

Synthesis and characterization of a monomeric octahedral C_2 -symmetric titanium complex bearing two 3,3'-diphenyl-2,2'-biphenol ligands†

Carine Diebold,^a Pierre Mobian,^a Clarisse Huguenard,^a Lionel Allouche^b and Marc Henry^{*a}

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The 3,3'-diphenyl-2,2'-biphenol (dpbpH₂) ligand is shown to react with Ti(OPr)₄ in a 2:1 ratio to yield a novel C_2 -symmetric mononuclear octahedral Ti(IV) bis-biphenolate complex, *cis*-Ti(dpbpO)₂(HOPr)₂.

The synthesis of complexes with controlled architectures is a fundamental purpose in coordination chemistry. The well-known family of titanium(IV) complexes bearing diphenolate ligands¹ illustrates well some of the difficulties encountered in designing complexes with predictable structures. Diphenolate-based Ti(IV) complexes display generally complex behaviours in solution due to their strong tendencies for oligomerisation *via* the formation of oxo and/or alkoxo-bridges between Ti-atoms.² Thus, the rational design of flexible monomeric Ti(IV) complexes with a controlled architecture and chirality that are able to keep their chemical integrity in solution is a challenging task.

We would like to report herein the synthesis, the solid-state characterization and the solution NMR study of a novel C_2 -symmetric octahedral monomeric Ti(IV) complex having two labile alcoholic ligands in *cis* positions. A sterically hindered biphenol ligand, *i.e.* 3,3'-diphenyl-2,2'-biphenol (dpbpH₂),³ was selected; its bulkiness is expected to prevent the formation of aggregates.⁴ The addition of Ti(OPr)₄ to a dry CD₂Cl₂ solution of dpbpH₂ in a 1:2 ratio, resulted immediately in the formation of a homogeneous red-orange mixture. ¹H NMR spectrum of this mixture recorded at room temperature showed that the reaction was quasi-quantitative with the disappearance of the signal of the phenolic protons of the free ligand at 5.82 ppm. Aromatic protons of dpbpH₂ as well as isopropoxide methine proton of Ti(OPr)₄ were all shifted to lower frequencies (Fig. S1 in ESI†). Moreover, the presence of a limited number of signals and a single set of resonance on the ¹H NMR spectrum suggests the selective formation of a unique and symmetrical compound. ¹³C NMR analysis is also in accordance with these assumptions. Unfortunately at this stage, a complete structural assessment of the complex was not possible, owing to the occurrence of broad resonances in the aromatic region of the ¹H NMR spectrum.†

In order to characterise this new complex, red-orange crystals⁵ suitable for X-ray diffraction (XRD) were obtained after two days

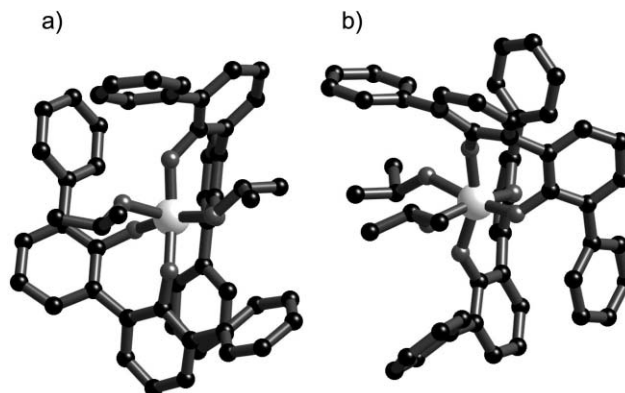


Fig. 1 Two views of the molecular structure of *cis*-(Λ , *aR*, *aS*)-Ti(dpbpO)₂(HOPr)₂. (a) Octahedral coordination of the Ti-atom. (b) View evidencing the two coordinated isopropanol ligands located in a confined chiral environment created by the presence of two phenyl rings. Hydrogens are omitted for clarity.

at 4 °C from CH₂Cl₂/*n*-pentane mixtures (75% yield). Crystal structure determination indicates the formation of a strongly distorted pseudo C_2 -symmetric octahedral mononuclear Ti(IV) complex formulated as *cis*-Ti(dpbpO)₂(HOPr)₂ (Fig. 1).‡

In this structure, two dpbpO ligands are wrapped around the metal centre leading to a complex which adopts a Λ or Δ configuration. Interestingly, upon coordination of the two dpbpH₂ ligands to the metal, an opposite configuration between these two biphenyl derivatives (*aR* and *aS*) is observed. Consequently, the unit cell contains two enantiomers adopting respectively a (Λ , *aR*, *aS*) and a (Δ , *aS*, *aR*) configuration. Concerning the Ti–O_(dpbpO) bonds, distances between 1.818 Å and 1.900 Å were measured. In the complex, the two remaining *cis* positions are occupied by coordinated HOPr ligands with much longer Ti–O distances (2.17 Å) that are in line with other isopropanol molecules found coordinated to Ti(IV) centres.⁶ To the best of our knowledge, the localization of these two isopropanol molecules between two phenyl rings belonging to the dpbpO ligands creates a unique confined chiral environment reported here for the first time.

