

Titanium(III) paramagnetic complexes for radical coupling of organic substrates

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A new class of titanium(III) complexes bearing a tripodal diamine bis(phenolate) ligand was investigated through electron transfer reactions. The ligand (Me₂NCH₂CH₂N(CH₂-2-HO-3,5-C₆H₂^tBu₂)₂) (**30**) was prepared by a well-established Mannich reaction between 2,4-C₆H₃^tBu₂, Me₂NCH₂CH₂NH₂ and formaldehyde. Reaction of titanium trichloride with 1 equiv of sodium salt of **30** led to formation of TiCl(L)N₂O₂^{tBu} (L = THF, **31**; py, **32**). Exposure of **31** and **32** to air led to the titanium oxo-bridged dimer [TiClN₂O₂^{tBu}]₂(μ-O) (**37**). Reaction of **37** with excess of water led to formation of insoluble hydrolysis products, possibly polymeric. From reaction of **31** with PhCH₂MgCl a green product was obtained, tentatively formulated as Ti(CH₂Ph)N₂O₂^{tBu} (**38**). Further reactions of **31** and **32** with [Cp₂Fe(III)][BPh₄] were performed and led to formation of [TiCl(L)N₂O₂^{tBu}][BPh₄] (L = THF, **44**; py, **45**). The cationic complexes readily undergo decomposition reactions to generate TiCl₂N₂O₂^{tBu} (**46**) as the major product. The reaction of **31** with CH₃CN gave TiCl(NCCH₃)N₂O₂^{tBu} which upon heating converts to a new paramagnetic species that is likely a chloride-bridged Ti(III) dimer. Oxidation of this chloride-bridged dimer with [Cp₂Fe(III)][BPh₄] gave a mixture of products where **37** and **46** could be identified.

Keywords: titanium(III); diamine bis(phenolate); C-C bond formation; electron-transfer process; radical coupling; cationic complexes

Introduction

The formation of new carbon-carbon bonds is a fundamental key in organic synthesis. From all types of reactions used for this purpose, the radical ones (and particularly with titanium compounds) were the less investigated, although having a very rich and unique chemistry^{1,2}. For that reason they deserved our attention.

Since 1950's metallocene chemistry boom, a large variety of titanium(III) complexes has been developed. Complexes bearing cyclopentadienyl ligands³⁻⁹, often used for the radical coupling of organic substrates¹⁰⁻²⁹, were following replaced by others supported by alkoxy^{30,31} and amido³²⁻³⁵ ligands. These novel non-organotitanium compounds demonstrated successful results in reductive coupling transformations and the respective titanium(IV)-substrate adducts were also characterized.

Recently, a new class of titanium(III) complexes with a tripodal diamine bis(phenolate) supporting ligand were

prepared³⁶⁻⁴⁰. Complexes **31** and **32** (**figure 1**) were the first neutral titanium(III) complexes of this type being described⁴¹ and they seemed to be able to perform reductive coupling reactions, aimed for this work. Thus, the stability and reactivity of complexes **31** and **32** were investigated to assess their potential in single-electron transfer processes.

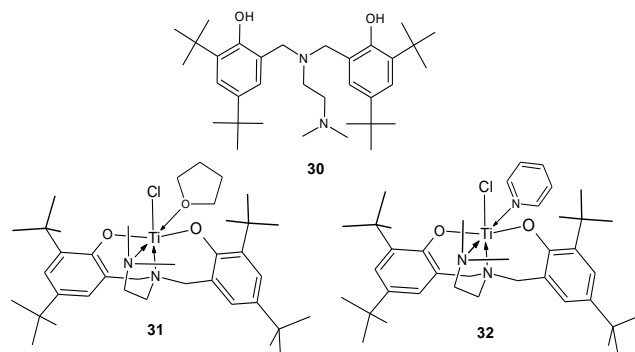


Figure 1 – Titanium(III) complexes **31** and **32** supported by diamine bis(phenolate) ligand **30**

