Electronic Supplementary Information

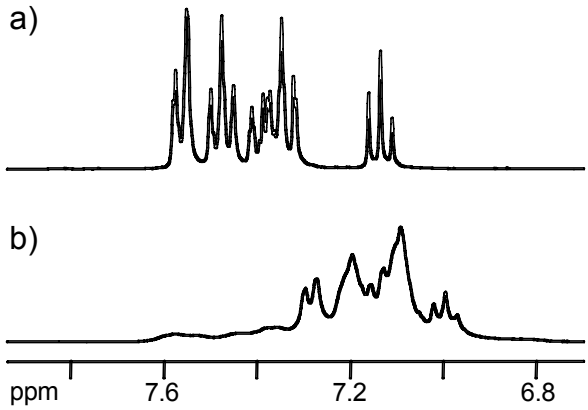

Fig. S1 a) Aromatic region of the **dpbpolH$_2$** ^{1}H NMR spectrum (CD_2Cl_2, 300 MHz) ; b) ^{1}H NMR aromatic region of a mixture obtained when Ti(OPr^i)$_4$ reacted with **dpbpolH$_2$** in a 1 : 2 ratio (CD_2Cl_2, 300 MHz)

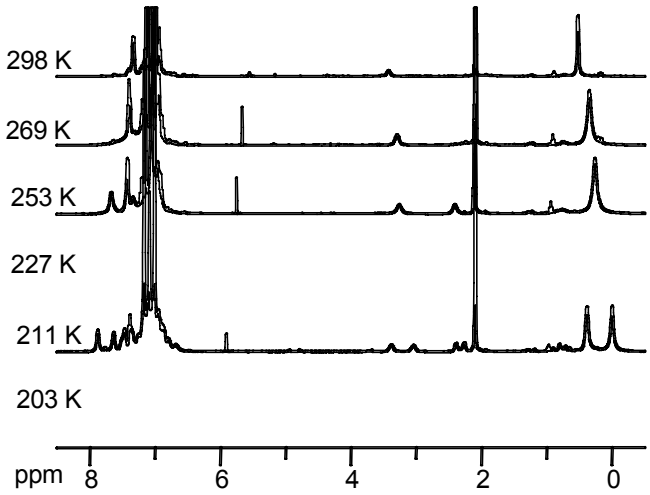

Fig. S2 Temperature dependence of *cis*-Ti(**dpbpol**)$_2$(HOPr^i)$_2$ proton resonances in toluene-d$_8$ (400 MHz). Note : signals attributed to the free **dpbpolH$_2$** ligand are also present in this series of spectra.[1]

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[1] The sample was prepared in a glove bag under nitrogen atmosphere by dissolving *cis*-Ti(**dpbpol**)$_2$(HOPr^i)$_2$ crystals in toluene-d$_8$.

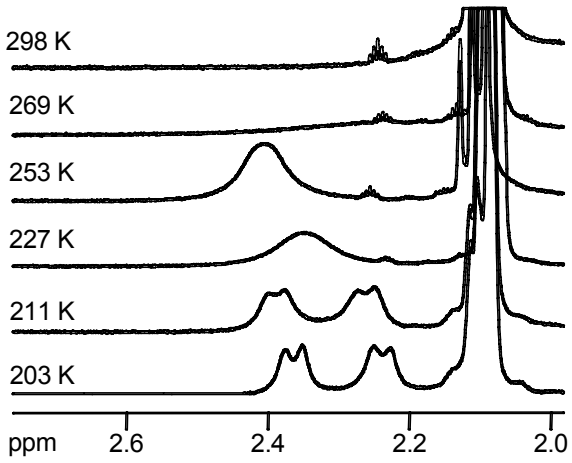

Fig. S3 Temperature dependence of the alcoholic proton resonances (HOPr^i) of the *cis*-Ti(**dpbpol**)$_2$(HOPr^i)$_2$ complex in toluene-d$_8$ (400 MHz).