¹³C CPMAS solid-state NMR analysis of the as-synthesized powders showed the existence of a pure, well-crystallized phase with a signature in perfect agreement with the XRD structure (Fig. S5 in ESI†). The best resolved aromatic ¹³C signals show that two chemically equivalent C sites observed in the ¹³C CPMAS spectrum of the free ligand may be related to a set of four peaks in the complex in agreement with the *P*-1 space group of the crystal. Similarly, the methyl groups of the two HOPr ligands give rise to four neighbouring signals around 22 ppm again in good agreement with the *P*-1 space group of the crystal. However, if

^aLaboratoire de Chimie moléculaire de l'Etat Solide, Université de Strasbourg, 67000, Strasbourg, France. E-mail: henry@chimie.u-strasbg.fr

^bService de RMN, Institut de Chimie, Université de Strasbourg, 67000, Strasbourg, France. E-mail: allouche@chimie.u-strasbg.fr

† Electronic supplementary information (ESI) available: ¹H solution NMR spectra, including variable temperature measurements and corresponding Eyring plot, ¹³C solid-state CP-MAS spectra of dpbpO ligand and *cis*-Ti(dpbpO)₂(HOPr)₂ and TGA curve. CCDC reference number 727138. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b912694p

two distinct signals are expected for CH groups in the complex according to XRD, only one peak is detected at 70.10 ppm in the ^{13}C CPMAS spectrum, suggesting a fortuitous overlap of resonance frequencies.

The next step was to examine in detail the behaviour of *cis*-Ti(dpbpol) $_2$ (HOPr i) $_2$ in solution. It is well documented that six-coordinate bis(chelate)-titanium complexes can undergo rapid $\Delta \rightleftharpoons \Lambda$ inversion of configuration at the metal centre.⁷ Accordingly, the observation of broad resonances in the room temperature ^1H NMR spectrum tends to indicate that *cis*-Ti(dpbpol) $_2$ (HOPr i) $_2$ adopts a fluxional behaviour in solution.[†] Important changes in the ^1H spectrum of *cis*-Ti(dpbpol) $_2$ (HOPr i) $_2$ recorded in toluene- d_8 were indeed observed by lowering the temperature from +25 °C down to -70 °C. Upon cooling, the aromatic resonances become strongly disturbed (Fig. S2 in ESI †), but a close examination of the isopropanol ligand resonances was particularly informative. At room temperature, these diastereotopic groups exhibit two broad signals at 0.52 ppm and 3.42 ppm attributed respectively to the methyl groups and the methine protons of the HOPr i ligands. Each of these signals split into two peaks of equal integration upon cooling. The presence in solution of the same pair of enantiomers *i.e.* (Δ , *aR*, *aS*) and (Δ , *aS*, *aR*) as the one characterized in the solid state matches well with these observations. It is also worth noticing that a new broad signal appears around 2.40 ppm at -20 °C which divides into two doublets at -70 °C. This observation is consistent with the NMR signature of the alcoholic protons of coordinated HOPr i (Fig. S3 in ESI †). The rate constants governing the exchange process of isopropanol ligands, $k(25\text{ °C}) = 7000\text{ s}^{-1}$, were thus determined using a NMR line-shape program (Win-DYNA \S) to simulate the spectra (Fig. 2). Corresponding Eyring plots yielded activation parameters: $\Delta H^\ddagger = 24.3 \pm 1\text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -91.5 \pm 2\text{ J K}^{-1}\text{ mol}^{-1}$, and $\Delta G^\ddagger_{298}(\text{calc}) = 51.6 \pm 2\text{ kJ K}^{-1}\text{ mol}^{-1}$, $T_c \approx -46\text{ °C}$ (Fig. S4 in ESI †).