Results and Discussion

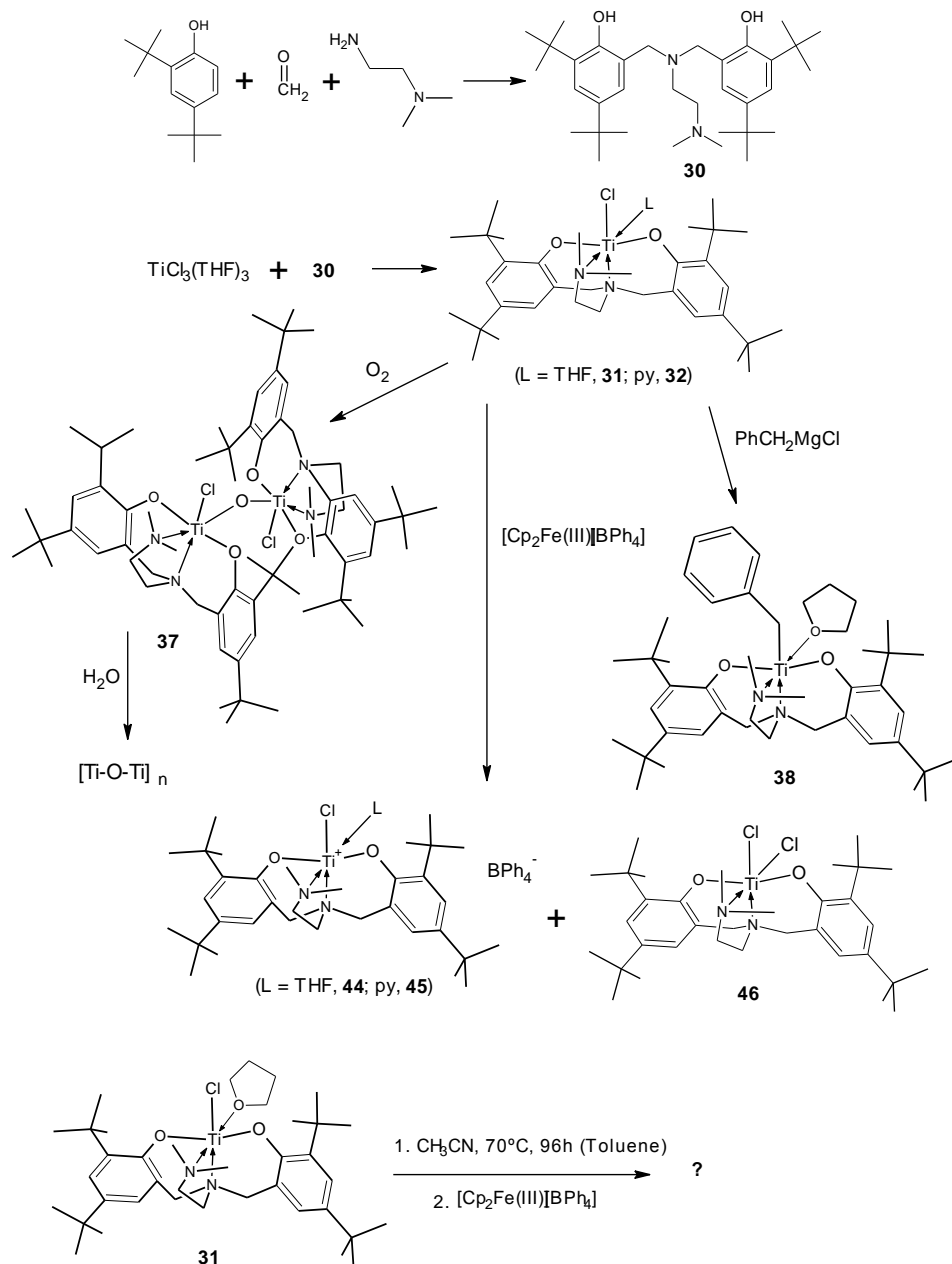


Figure 2 – Resume of the reactions performed

All the reactions performed in this work are summarized in the **Figure 2**.

Refluxing a solution of 2 equiv of 2,5-di-*tert*-butyl-phenol, 2.7 equiv of formaldehyde and 1 equiv of *N,N*-dimethyl-ethylenediamine in methanol, over 48 hours, led to the formation of **30** (abbreviated as $\text{H}_2\text{N}_2\text{O}_2^{t\text{-Bu}}$ and as $\text{N}_2\text{O}_2^{t\text{-Bu}}$ in the anionic form), as the major product of a well-established Mannich condensation. A small amount of the correspondent

benzoxazine was also achieved, as a yellowish oil, indicating a second possible pathway⁴² for the reaction to form more stable products. The room-temperature ^1H NMR spectrum of **30** shows only one set of resonances in accordance with the proposed structure.

Treatment of $\text{TiCl}_3(\text{THF})_3$ with the sodium salt of **30** ($\text{NaN}_2\text{O}_2^{t\text{-Bu}}$), in THF, resulted in the orange complex **31**, $\text{TiCl}(\text{THF})\text{N}_2\text{O}_2^{t\text{-Bu}}$. Complex **32**, $\text{TiCl}(\text{py})\text{N}_2\text{O}_2^{t\text{-Bu}}$, was obtained by addition of an excess of pyridine to a

solution of **31** in THF, resulting in an instantaneous color change from orange to purple, indicative of THF replacement by pyridine. The tetracoordinating diamine bis(phenolate) ligand **30** forces the two free coordination positions (typically occupied by chlorine and THF or pyridine) to a *cis* configuration. Thus, the phenolate rings adjust themselves in a *trans* configuration with less steric hindrance, resulting in a C_s symmetry for complexes **31** and **32**. The structures of **31** and **32** have been determined by single crystal X-ray diffraction and the compounds were also characterized by EPR⁵⁵ and its magnetic susceptibility was measured⁵⁵.

When a solution of $TiCl(THF)N_2O_2^{t-Bu}$ in THF is exposed to air, it immediately changes its color from yellow/orange to dark orange, confirming the high instability of these compounds to air and moisture. The only Ti(IV) product was identified as the crystalline oxide **37**, $[TiClN_2O_2^{t-Bu}]_2(\mu-O)$, with an oxygen bridge between the two metal centers, quite different from the multinuclear oxidized product that might have been formed. This result suggests a radical coupling with O_2 , followed by oxygen-oxygen bond cleavage. The 1H NMR spectrum of **37** shows only a set of resonances, with only one AX system for the benzylic protons, which is consistent with an average C_s symmetry.

Several diamine bis(phenolate) compounds of Ti(IV) studied by other research groups^{43,44} were found to exhibit good cytotoxic properties. The assumption of potential anti-tumoral activity for oxide **37** drove us to study the reaction of $[TiClN_2O_2^{t-Bu}]_2(\mu-O)$ with an excess of water, in view to predict its stability in aqueous media. A yellow precipitate was obtained, insoluble in most of the common organic solvents, pointed as a possible product of hydrolysis. From IR analysis of the product, the absence of Ti-Cl bands (in general between $\nu = 510$ e 370 cm^{-1})⁴⁵ and the shift of the more intense Ti-O-Ti peak to a higher wavenumber value ($\nu = 803\text{ cm}^{-1}$), are in agreement with the formation of polymeric species of $[Ti-O-Ti]_n$ type with elimination of Cl^- ions. The formation of insoluble hydrolysis products may possibly compromise the cytotoxic activity of compound **37**.

The alkylation reaction of complex **31** with benzylmagnesium chloride, $PhCH_2MgCl$, was expected to give compound $Ti(CH_2Ph)(THF)N_2O_2^{t-Bu}$, **38**. The product of the reaction was a green microcrystalline solid, with Ti(III) characteristic color. However, the full characterization of **38** was not yet possible. Previous reactions of titanium complex **32** with $PhCH_2MgCl$ showed that this complex is susceptible to suffer a radical transfer rearrangement to generate a dibenzyl titanium complex, $[Ti(CH_2Ph)_2N_2O_2^{t-Bu}]$, co-crystallized with oxide **37** in a 1:1 ratio. The formation of **37** can't be attributed to the entrance of air because the dibenzyl complex is extremely sensitive to water and the titanium-carbon bonds would hydrolyse. Thus, a tentative explanation for these results is the transfer of a benzyl radical from one molecule of **38** to another. The formation of **37** may result from subsequent activation of Et_2O , existing as solvent, and abstraction of Cl^- from magnesium salts not removed during workup.

