\text{Cl})\text{Ti}]_2(\mu\text{-RN})_2$; substitution of the chloride ligands by organic groups is possible with the imido complexes, as is reversible reduction to stable anionic complexes.

Several nitrogen fixation systems based on organotitanium compounds are known,¹ but little information is available about the intermediate complexes that give, on protonation,

hydrazine, ammonia, or amines. With the importance of the formation of N-C bonds from molecular nitrogen in mind we decided to study amido- and imido-titanium compounds that

Scheme 1. R = Et, Pr^i , Bu^t , or Ph. i, thf, $-\text{Me}_3\text{SiCl}$; ii, heat, vacuum, $-\text{HCl}$; iii, CH_2Cl_2 , Bu^tNH_2 , $-\text{Bu}^t\text{NH}_2\cdot\text{HCl}$; iv, (R = Bu^t) Et_2O , MeLi , $-\text{LiCl}$, $-\text{MeH}$.

Scheme 2. i, thf, $-2\text{Me}_3\text{SiCl}$.

could act as model systems for intermediates in nitrogen fixation systems such as $\text{cp}_2\text{TiR-N}_2$ -reducing agent ($\text{cp} = \eta^5\text{-C}_5\text{H}_5$).²

The yellow to red-brown amido complexes $\text{cpTiCl}_2\text{N}(\text{H})\text{R}$ (1) (R = Et, Pr^i , Bu^t , or Ph) were prepared at room temperature by reaction of cpTiCl_3 with the corresponding trimethylsilylamine in tetrahydrofuran (thf) (Scheme 1). The yields were essentially quantitative. With an excess of amine further substitution was not observed. The use of Me_3Si as a leaving group for the syntheses of imido complexes is well known;³ evidently it is also an excellent method for introducing one amido group $\text{N}(\text{H})\text{R}$. The amido complexes (1) were fully characterized.[†] They are all very air sensitive and hydrolyse in moist air giving $\text{RNH}_2\cdot\text{HCl}$ and polymeric, oxygen-bridged cyclopentadienylorgano-titanium complexes. Under nitrogen they are indefinitely stable at room temperature.

The complexes (1) decompose on thermolysis giving the imido complexes (2) and hydrogen chloride (Scheme 1). Quantitative yields were obtained when the hydrogen chloride was trapped with a base; Bu^tNH_2 was excellent in this respect. The *t*-butylimido complex (2) (R = Bu^t) could not be prepared in this way, but it was formed in high yields by reaction of the amido complex (1) with MeLi . The methyl imido complex (2) (R = Me) was prepared directly from cpTiCl_3 and

[†] Satisfactory analytical data were obtained for all complexes. The ^1H n.m.r. spectra (25 °C, CD_2Cl_2) show the alkyl or phenyl resonances at normal positions. The cp resonances are found in the region 6.75–6.95 p.p.m. and the N–H resonances between 9.7 and 11.9 p.p.m. The i.r. spectra show the $\nu(\text{N-H})$ absorptions at 3330 cm^{-1} in all cases. The mass spectrum of $\text{cpTi}(\text{Cl})_2\text{N}(\text{H})\text{Ph}$ shows the molecular ion peak; in the case of the alkylamido complexes the parent peak is M^+-15 . Exact mass measurements prove that in these fragments one CH_3 group is missing, which is a normal phenomenon with alkylamines.

Figure 1

Scheme 3. i, MeLi , $-\text{LiCl}$.

$(\text{Me}_3\text{Si})_2\text{NMe}$; an intermediate trimethylsilylmethylamido compound was not observed (Scheme 2). The binuclear imido complexes (2) were completely characterized by elemental analysis and spectroscopy.[‡] The crystal structure of $[\text{cp}(\text{Cl})\text{Ti}]_2(\mu\text{-PhN})_2$, determined by X-ray diffraction,[§] shows that the imido nitrogen atoms are symmetrically bridging and that the molecule has a centre of inversion (Figure 1). The metal and nitrogen atoms are in a square planar arrangement with bond distances and angles very close to those of other imido-titanium complexes as reported by Nugent⁴ and Floriani *et al.*⁵

The imido complexes are thermally stable, but quite reactive. With hydrogen chloride $\text{RNH}_2\cdot\text{HCl}$ and cpTiCl_3 were formed. Reaction of (2) (R = Ph) with MeLi resulted in substitution of the chlorine ligands and formation of $[\text{cp}(\text{Me})\text{Ti}]_2(\mu\text{-PhN})_2$ (3) (Scheme 3). The redox behaviour of some imido complexes

[‡] Both ^1H n.m.r. (CDCl_3) and ^{13}C n.m.r. (CDCl_3) data show one resonance for the cp group (^1H : 6.3–6.6; ^{13}C : 114.8–118.1 p.p.m.) and one pattern for the group R, indicating the symmetry of the molecule. The i.r. spectra show the absorptions due to cp and phenyl groups; a broad absorption at about 600 cm^{-1} is assigned to the stretching vibrations of the $(\text{Ti-N})_2$ ring system. The mass spectra all show the molecular ion peak.