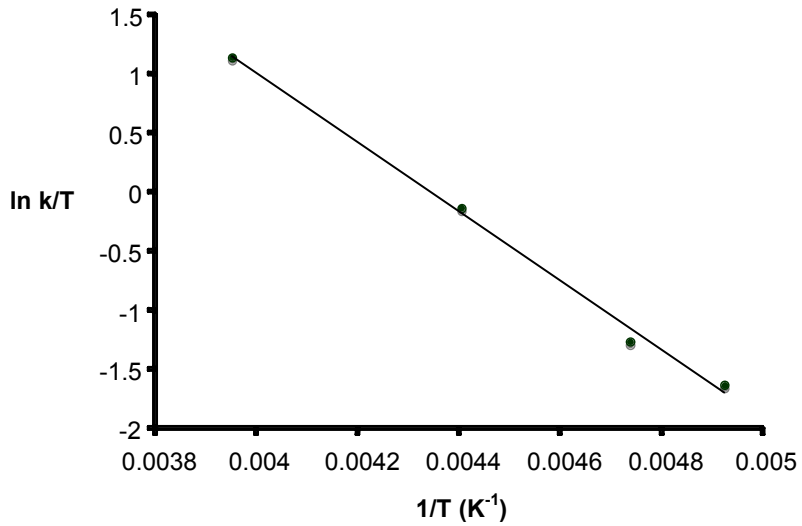

Fig. S4 Eyring plot for the exchange of isopropanol ligands in *cis*-Ti(**dpbpol**)$_2$(HOPr^i)$_2$. The Eyring plot have be constructed by taking into account only the dynamic process which is linked to the $\Delta \leftrightarrows \Lambda$ inversion of configuration.

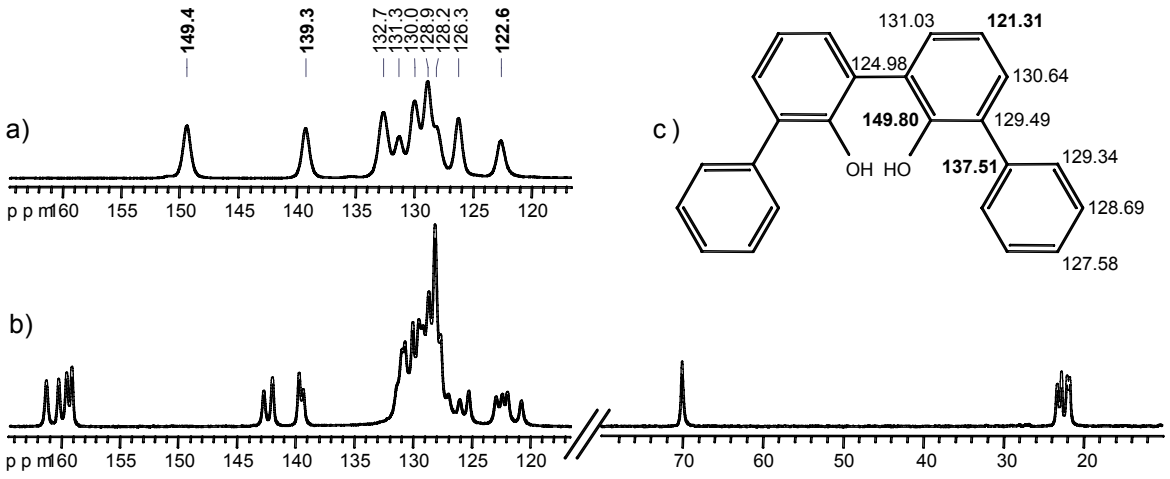

Fig. S5 a) ^{13}C CPMAS spectrum of free **dpbpolH$_2$** ligand; b) ^{13}C CPMAS spectrum of *cis*-Ti(**dpbpol**)$_2$(HOPr^i)$_2$; c) ^{13}C chemical shift attribution for free **dpbpolH$_2$** ligand in CD_2Cl_2 solution according to ^1H COSY, NOESY, ^1H-^{13}C HSQC and HMBC analyses.

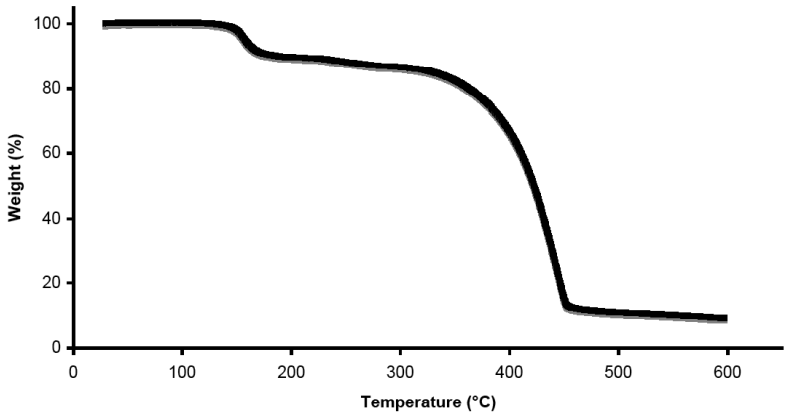

Fig. S6 Thermogravimetric analysis of *cis*-Ti(**dpbpol**)$_2$(HOPr^i)$_2$ under nitrogen at 10°C.min^{-1}.