To assess the success of single-electron transfer process, mediated by diamine bis(phenolate) complexes **31** and **32**, were oxidized by reaction with ferricinium tetraphenylborate, $[Cp_2Fe(III)][BPh_4]$. The slowly addition of a $TiCl(THF)N_2O_2^{t-Bu}$ solution in THF to a blue suspension of the ferricinium oxidant, in the same solvent, at $-60^\circ C$, resulted in the formation of the oxide **37**. Then, THF was replaced by toluene, but the same reaction led, initially, to the formation of a microcrystalline red/orange solid, identified as the dichloride compound **46**, $TiCl_2N_2O_2^{t-Bu}$. Crystals of **46** were obtained from a C_6D_6 solution at $-20^\circ C$ and the molecular structure of $TiCl_2N_2O_2^{t-Bu}$ is presented in **Figure 3** (the selected parameters are resumed in **Table 1**).

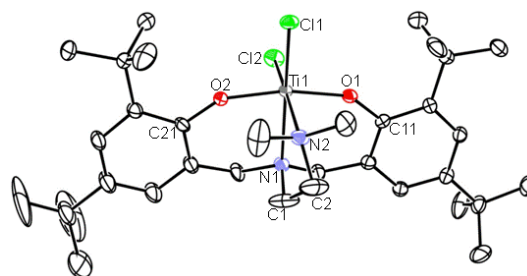


Figure 3 – ORTEP-3 diagram of $TiCl_2N_2O_2^{t-Bu}$ (**46**) using 40 % probability level ellipsoids. Hydrogen atoms are omitted for clarity.

Table 1 – Selected bond distances (Å) and angles (°) for $\text{TiCl}_2\text{N}_2\text{O}_2$ (**46**)

Distances (Å)			
Ti(1)-O(1)	1.842(2)	Ti(1)-N(2)	2.291(3)
Ti(1)-O(2)	1.833(2)	Ti(1)-Cl(1)	2.304(1)
Ti(1)-N(1)	2.254(2)	Ti(1)-Cl(2)	2.320(1)
Ti(1)-plano eq. ^a	0.191(1)		
Angles (°)			
O(1)-Ti(1)-O(2)	167.8(1)	N(1)-Ti(1)-N(2)	78.7(1)
O(1)-Ti(1)-N(1)	84.5(1)	N(1)-Ti(1)-Cl(1)	166.4(1)
O(1)-Ti(1)-N(2)	86.9(1)	N(1)-Ti(1)-Cl(2)	91.9(1)
O(1)-Ti(1)-Cl(1)	97.5(1)	N(2)-Ti(1)-Cl(1)	87.9(1)
O(1)-Ti(1)-Cl(2)	90.2(1)	N(2)-Ti(1)-Cl(2)	170.4(1)
O(2)-Ti(1)-N(1)	83.2(1)	Cl(1)-Ti(1)-Cl(2)	101.5(0)
O(2)-Ti(1)-N(2)	90.5(1)	Ti(1)-O(1)-C(11)	145.6(2)
O(2)-Ti(1)-Cl(1)	94.4(1)	Ti(1)-O(2)-C(21)	146.0(2)
O(2)-Ti(1)-Cl(2)	90.5(1)	Ti(1)-N(1)-C(1)-C(2)	-34.3(4)
θ^b	176.8(2)		

^a The equatorial plane is defined by atoms O1, O2, N2 and Cl2.

^b θ is the angle between the planes containing the aromatic rings

The titanium coordination geometry is distorted octahedral with the equatorial plane defined by atoms O1, O2 and N2 of the ligand and the chloride ligand Cl2, while the axial positions are occupied by the tripodal nitrogen N1 and the chloride ligand Cl1. The titanium is slightly away from the equatorial plane [0.191(1) Å] towards Cl1. The two phenolate moieties occupy *trans* positions with an angle of 176.8(2)° between the aromatic rings planes.

The most reasonable hypothesis for the formation of Ti(IV) complex **46** passes through the pre-formation of the cationic and particularly electrophilic species of Ti(IV), from oxidation with the ferricinium, followed by chloride abstraction of a second molecule that decomposes in solution. The other hypothesis for the source of extra chloride ions is the existence of NaCl, produced during the treatment of $\text{TiCl}_3(\text{THF})_3$ with the sodium salt of the ligand, that could remain in solution, eventually allowing the formation of a Ti(III) 'ate complex'. Evidences for this type of zwitterionic complexes had already been described by Sarazin *et al*, which obtained the complex

29,

$[\text{Ti}(\text{Me}_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_2-2-\text{O}-3\text{-}^t\text{Bu}-5\text{-MeC}_6\text{H}_2)_2(\text{O}^i\text{Pr})_2.\text{Na}(\text{THF})_2]$ (**Figure 4**) by reduction with sodium amalgam of the respective diamine bis(phenolate) Ti(IV) complex⁴⁶.