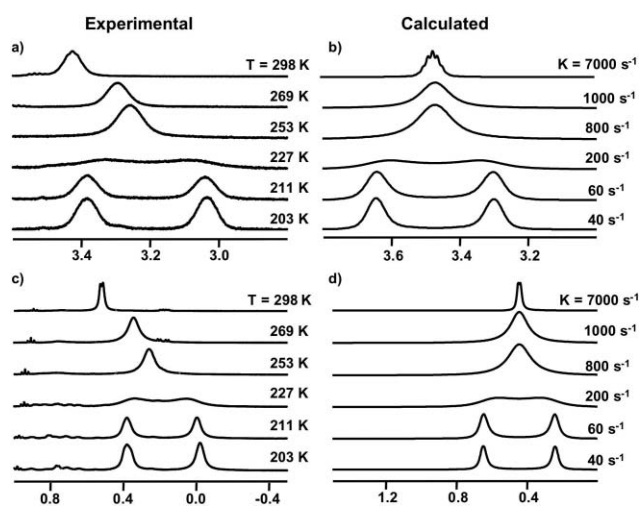


Fig. 2 Observed and simulated ^1H NMR line-shapes for the isopropanol ligand resonances of *cis*-Ti(dpbpol) $_2$ (HOPr i) $_2$ in toluene- d_8 at 400 MHz. (a) and (b) correspond to the resonances of methine protons. (c) and (d) correspond to the resonances of the CH_3 groups. Small amounts of undetermined products are also present (c).

Owing to the strong negative entropic contribution, a non-bond-rupture twist mechanism passing through a highly constrained

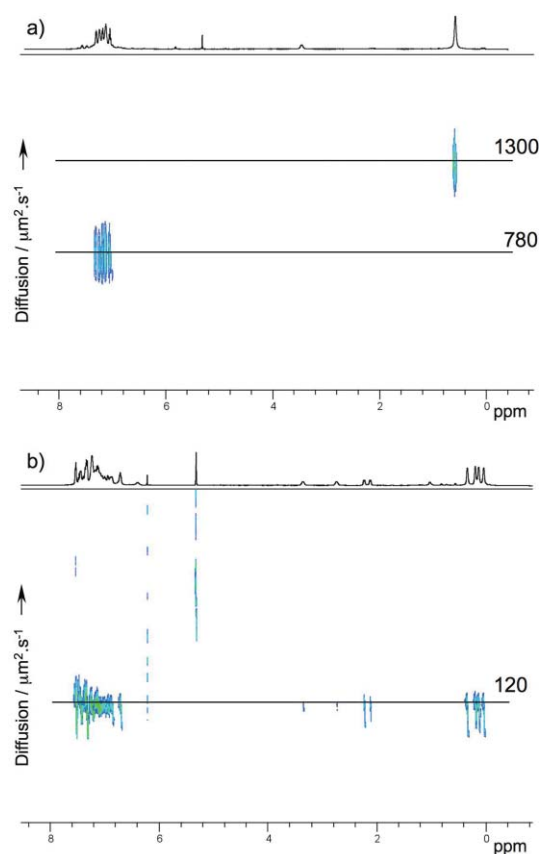


Fig. 3 (a) ^1H NMR DOSY spectrum of *cis*-Ti(dpbpol) $_2$ (HOPr i) $_2$ and ^1H NMR spectrum in CD_2Cl_2 (500 MHz) at 298 K. Two signals are observed, one attributed to the isopropanol ligands (on the right side of the spectrum), the other is related to the complex (on the left side of the spectrum). (b) ^1H NMR DOSY spectrum and ^1H NMR spectrum of *cis*-Ti(dpbpol) $_2$ (HOPr i) $_2$ in CD_2Cl_2 (500 MHz) at 193 K. One single diffusion attributed to the titanium complex coordinated by the isopropanol ligands is observed. Minor signals in ^1H NMR spectra in (a) and (b) reveal the presence of small amounts of free dpbpolH $_2$ ligand.

transition may be proposed for this exchange process in agreement with previous studies on related Ti(chelate) $_2$ (OR) $_2$ (chelate = diketone ligand, OR = alkoxide ligand) complexes.⁸ It is also worth noticing that the signal attributed to isopropanol methine and methyl protons are slightly shifted to lower frequencies between +25 °C and -20 °C ($\Delta\delta = 0.16$ and 0.26 ppm respectively).

A clear and unambiguous explanation of this phenomenon was obtained from DOSY (Diffusion Ordered SpectroscopY) measurements. Figs. 3a and b show two DOSY maps corresponding to the spectrum of *cis*-Ti(dpbpol) $_2$ (HOPr i) $_2$ in CD_2Cl_2 at +25 °C and -80 °C respectively evidencing again the temperature-dependent behaviour in solution of *cis*-Ti(dpbpol) $_2$ (HOPr i) $_2$. At low temperature, a $120\text{ }\mu\text{m}^2\text{ s}^{-1}$ diffusion coefficient was measured corresponding to a hydrodynamic radius of $r_s \approx 7\text{ Å}$ for the species in solution. This value matches well with the mean radius 7.0 Å evaluated from the crystalline structure using a standard set of van der Waals radii.⁸ At +25 °C the situation changes drastically, with the isopropanol molecule ($\delta = 3.44$ and 0.57 ppm) and the complex ($\delta = 7.40\text{--}7.00$ ppm) diffusing in solution at $D_{\text{isopropanol}} = 1300\text{ }\mu\text{m}^2/\text{s}$ and $D_{\text{complex}} = 780\text{ }\mu\text{m}^2/\text{s}$. These values

