

New Amido- and Imido-titanium Complexes

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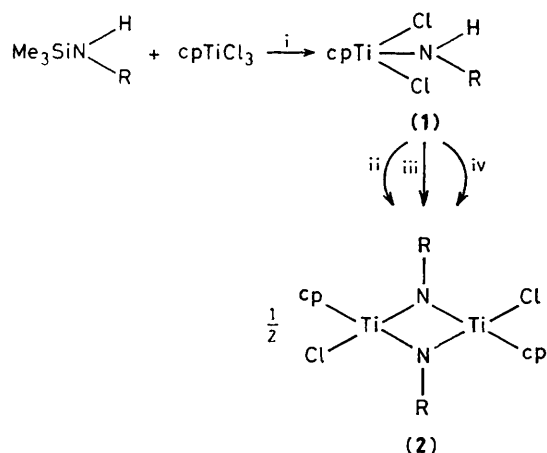
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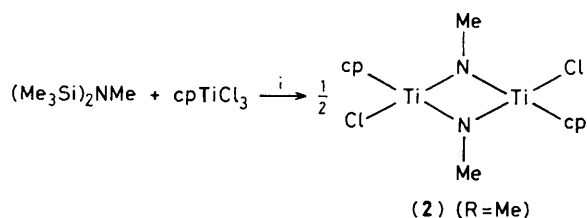
cpTiCl_3 (cp = $\eta^5\text{-C}_5\text{H}_5$) in reaction with $\text{Me}_3\text{SiN(H)R}$ (R = Et, Prⁱ, Bu^t, or Ph) yields the amido complexes $\text{cpTi(Cl)}_2\text{N(H)R}$, which react further by HCl abstraction to give the corresponding centrosymmetric binuclear imido complexes $[\text{cp(Cl)Ti}]_2(\mu\text{-RN})_2$; 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^t, Bu^t, or Ph. i, thf, -Me₃SiCl; ii, heat, vacuum, -HCl; iii, CH₂Cl₂, Bu^tNH₂, -Bu^tNH₂·HCl; iv, (R = Bu^t) Et₂O, MeLi, -LiCl, -MeH.



Scheme 2. i, thf, -2Me₃SiCl.

could act as model systems for intermediates in nitrogen fixation systems such as cp₂TiR-N₂-reducing agent (cp = η⁵-C₅H₅).²

The yellow to red-brown amido complexes cpTiCl₂N(H)R (1) (R = Et, Pr^t, Bu^t, or Ph) were prepared at room temperature by reaction of cpTiCl₃ 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 Me₃Si 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 N(H)R. The amido complexes (1) were fully characterized.† They are all very air sensitive and hydrolyse in moist air giving RNH₂·HCl and polymeric, oxygen-bridged cyclopentadienylorganotitanium 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^tNH₂ 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 methylimido complex (2) (R = Me) was prepared directly from cpTiCl₃ and

† Satisfactory analytical data were obtained for all complexes. The ¹H n.m.r. spectra (25 °C, CD₂Cl₂) 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 ν(N–H) absorptions at 3330 cm⁻¹ in all cases. The mass spectrum of cpTi(Cl)₂N(H)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 CH₃ group is missing, which is a normal phenomenon with alkylamines.

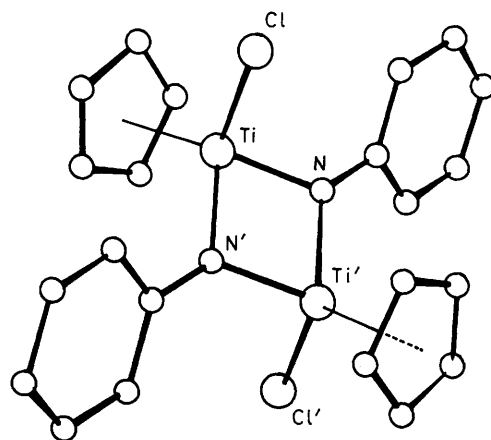
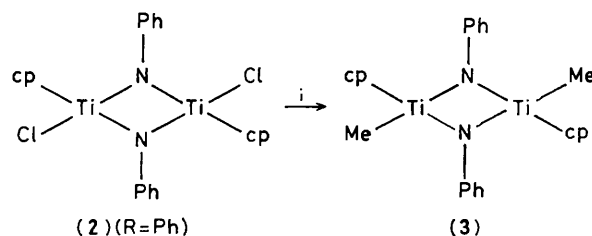


Figure 1



Scheme 3. i, MeLi, -LiCl.

(Me₃Si)₂NMe; 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 [cp(Cl)Ti]₂(μ-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 RNH₂·HCl and cpTiCl₃ were formed. Reaction of (2) (R = Ph) with MeLi resulted in substitution of the chlorine ligands and formation of [cp(Me)Ti]₂(μ-PhN)₂ (3) (Scheme 3). The redox behaviour of some imido complexes

‡ Both ¹H n.m.r. (CDCl₃) and ¹³C n.m.r. (CDCl₃) data show one resonance for the cp group (¹H: 6.3–6.6; ¹³C: 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 (Ti–N)₂ ring system. The mass spectra all show the molecular ion peak.

§ *Crystal data* for (2) (R = Ph): C₂₂H₂₀Cl₂N₂Ti₂, 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) Å; U = 2180.9 (2.1) Å³, Z = 4, D_c = 1.459 g cm⁻³; F(000) = 976, λ(Cu–Kα) = 1.5418 Å, μ(Cu–Kα) = 87.7 cm⁻¹; the crystals were rather imperfect; intensities were measured with a Nonius-CAD 4F diffractometer (1.0 < 2θ < 154.0°) on a crystal with dimensions 0.20 × 0.35 × 0.40 mm³, 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 > 3σ(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 M Bu₄NClO₄). 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) (R = Bu^t) at -0.78 V in CH₂Cl₂ 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) (R = Ph) and (3) with Na amalgam or Na₂[Fe(CO)₄] results in the formation of the ionic complexes Na{[cp(X)Ti]₂(μ-PhN)₂}-

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

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