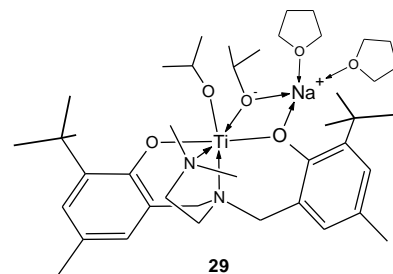


Figure 4 – Chemical structure for zwitterionic complex $[\text{Ti}(\text{Me}_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_2-2-\text{O}-3\text{-}^t\text{Bu}-5\text{-MeC}_6\text{H}_2)_2(\text{O}^i\text{Pr})_2.\text{Na}(\text{THF})_2]$ (**29**)

The single-electron transfer studies to the ferricinium cation continued with complex **32** with the hope to achieve more satisfactory results. Pyridine was tried as a more stabilizing ligand by the fact that the sp_2 hybridized nitrogen atom doesn't allow the C-H activation to occur so easily and, on the other hand, it is a more efficient electron donor due to the more extended and directional sp_2 orbital, when compared with the sp_3 hybridized oxygen atom in THF. Indeed, the mixture of a solution of **32** in toluene with a suspension of ferricinium oxidant, at -60°C in the same solvent, resulted in $[\text{TiCl}(\text{py})\text{N}_2\text{O}_2^{t\text{Bu}}][\text{BPh}_4]$, **45**, as a red/orange crystalline solid. This result confirmed the oxidation of Ti(III) to Ti(IV) that could not previously be obtained when $L = \text{THF}$. A new attempt of this reaction, with isolation and characterization of the product immediately after the work up, allowed the NMR identification of $[\text{TiCl}(\text{THF})\text{N}_2\text{O}_2^{t\text{Bu}}][\text{BPh}_4]$, **44**, together with **46**.

The proton and carbon NMR spectra for **44** and **45** only showed a set of resonances for the ancillary ligand, coherent with an average C_s symmetry. However, both cationic complexes decompose, in solution, to $\text{TiCl}_2\text{N}_2\text{O}_2^{t\text{Bu}}$. The NMR spectra reveal that **45** is much more stable and isolable than **44**. These results suggest that the formation of the cations strongly increases the polarity of the Ti-Cl bond, which, in result, is not able to provide the sufficient electronic stabilization required for the tremendously electrophilic Ti(IV)^+ center, and, by a

decomposition process leads to chloride ions abstraction when this ion is the only electron-donor in the reaction medium.

Finally, the reaction of $\text{TiCl}(\text{THF})\text{N}_2\text{O}_2^{\text{t-Bu}}$ with acetonitrile, already performed and described in literature⁴¹, was made. Upon addition of one equivalent of CH_3CN to a THF solution of complex **31**, a new titanium(III) species with $g = 1.962$ was formed. The new species is tentatively assigned to $\text{TiCl}(\text{CH}_3\text{CN})\text{N}_2\text{O}_2^{\text{t-Bu}}$ that results from the replacement of THF by acetonitrile. On heating the solution at $70\text{ }^\circ\text{C}$, another titanium(III) complex displaying $g = 1.957$ starts to form and after heating for 96 h either $\text{TiCl}(\text{THF})\text{N}_2\text{O}_2^{\text{t-Bu}}$ or $\text{TiCl}(\text{CH}_3\text{CN})\text{N}_2\text{O}_2^{\text{t-Bu}}$ are completely converted into the new compound that is formulated as a chloride-bridged titanium(III) dimer, $[\text{TiN}_2\text{O}_2^{\text{t-Bu}}]_2(\mu\text{-Cl})_2$. The main goal of an electron transfer reaction to acetonitrile was unfruitful and to get evidence about the postulated chloride-bridged dimer, a solution of the hypothetical $[\text{TiN}_2\text{O}_2^{\text{t-Bu}}]_2(\mu\text{-Cl})_2$ complex was added to a suspension of $[\text{Cp}_2\text{Fe}(\text{III})][\text{BPh}_4]$, both in toluene, at -60°C . The oxidation of $[\text{TiN}_2\text{O}_2^{\text{t-Bu}}]_2(\mu\text{-Cl})_2$ complex resulted in a microcrystalline red/orange solid which was characterized by ^1H , ^{13}C and ^{11}B NMR spectroscopy. ^1H and ^{13}C spectra revealed 3 sets of resonances, supported by the existence of 3 AX systems and 3 peak sets assigned to ^tBu groups in phenolate moieties. ^{11}B spectrum also revealed a broad sign attributed to BAR_3 species mixed with a low intensity and sharp peak at -5.84 ppm, still confirming the existence of the BPh_4^- anion. These results point to a possible phenyl transfer from BPh_4^- to generate BPh_3 species. Nevertheless, the assignment of NMR spectra peaks was impossible and the characterization of this system remained inconclusive.

Concluding Remarks

Titanium(III) complexes bearing a tripodal a diamine bis(phenolate) ligand are described. The stability and reactivity of these complexes towards single-electron transfer are also presented. All complexes display distorted octahedral geometry with a *trans*-configuration for phenolate rings, forced by the tripodal ligand.

Complexes **31** and **32** are extremely reactive and when exposed to air or moisture, form the Ti(IV) oxo-bridged dimer **37**. Showing potential cytotoxic properties, **37** was investigated through hydrolysis resistance in aqueous media, but polymeric and insoluble species were obtained, perhaps with compromise of its biological activity.

Very instable benzylic complex **38** was prepared, although its full characterization was not possible. When a source of chloride ions is present, **38** can decompose and transfer a benzyl radical, producing a dibenzylic complex and oxide **37**.

The reactions of **31** and **32** with the ferricinium cation were performed and the respective cationic complexes of Ti(IV) were characterized. Pyridine cationic complex is more stable than the THF analogue, but both complexes decompose to give $\text{TiCl}_2\text{N}_2\text{O}_2^{\text{t-Bu}}$, **46**. The existence of a Ti-Cl bond with high polarization preclude the stabilization of such Ti(IV) cationic species.

Heating a solution of **31** with acetonitrile in toluene resulted on the $[\text{TiN}_2\text{O}_2^{\text{t-Bu}}]_2(\mu\text{-Cl})_2$ formation. The oxidation with the ferricinium salt gave a mixture of three compounds, two of them probably assigned as **37** and **46**.

Experimental Section

General Procedures. All preparations and subsequent manipulations were carried out using standard Schlenk line and drybox techniques in an atmosphere of dinitrogen. The used solvents were dried prior to use with 4 \AA molecular sieves and refluxed over Na/benzophenone (THF, toluene, Et_2O and 1,4-dioxane) or CaH (*n*-hexane and pyridine). Deuterated solvents were also dried over Na and distilled. All the other reagents are from commercial sources. $\text{TiCl}_3(\text{THF})_3$ was prepared as described in literature⁴⁷.