[§] Crystal data for (2) (R = Ph): $\text{C}_{22}\text{H}_{20}\text{Cl}_2\text{N}_2\text{Ti}_2$, $M = 479.1$, orthorhombic, space group $Pbca$ (from Weissenberg photographs of zero and higher layer lines), $a = 8.705(3)$, $b = 14.595(7)$, $c = 17.166(3)\text{ Å}$; $U = 2180.9(2.1)\text{ Å}^3$, $Z = 4$, $D_c = 1.459\text{ g cm}^{-3}$; $F(000) = 976$, $\lambda(\text{Cu-K}\alpha) = 1.5418\text{ Å}$, $\mu(\text{Cu-K}\alpha) = 87.7\text{ cm}^{-1}$; the crystals were rather imperfect; intensities were measured with a Nonius-CAD 4F diffractometer ($1.0 < 2\theta < 154.0^\circ$) on a crystal with dimensions $0.20 \times 0.35 \times 0.40\text{ mm}^3$, which was sealed in a thin-walled capillary under nitrogen; no corrections were made for absorption. $R(w = 1) = 0.116$ for 1506 intensities with $I > 3\sigma(I)$.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

Table 1. Half-wave potentials for binuclear imido titanium complexes.

Compound	$E_{1/2}/V^a$
$[\text{cp}(\text{Cl})\text{Ti}]_2(\mu\text{-Bu}^t\text{N})_2$	-0.58
$[\text{cp}(\text{Cl})\text{Ti}]_2(\mu\text{-PhN})_2$	-0.39
$[\text{cp}(\text{Me})\text{Ti}]_2(\mu\text{-PhN})_2$	-1.02

^a From pulse voltammetry vs. an Ag-AgI reference electrode (ref. 6), at a scan rate of 5 mV s^{-1} and 2 pulses per second.

at a platinum electrode was investigated in dichloromethane solutions ($0.1 \text{ M Bu}_4\text{NClO}_4$). All complexes exhibit one reduction wave, the half-wave potentials of which are clearly dependent on the substituent present on titanium or nitrogen (Table 1). Controlled potential reduction of (2) ($\text{R} = \text{Bu}^t$) at -0.78 V in CH_2Cl_2 revealed that only one electron is transferred per molecule. Cyclic voltammetry shows that this reduction is nearly completely reversible, for i_p/i_f ratios were in the range 0.9-1.0 at 0.2 V s^{-1} . The observed reversibility indicates that the one-electron reduction product is stable and that it should be possible to generate and isolate it *via* a chemical route. Indeed, careful chemical reduction of (2) ($\text{R} = \text{Ph}$) and (3) with Na amalgam or $\text{Na}_2[\text{Fe}(\text{CO})_4]$ results in the formation of the ionic complexes $\text{Na}\{[\text{cp}(\text{X})\text{Ti}]_2(\mu\text{-PhN})_2\}$ -

(thf)₄ ($\text{X} = \text{Cl}, \text{Me}$), which could be isolated and characterized.¶ The chloro complex is not very stable and decomposes slowly in thf solution at room temperature.

Received, 6th January 1983; Com. 030

References

- 1 J. Chatt, J. R. Dilworth, and R. L. Richards, *Chem. Rev.*, 1978, **78**, 589.
- 2 F. W. van der Weij and J. H. Teuben, *J. Organomet. Chem.*, 1976, **105**, 203.
- 3 M. Pierce-Butler and G. R. Willey, *J. Organomet. Chem.*, 1973, **54**, C19; N. W. Alcock, M. Pierce-Butler, and G. R. Willey, *J. Chem. Soc., Dalton Trans.*, 1976, 707.
- 4 W. A. Nugent and B. L. Haymore, *Coord. Rev.*, 1980, **31**, 123; W. A. Nugent, D. L. Thorn, and R. L. Harlow, *J. Am. Chem. Soc.*, 1981, **103**, 357.
- 5 S. Gambarotta, C. Floriani, A. Chiesi-Villa, and C. Guastini, *J. Chem. Soc., Chem. Commun.*, 1982, 1015.
- 6 D. Coucouvanis, S. J. Lippard, and J. A. Zubieta, *J. Am. Chem. Soc.*, 1970, **92**, 3342.

¶ Characterization by elemental analysis and i.r. spectroscopy. The e.s.r. spectra (thf) show in both cases a five-line spectrum ($g = 1.973 \text{ G}$, $a = 6.7 \text{ G}$, $\text{X} = \text{Cl}$; $g = 1.971 \text{ G}$, $a = 6.4 \text{ G}$, $\text{X} = \text{Me}$) due to interactions with two equivalent N nuclei ($I = 1$).