

Supporting Information

Choosing between Ti(II) and Ti(III): selective reduction of titanocene dichloride by elemental lanthanides

Guillaume Bousrez,^{a,b} Dominique Harakat,^a Sylviane Chevreux,^{a,c} Isabelle Déchamps - Olivier,^a Florian Jaroschik^{*a,d,e}

^a *Institut de Chimie Moléculaire de Reims, CNRS UMR 7312, Université de Reims Champagne-Ardenne, BP 1039, 51687 Reims, France*

^b *Department of Biological and Chemical Engineering, Aarhus University, 8000 Aarhus C, Denmark*

^c *Institut de Recherche de Chimie Paris, UMR CNRS 8247, Chimie ParisTech, PSL Université, 75005 Paris, France*

^d *ICGM, Univ. Montpellier, CNRS, ENSCM, 34090 Montpellier, France*

^e *Email : florian.jaroschik@enscm.fr*

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I. SCXRD data

Table S1. Crystallographic data of $[\text{Cp}_2\text{Ti}(\mu\text{-Cl})_2\text{SmCl}_2(\text{THF})_3]\cdot\text{THF}$ (CCDC-2369904)

Empirical formula	$\text{C}_{12}\text{H}_{19}\text{Cl}_2\text{O}_{1.75}\text{Sm}_{0.5}\text{Ti}_{0.5}$
Formula weight	361.30
Space group	Fdd2
a/Å	22.5099(15)
b/Å	44.910(3)
c/Å	11.2932(6)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
Volume/Å ³	11416.5(12)
Z	32
$\rho_{\text{calc}}/\text{g}/\text{cm}^3$	1.682
μ/mm^{-1}	2.717
Reflections collected	120177
Goodness-of-fit on F^2	1.126
Final R indexes [$ I \geq 2\sigma(I)$]	$R_1 = 0.0165$, $wR_2 = 0.0350$
Final R indexes [all data]	$R_1 = 0.0174$, $wR_2 = 0.0353$