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance II+ 300 MHz (UltraShield Magnet) spectrometer at room temperature. ^1H and ^{13}C NMR spectra were referenced internally to residual protio-solvent (^1H) or solvent (^{13}C) resonances and reported relative to tetramethylsilane (δ 0). ^{11}B spectra

were reported relative to $\text{BF}_3 \cdot \text{OEt}_2$ (δ 0). Chemical shifts are quoted in δ (ppm) and coupling constants in hertz. The assessment of proton and carbon resonances has been based on COSY, HSQC and NOESY experiments.

Infrared (IR) spectra were prepared as KBr pellets and were recorded on Jasco FT/IR-4100 spectrometer. Infrared data are quoted in wavenumbers (cm^{-1}).

Elemental analyses were performed in CE Instruments EA110 automatic analyzer.

Crystals of **46** suitable for single-crystal X-ray analysis were grown as described in the synthetic procedures. Crystallographic data were collected using graphite monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) on a Bruker AXS-KAPPA APEX II diffractometer equipped with an Oxford Cryosystem open-flow nitrogen cryostat. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT on all observed reflections. Absorption corrections were applied using SADABS⁴⁸. The structures were solved and refined using direct methods with programs SIR 97⁴⁹, SIR2004⁵⁰ or SHELXS-97⁵¹. All programs are included in the package of programs WINGX-Version 1.80.01⁵² SHELXL⁵³. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were inserted in idealized positions and allowed to refine riding on the parent carbon atom. The molecular diagram was drawn with ORTEP-3 for Windows⁵⁴ included in the software package.

Table 2 - Selected crystallographic experimental data and structure refinement parameters for $\text{TiCl}_2\text{N}_2\text{O}_2$

Empirical formula	$\text{C}_{34}\text{H}_{54}\text{Cl}_2\text{N}_2\text{O}_2\text{Ti}$	$V(\text{\AA}^3)$	18780.0(14)
Formula weight	641.59	$Z, \rho_{\text{calc}} (\text{gcm}^{-3})$	16, 0.908
Temperature (K)	150(2)	$\mu(\text{mm}^{-1})$	0.319
Crystal system	Tetragonal	Crystal size	0.40×0.40×0.10
Space group	$P4/nnc$	Crystal colour	orange
a(Å)	24.7045(9)	Crystal shape	prism
b(Å)	24.7045(9)	Refl. collected	326467
c(Å)	30.7712(16)	Unique refl. [R(int)]	8344 [0.0769]
α (°)	90	R1 [$ \gt 2\sigma(I) $]	0.0694
β (°)	90	wR2 [$ \gt 2\sigma(I) $]	0.1843

γ (°)	90	GooF	1.084
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$\text{H}_2\text{N}_2\text{O}_2^{\text{t-Bu}}$ (30). A solution of 2,4-di-*tert*-butyl-phenol (5.01 g, 24.2 mmol), *N,N*-dimethylethylenediamine (1.35 mL, 12.3 mmol) and formaldehyde (37%) (2.5 ml, 33.6 mmol) in methanol was refluxed over 48h. The solution was cooled down and left at -20°C overnight, to induce complete precipitation. The precipitate obtained was filtrated and washed with cold methanol. Then, the precipitate was recrystallized from hexane as a crystalline white powder (5.67 g, 10.8 mmol, 90%). ^1H RMN (300 MHz, CDCl_3 , δ (ppm)): 9.81 (s, 2H, OH), 7.21 ($^4J_{\text{HH}} = 2.3$ Hz, d, 2H, p-ArH), 6.89 ($^4J_{\text{HH}} = 2.3$ Hz, d, 2H, o-ArH), 3.62 (s, 4H, CH_2), 2.61 (m, 4H, CH_2), 2.33 (s, 6H, $\text{N}(\text{CH}_3)_2$), 1.41 (s, 18H, $\text{C}(\text{CH}_3)_3$), 1.29 (s, 18H, $\text{C}(\text{CH}_3)_3$).

$\text{TiCl}(\text{THF})\text{N}_2\text{O}_2^{\text{t-Bu}}$ (31). A solution of $\text{H}_2\text{N}_2\text{O}_2^{\text{t-Bu}}$ (30) (0.52 g, 1 mmol) in THF was added to a suspension of NaH (0.053 g, 2.2 mmol) in the same solvent at -30°C . The temperature was allowed to rise slowly to room temperature and further stirred for 2h. The colorless solution of $\text{NaN}_2\text{O}_2^{\text{t-Bu}}$ obtained was filtered through Celite and added to a suspension of $\text{TiCl}_3(\text{THF})_3$ (0.37 g, 1 mmol) in THF at -80°C . The mixture was stirred for 4h and allowed to reach room temperature slowly. The orange solution obtained was evaporated to dryness, and the residue was extracted in Et_2O and filtered. Evaporation of the solution to dryness led to microcrystalline orange solid (0.58 g, 0.86 mmol, 86%).

$\text{TiCl}(\text{py})\text{N}_2\text{O}_2^{\text{t-Bu}}$ (32). A solution of $\text{H}_2\text{N}_2\text{O}_2^{\text{t-Bu}}$ (30) (1.57 g, 3 mmol) in THF was added to a suspension of NaH (0.16 g, 6.6 mmol) in the same solvent at -30°C . The temperature was allowed to rise slowly to room temperature and further stirred for 2h. The colorless solution of $\text{NaN}_2\text{O}_2^{\text{t-Bu}}$ obtained was filtered through Celite and added to a suspension of $\text{TiCl}_3(\text{THF})_3$ (1.11 g, 3 mmol) in THF at -80°C , followed by quickly addition of pyridine (0.36 mL, 4.5 mmol). The mixture was stirred for 4h and allowed to reach room temperature slowly. The purple solution obtained was evaporated to dryness, and the residue was extracted in Et_2O and filtered.