correspond respectively to hydrodynamic radii of 5 and 3 Å. Free isopropanol molecules having a mean structural radius of 3.0 Å,⁹ our DOSY experiment at +25 °C suggests a possible decoordination of the HOPrⁱ ligands in solution. This rather weak coordination of the isopropanol ligands was also verified through thermogravimetric analysis (TGA) showing a weight loss of 14% upon heating *cis*-Ti(dpbpol)₂(HOPrⁱ)₂ crystals between 110 °C and 280 °C corresponding to the departure of two isopropanol molecules, followed by decomposition above 300 °C (Fig. S6 in ESI†). Consequently, variable-temperature and DOSY ¹H NMR experiments have highlighted the unique behaviour of *cis*-Ti(dpbpol)₂(HOPrⁱ)₂ in solution. Above −4 °C, the two isopropanol molecules undergo a rapid coordination/decoordination process, while at lower temperatures the two HOPrⁱ ligands remain bonded to the metal leading to a structurally stable C₂-symmetric complex with the occurrence of another dynamic process that may be attributed to a $\Lambda \rightleftharpoons \Delta$ inversion of configuration at the metal centre *via* a non-bond-rupture twist mechanism.

In conclusion, we have reported here the synthesis of a novel monomeric C₂-symmetric octahedral titanium complex incorporating a Ti(chelate)₂ moiety (chelate = 3,3'-diphenyl-2,2'-biphenolate). This complex was fully characterized in the solid state and in solution. The arrangement of the two bisphenol derivatives around the metal leads to a chiral confined environment close to the titanium atom including two coordinated isopropanol molecules. Two different temperature dependent dynamic processes were characterized by the use of NMR techniques; one is related to the lability of the isopropanol ligands (¹H NMR DOSY), whereas the other implies a configurational fluctuation (¹H variable temperature NMR). We believe that our investigation of the solid-state structure and the solution behaviour of *cis*-Ti(dpbpol)₂(HOPrⁱ)₂ may help in the rational design of new titanium complexes. In particular, we believe that the structural features of this C₂-symmetric complex are well-suited for the future design of new catalysts which incorporate a *cis*-Ti(dpbpol)₂(HOPrⁱ)₂ motif. Current investigations are now focusing on the stereocontrol of this complex.

Acknowledgements

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Notes and references

‡ **X-Ray data for *cis*-Ti(dpbpol)₂(HOPrⁱ)₂.** C₅₄H₄₆O₆Ti; *M* = 838.81 Triclinic, Space group *P*-1, *a* = 9.9778(3) Å, *b* = 10.8481(3) Å, *c* = 20.9057(5) Å, α = 86.959(2)°, β = 80.036(2)°, γ = 79.613(2)°, *V* = 2191.62(10) Å³, *T* = 173(2) K, *Z* = 2, *D*_c = 1.271 Mg/m³, Reflections collected 29806, *R*_{int} = 0.0480, Refinement factors: *R* = 0.0759, *R*_w = 0.2007, GOF = 1.050. CCDC 727138.

§ NMR experimental: ¹³C CPMAS spectra were acquired on a Bruker Avance-300 apparatus operating at 75.52 MHz equipped with a standard 4 mm H/X probe, with rotor spinning at 10 kHz, contact time equal to 2.5 ms, 53 kHz and 63 kHz as ¹H and ¹³C RF frequencies respectively and spinlock composite pulse decoupling with 90 kHz ¹H RF frequency. Bruker Avance-300, Avance-400 and Avance-500 were used for solution NMR analysis. ¹H NMR DOSY measurements were performed at 500.13 MHz with a 5 mm ¹H/X z-gradient BBI probe and applying a PFGSTE pulse sequence using bipolar gradients. DOSY spectra were generated with the DOSY module of the NMR Notebook™ software, *via* maximum entropy and inverse Laplace transform calculations. Line shape analysis was carried out using WIN-DYNA, version 1.01, Bruker BioSpin GmbH.

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- 9 *R*_{max} = 3.4 Å, *R*_{min} = (3*V*/4π)^{1/3} = 2.6 Å with *V* = 70 Å³, see ref. 8 for methods and references.