II. ESI-MS for bimetallic Ti-Yb complex $\{[\text{Cp}_2\text{TiCl}][\text{YbCl}_3]\text{Cl}\}^-$

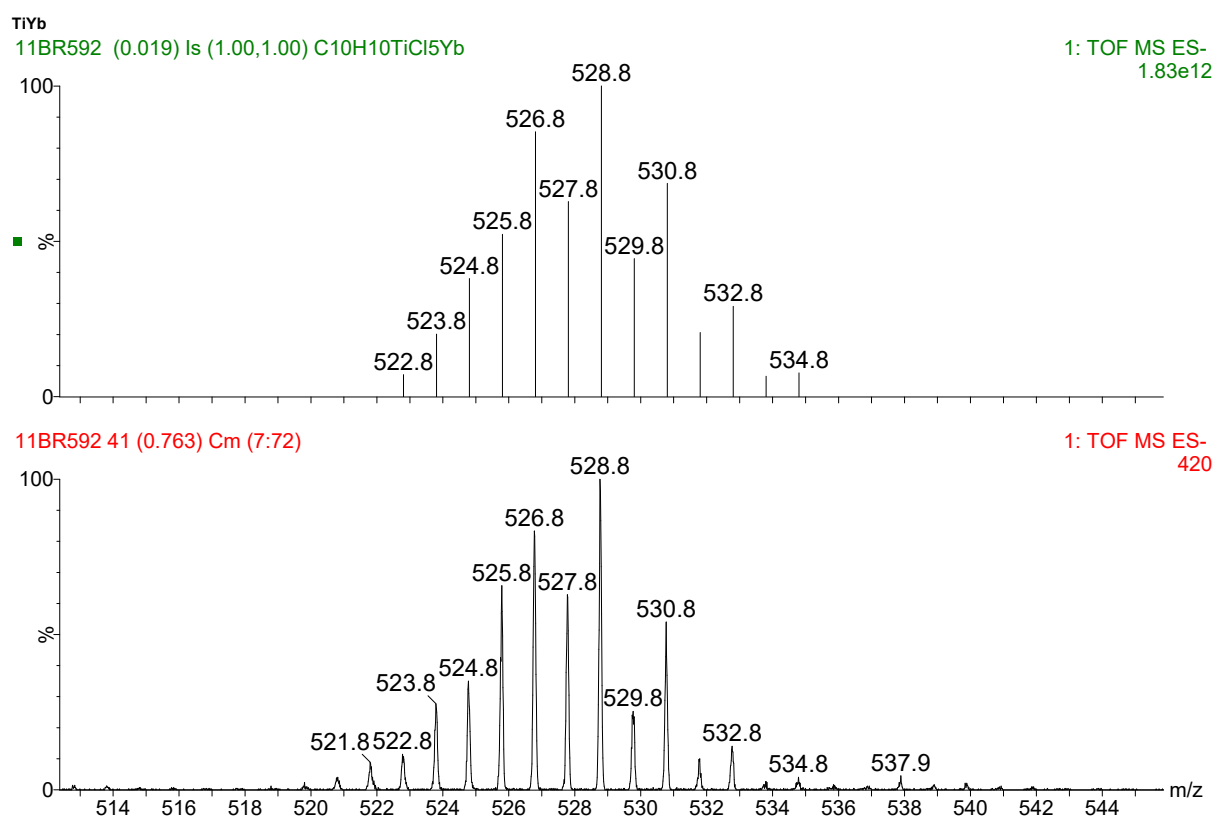


Figure S1. ESI-MS spectrum (negative mode) of bimetallic complex $\{[\text{Cp}_2\text{TiCl}][\text{YbCl}_3]\text{Cl}\}^-$: calculated (top) and observed (bottom) isotope distribution.

III. EPR spectra

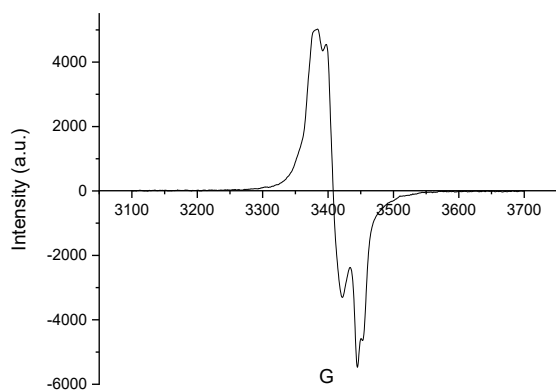


Figure S2. EPR spectra at 150 K of reaction: $\text{Cp}_2\text{TiCl}_2 + \text{Yb}$ in THF

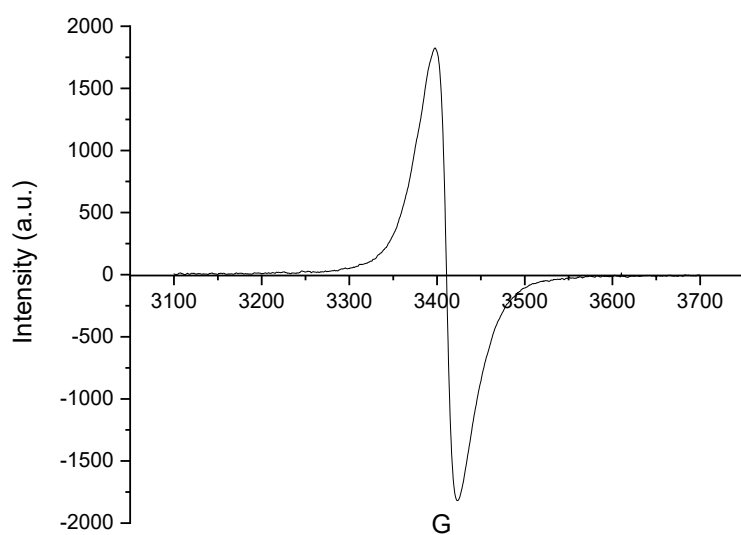


Figure S3. EPR spectra at 150 K of reaction: $\text{Cp}_2\text{TiCl}_2 + \text{Sm}$ in THF