Evaporation of the solution to dryness led to microcrystalline orange solid (1.66 g, 2.4 mmol, 81%).

[Cp₂Fe(III)][BPh₄]. On an Erlenmeyer were added 25 mL of concentrated H₂SO₄ over ferrocene (2.50 g, 13.4 mmol). The mixture was further stirred for 40 minutes and the resulting dark blue solution was carefully added over 600 mL of ice-cold water. This blue solution was then filtered and added to 500 mL of an aqueous solution of NaBPh₄ (4.03 g, 11.8 mmol). The blue precipitate formed (5.37 g, 10.6 mmol, 89%) was filtered, washed with water (5 x 0.5 mL) and dried in vacuum line. Anal. Calcd for C₃₄H₃₀BF_e: C, 80.82; H, 5.98; N, 0.00; found: C, 78.59; H, 5.00; N, <0.5.

[TiCl(THF)N₂O₂^{tBu}][BPh₄] (44). A blue suspension of [Cp₂Fe(III)][BPh₄] (0.43 g, 0.86 mmol) in toluene was slowly added to a solution of TiCl(THF)N₂O₂^{tBu} (0.58 g, 0.86 mmol) in the same solvent at -80°C, followed by instantaneous color exchange from yellow/orange to dark orange. The temperature was allowed to rise slowly to room temperature and further stirred overnight. Next, the mixture was evaporated to dryness and washed with hexane (excess) and filtered. The dark orange residue obtained was dried in the vacuum line (0.73 g, 0.74 mmol, 86%). ¹H RMN (75 MHz, C₆H₅Br, δ(ppm)): 7.32 (m, 20H, B(C₆H₅)₄), 7.12 (d, 2H, ⁴J_{HH} = 2.3 Hz, *p*-CH-Ar), 6.94 (d, 2H, ⁴J_{HH} = 2.3 Hz, *o*-CH-Ar), 4.39 (d, ²J_{HH} = 13.8 Hz, 2H, NCH₂Ar), 3.77 (s, 4H, CH₂OCH₂, THF), 3.14 (d, ²J_{HH} = 13.3 Hz, 2H, NCH₂Ar), 2.57 (m, 2H, CH₂), 2.06 (s, 6H, N(CH₃)₂), 1.93 (s, 4H, CH₂CH₂, THF), 1.57 (s, 18H, 5-C(CH₃)₃), 1.45 (m, 2H, CH₂), 1.39 (s, 18H, 3-C(CH₃)₃). ¹³C-¹H NMR (75 MHz, C₆H₅Br, δ(ppm)): 163.7 (C_{ipso}-BAr₄), 158.4 (C_{ipso}-Ar), 143.1 (C_{ipso}-Ar), 136.6 (*o*-CH, BAr₄), 135.4 (C_{ipso}-Ar), 127.3 (*m*-CH, BAr₄), 126.2 (C_{ipso}-Ar), 125.2 (*p*-CH-Ar), 124.1 (*o*-CH-Ar), 121.7 (*p*-CH, BAr₄), 67.3 (CH₂OCH₂, THF), 66.5 (NCH₂Ar), 60.2 (CH₂), 53.9 (CH₂), 51.3 (N(CH₃)₂), 35.2 e 34.3 (C(CH₃)₃), 31.6 e 31.4 (C(CH₃)₃), 25.2 (CH₂CH₂, THF). ¹¹B RMN (300 MHz, C₆H₅Br, δ(ppm)): -5.86 (s, BPh₄⁻).

TiCl(py)N₂O₂^{tBu}][BPh₄] (45). A blue suspension of [Cp₂Fe(III)][BPh₄] (1.21 g, 2.4 mmol) in toluene was

slowly added to a solution of TiCl(py)N₂O₂^{tBu} (1.66 g, 2.4 mmol) in the same solvent at -80°C, followed by instantaneous color exchange from yellow/orange to dark orange. The temperature was allowed to rise slowly to room temperature and further stirred overnight. Next, the mixture was evaporated to dryness and washed with hexane (excess) and filtered. The dark orange residue obtained was dried in the vacuum line (2.09 g, 2.2 mmol, 93%). ¹H RMN (75 MHz, C₆H₅Br, δ(ppm)): 8.35 (s, 2H, *o*-py), 7.52 (s, 1H, *p*-py), 7.30 (m, 20H, B(C₆H₅)₄), 7.10 (d, 2H, ⁴J_{HH} = 2.3 Hz, *p*-CH-Ar), 6.93 (d, 2H, ⁴J_{HH} = 2.3 Hz, *o*-CH-Ar), 6.72 (s, 2H, *m*-py), 4.39 (d, ²J_{HH} = 13.8 Hz, 2H, NCH₂Ar), 3.14 (d, ²J_{HH} = 13.3 Hz, 2H, NCH₂Ar), 2.58 (m, 2H, CH₂), 2.21 (s, 6H, N(CH₃)₂), 1.73 (s, 18H, 5-C(CH₃)₃), 1.54 (m, 2H, CH₂), 1.42 (s, 18H, 3-C(CH₃)₃). ¹³C-¹H NMR (75 MHz, C₆H₅Br, δ(ppm)): 163.7 (C_{ipso}-BAr₄), 158.4 (C_{ipso}-Ar), 147.8 (*o*-CH, py), 143.1 (C_{ipso}-Ar), 136.6 (*o*-CH, BAr₄), 135.4 (C_{ipso}-Ar), 134.7 (*p*-CH, py), 127.2 (*m*-CH, BAr₄), 126.6 (C_{ipso}-Ar), 125.3 (*m*-CH, py), 124.3 (*p*-CH-Ar), 124.0 (*o*-CH-Ar), 121.7 (*p*-CH, BAr₄), 66.5 (NCH₂Ar), 60.8 (CH₂), 53.9 (CH₂), 51.3 (N(CH₃)₂), 35.3 e 34.3 (C(CH₃)₃), 31.7 e 31.4 (C(CH₃)₃). ¹¹B RMN (300 MHz, C₆H₅Br, δ(ppm)): -5.82 (s, BPh₄⁻).

[TiClN₂O₂^{tBu}]₂(μ-O) (37). A solution of TiCl(THF)N₂O₂^{tBu} (0.70 g, 1.9 mmol) in THF was exposed to air for 12 h. The red/orange solution obtained was evaporated to dryness, and the residue was extracted with Et₂O and filtered. Evaporation of the Et₂O solution to dryness led to an orange crystalline solid (1.06 g, 0.86 mmol, 91%). ¹H RMN (300 MHz, CDCl₃, δ(ppm)): 7.15 (⁴J_{HH} = 2.4 Hz, d, 4H, *p*-ArH), 6.91 (⁴J_{HH} = 2.3 Hz, d, 4H, *o*-ArH), 5.43 (²J_{HH} = 13.8 Hz, d, 4H, NCH₂Ph), 3.38 (²J_{HH} = 13.9 Hz, d, 4H, NCH₂Ph), 2.77 (s, 4H, NCH₂), 2.15 (s, 12H, N(CH₃)₃), 2.01 (s, 4H, CH₂N(CH₃)₃), 1.28 (s, 36H, 5-C(CH₃)₃), 1.00 (s, 36H, 3-C(CH₃)₃). IR spectrum (KBr) ν cm⁻¹: 2955 s, 2901 m, 2868 m, 1600 w, 1475 s, 1411 w, 1391 w, 1361 w, 1294 m, 1264 s, 1239 m, 1203 w, 1169 m, 1129 w, 1104 w, 1022 vw, 961 vw, 911 w, 873 w, 850 s, 808 w, 759 m, 696 s (broad), 621 w, 588 w, 575 m, 542 w, 508 vw, 475 m, 454 w, 404 w.

Reaction of $[\text{TiClN}_2\text{O}_2^{\text{t-Bu}}]_2(\mu\text{-O})$ with water. To an orange solution of $[\text{TiClN}_2\text{O}_2^{\text{t-Bu}}]_2(\mu\text{-O})$ in THF was added an excess of water, and the mixture was left unstirred over 24h. A yellow precipitate was obtained while the solution remained with a light orange color. The solvent was carefully pumped off and the residue was dried, resulting in a light yellow precipitate, insoluble in the most common solvents. Anal. Found: C, 9.57, H, 2.56, N, 0.69. IR spectrum (KBr) ν cm^{-1} : 3430 s (broad), 2958 s, 2867 w, 1631 m, 1477 m, 1415 w, 1391 w, 1362 w, 1261 m, 1169 w, 1098 m, 1025 m, 878 w, 803 s (broad), 612 w, 449 w, 415 w.

$\text{Ti}(\text{CH}_2\text{Ph})\text{N}_2\text{O}_2^{\text{t-Bu}}$ (47). A colorless solution of PhCH_2MgCl (1M, 2.28 mL, 2.28 mmol) in Et_2O was slowly added to a solution of $\text{TiCl}(\text{THF})\text{N}_2\text{O}_2^{\text{t-Bu}}$ (1.54 g, 2.28 mmol) in THF at -80°C . The temperature was allowed to rise slowly to room temperature and it was further stirred overnight. An excess of 1,4-dioxane (aprox. 50 mL) was added to the resulting brown mixture and then it was filtered. The brownish filtered solution was evaporated to dryness and the brown-greenish residue was extracted with hexane and filtered again. The hexane washing procedure was repeated. A green solution was achieved and it was evaporated to dryness, leading to the formation of a microcrystalline green solid (0.84 g, 1.14 mmol, 55%).

Oxidation of the $\text{TiCl}(\text{THF})\text{N}_2\text{O}_2^{\text{t-Bu}}$ + CH_3CN system. To a solution of $\text{TiCl}(\text{THF})\text{N}_2\text{O}_2^{\text{t-Bu}}$ (0.48 g, 0.70 mmol) in toluene was added acetonitrile (0.04 mL, 0.70 mmol). On heating at 70°C the orange solution, over 96 hours, a color change to red/orange was observed. The temperature was allowed to rise slowly to room temperature and the solution was slowly added to a blue suspension of $[\text{Cp}_2\text{Fe}][\text{BPh}_4]$ (0.35 g, 0.70 mmol) in toluene at -60°C . It was further stirred overnight and then evaporated to dryness. The residual ferrocene was removed by vacuum sublimation from a microcrystalline red/orange solid.

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References

- Nair, V.; Mathew, J.; Prabhakaran, J., *Chem. Soc. Rev.*, **1997**, 26, 127-132
- Reetz, M. T., *Topics in Current Chemistry*, Volume 106, **1982**, 1-54
- Kealy, T. J.; Pauson, P. L., *Nature*, **1951**, 168, 1039-1040
- Stahl, L.; Ernest, R. D., *Advances in Organometallic Chemistry*, Elsevier, Volume 55, **2008**, 137-195
- Tamelen, E. E.; Seeley, D.; Schneller, S.; Rudler, H.; Cretney, W., *J. Am. Chem. Soc.*, **1970**, 92, 5251-5253
- Hanna, T. E.; Lobkovsky, E.; Chirik, P. J., *J. Am. Chem. Soc.*, **2004**, 126, 14688-14689
- Hanna, T. E.; Lobkovsky, E.; Chirik, P. J., *Organometallics*, **2009**, 28, 4079-4088
- Brintzinger, H. H.; Bercaw, J. E., *J. Am. Chem. Soc.*, **1970**, 92, 6182-6185
- Petasis, N. A.; Hu, Y. H., *Curr. Org. Chem.*, **1997**, 1, 249-286
- De Boer, E. J. M.; Teuben, J. H., *J. Organomet. Chem.*, **1978**, 153, 53-57
- Cuerva, J. M.; Campaña, A. G.; Justicia, J.; Rosales, A.; Oller-López, J. L.; Robles, R.; Cárdenas, D. J.; Buñuel, E.; Oltra, J. E., *Angew. Chem. Int. Ed.*, **2006**, 45, 5522-5526
- RajanBabu, T. V.; Nugent, W. A., *J. Am. Chem. Soc.*, **1994**, 116, 986-997
- Barrero, A. F.; Oltra, J. E.; Cuerva, J. M.; Rosales, A., *J. Org. Chem.*, **2002**, 67, 2566-2571
- Barrero, A. F.; Quílez del Moral, J. F.; Sánchez, E. M.; Arteaga, J. F., *Org. Lett.*, **2006**, 8, 669-672
- Yamamoto, Y.; Hattori, R.; Miwa, T.; Nakagai, Y.; Kubota, T.; Yamamoto, C.; Okamoto, Y.; Itoh, K., *J. Org. Chem.*, **2001**, 66, 3865-3870.

16. Barden, M. C.; Schwartz, J.; *J. Am. Chem. Soc.*, **1996**, *118*, 5484-5485
17. Spencer, R. P.; Schwartz, J., *J. Org. Chem.*, **1997**, *62*, 4204-4205
18. Spencer, R. P.; Schwartz, J., *Tetrahedron*, **2000**, *56*, 2103-2112
19. Manzer, L. E., *Inorg. Syn.* 1982, *21*, 84-86.
20. Tanaka, K.; Kishigami, S.; Toda, F., *J. Org. Chem.* **1990**, *55*, 2981-2983
21. McMurry, J. E., *Chem. Rev.*, **1989**, *89*, 1513-1524
22. Ephritikhine, M., *Chem. Comm.*, **1998**, *6*, 2549-2554
23. Detsi, A.; Koufaki, M.; Calogeropoulou, T., *J. Org. Chem.* **2002**, *67*, 4608-4611
24. Alberto, S.; Pelayo, C.; Gloria, R.; Bosch, Onrubia, J.; Carmen, M., U.S. Patent 6084100, 2000
25. Dunlap, M. S.; Nicholas, K. M., *J. Organomet. Chem.*, **2001**, *630*, 125-131
26. Handa, Y.; Inanaga, J., *Tetrahedron Lett*, **1987**, *28*, 5717-5718
27. Liu, Y.; Schwartz, J., *J. Org. Chem.*, **1994**, *59*, 940-942
28. Liu, Y.; Schwartz, J., *Tetrahedron*, **1995**, *51*, 4471-4482
29. Barden, M. C.; Schwartz, J., *J. Org. Chem.*, **1995**, *60*, 5963-5965
30. Covert, K. J.; Wolczanski, P. T.; Hill, S. A.; Krusic, P. J., *Inorg. Chem.*, **1992**, *31*, 66-78
31. Huffman, J. C.; Moloy, K. G.; Marsella, J. A.; Caulton, K. G., *J. Am. Chem. Soc.*, **1980**, *102*, 3009-3014
32. Mendiratta, A.; Cummins, C. C., *Inorg. Chem.*, **2005**, *44*, 7319-7321
33. Wanandi, P. W.; Davis, W. M.; Cummins, C. C., *J. Am. Chem. Soc.*, **1995**, *117*, 2110-2111
34. Peters, J. C.; Johnson, A. R.; Odom, A. L.; Wanandi, P. W.; Davis, W. M.; Cummins, C. C., *J. Am. Chem. Soc.*, **1996**, *118*, 10175-10188
35. Agapie, T.; Diaconescu, P. L.; Mindiola, D. J.; Cummins, C. C., *Organometallics*, **2002**, *21*, 1329-1340
36. Tshuva, E. Y.; Versano, M.; Goldberg, I.; Kol, M.; Weitman, H.; Goldschmidt, Z., *Inorg. Chem. Commun.*, **1999**, *2*, 371-373
37. Tshuva, E. Y.; Goldberg, I.; Kol, M., *Inorg. Chem.*, **2001**, *40*, 4263-4270
38. Groysman, S.; Goldberg, I.; Kol, M., *Organometallics*, **2003**, *22*, 3013-3015
39. Boyd, C. L.; Toupance, T.; Tyrrell, B. R.; Ward, B. D.; Wilson, C. R.; Cowley, A. R.; Mountford, P., *Organometallics*, **2005**, *24*, 309-330
40. Toupance, T.; Dubberley, S. R.; Rees, N. H.; Tyrrell, B. R.; Mountford, P., *Organometallics*, **2002**, *21*, 1367-1382
41. Barroso, S.; Cui, J.; Carretas, J. M.; Cruz, A.; Santos, I. C.; Duarte, M. T.; Telo, J. P.; Marques, N.; Martins, A. M., *Organometallics*, **2009**, *28*, 3449-3458
42. Barroso, S.; Abreu, A. M.; Araújo, A. C.; Coelho, A. M.; Maulide, N.; Martins, A. M.; *Synlett*, **2010**, *publicado*
43. Perí, D.; Meker, S.; Shavit, M.; Tshuva, E. Y., *Chem. Eur. J.*, **2009**, *15*, 2403-2415
44. Manna, C. M.; Tshuva, E. Y., *Dalton Trans.*, **2010**, *39*, 1182-1184
45. Socrates, G., *Infrared and Raman Characteristic Group Frequencies – Tables and Charts*, Wiley, 3rd edition, **2001**, 304-306
46. Sarazin, Y.; Howard, R. H.; Hughes, D. L.; Humphrey, S. M.; Bochmann, M., *Dalton Trans.*, **2006**, 340-350
47. Manzer, L. E., *Inorg. Synth.*, **1982**, *21*, 135-136
48. Sheldrick, G. M. SADABS, Program for Empirical Absorption Correction; University of Göttingen: Göttingen, Germany, **1996**
49. Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115
50. Burla, M. C.; Caliandro, R.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; De Caro, L.; Giacovazzo, C.; Polidori, G.; Spagna, R. *J. Appl. Cryst.* **2005**, *38*, 381
51. Sheldrick, G. M. *Acta Cryst.* **1990**, *A46*, 467
52. Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837
53. Sheldrick, G. M. (a) SHELXL-97 – Programs for Crystal Structure Analysis (Release 97-2), Göttingen, Germany, **1998**; (b) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 122
54. Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565