

Cite this: *Dalton Trans.*, 2024, **53**, 15595

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

Guillaume Bousrez,<sup>a,b</sup> Dominique Harakat,<sup>a</sup> Sylviane Chevreux,<sup>a,c</sup> Isabelle Déchamps-Olivier<sup>a</sup> and Florian Jaroschik<sup>b,\*a,d</sup>

The reduction of titanocene dichloride  $\text{Cp}_2\text{TiCl}_2$  with lanthanide metals has led to the discovery of a surprising lanthanide effect: while with most lanthanides, a divalent  $[\text{Cp}_2\text{Ti}]$  equivalent was obtained, the use of samarium or ytterbium only led to the reduction to trivalent  $[\text{Cp}_2\text{TiCl}]$ -type complexes, including the structurally characterized heterobimetallic complex  $[\text{Cp}_2\text{Ti}(\mu\text{-Cl})_2\text{SmCl}_2(\text{THF})_3]$ . These results were corroborated by reactivity studies (alkyne coupling and radical reactions), EPR spectroscopy and electrospray mass spectrometry, providing new insights into the reduction chemistry of lanthanide metals.

Received 11th July 2024,  
Accepted 20th August 2024  
DOI: 10.1039/d4dt02004a

rsc.li/dalton

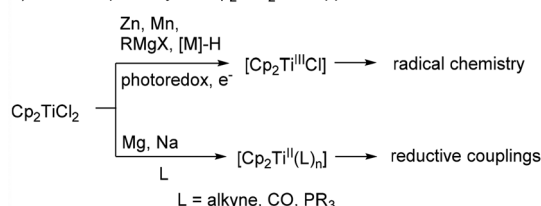
## Introduction

Low-valent titanocene complexes have found widespread applications in organic and organometallic transformations.<sup>1</sup> Trivalent  $[\text{Cp}_2\text{TiCl}]$  is a reliable source of radicals, which can be applied in stoichiometric or catalytic amounts for the synthesis of complex organic molecules, involving, for example, epoxide openings, free radical additions, cycloadditions or reductive umpolung reactions.<sup>2</sup> The synthesis of  $[\text{Cp}_2\text{TiCl}]$  is mainly achieved by reduction of the tetravalent precursor  $\text{Cp}_2\text{TiCl}_2$  employing Grignard reagents, metal hydrides, dihydropyrazines or mild metallic reducing agents, such as Zn or Mn metal. Electrochemical preparation,<sup>3</sup> and more recently, photocatalytic pathways have also been described (Scheme 1a).<sup>4</sup>

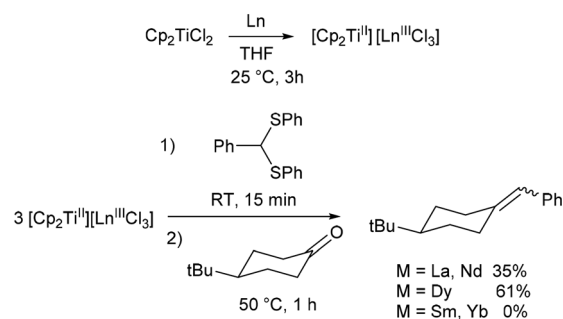
On the other hand, divalent  $[\text{Cp}_2\text{Ti}]$  equivalents, such as  $[\text{Cp}_2\text{Ti}(\text{CO})_2]$ ,  $[\text{Cp}_2\text{Ti}(\text{alkyne})]$ , and  $[\text{Cp}_2\text{Ti}(\text{P}(\text{OEt})_3)_2]$ , have been investigated in dinitrogen activation and cleavage, water splitting, diene transformations or carbonyl olefination.<sup>5</sup> For accessing these divalent  $[\text{Cp}_2\text{Ti}]$  equivalents from  $\text{Cp}_2\text{TiCl}_2$ , strong

reducing agents, such as Mg or Na, and the presence of stabilising ligands or Lewis bases (phosphines, alkynes, and CO) are required (Scheme 1a).<sup>6</sup> Base-free titanocenes were only obtained with highly bulky Cp ligands.<sup>7</sup>

Lanthanide metals are strong reducing agents ( $E^\circ(\text{Ln}^{3+}/\text{Ln}^0) = -2.3$  V), and have been employed in organic chemistry, e.g. for radical generation, for the formation of Grignard-type reagents, in C–F bond activation and in bimetallic systems combined with transition metals.<sup>8,9</sup> They are also excellent

a) reduction pathways of  $\text{Cp}_2\text{TiCl}_2$  and applications

## b) Lanthanide effect in the Takeda carbonyl olefination without phosphite



**Scheme 1** (a) Reduction of  $\text{Cp}_2\text{TiCl}_2$  leading to low-valent titanocene species and (b) Takeda carbonyl olefination using  $\text{Cp}_2\text{TiCl}_2/\text{Ln}$  systems.

<sup>a</sup>Université de Reims Champagne Ardenne, CNRS UMR 7312, ICMR, URCA Tech, 51100 Reims, France

<sup>b</sup>Department of Biological and Chemical Engineering, Aarhus University, 8000 Aarhus C, Denmark

<sup>c</sup>Institut de Recherche de Chimie Paris, UMR CNRS 8247, Chimie ParisTech, PSL University, 75005 Paris, France

<sup>d</sup>ICGM, Univ. Montpellier, CNRS, ENSCM, 34090 Montpellier, France.

E-mail: florian.jaroschik@enscm.fr

† Electronic supplementary information (ESI) available: Details of X-ray diffraction, EPR spectroscopy, and ESI-MS analysis. CCDC 2369904. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d4dt02004a>



starting materials for the synthesis of organometallic complexes using redox transmetalation approaches.<sup>10</sup> Despite the similar redox potential of these metals along the series from La to Lu, their reactivity and efficiency are not necessarily the same, which may be related to their different size, density or activation methods.<sup>8,11</sup>

The reduction of Cp<sub>2</sub>TiCl<sub>2</sub> with lanthanides, especially Sm, has been investigated since 1995, and this bimetallic system has been employed successfully in radical reactions.<sup>12</sup> The formation of a bimetallic complex comprising Ti(III) and Sm(II) moieties was suggested,<sup>12a</sup> but to date, no structurally characterized complex has been reported. Another rare example of the combination of TiCl<sub>4</sub> with Yb metal has shown its utility in the McMurry carbonyl olefination reaction, in which the involvement of a Ti(III) complex was proposed.<sup>13</sup>

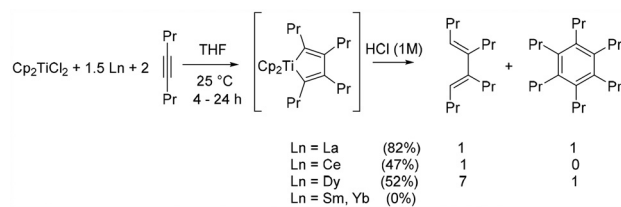
At the same time, in 2015, we reported on the reduction of Cp<sub>2</sub>TiCl<sub>2</sub> with different lanthanide metals in the absence of any Lewis base to access a new [Cp<sub>2</sub>Ti] equivalent, solely stabilised by the *in situ* formed LnCl<sub>3</sub> salt.<sup>14</sup> Dysprosium was shown to be most efficient among a selection of lanthanides, as evidenced by the application of the Cp<sub>2</sub>TiCl<sub>2</sub>/Dy system in the Takeda carbonyl olefination reaction (Scheme 1b). In this reaction, initially, Ti(IV) was reduced to Ti(II), which then reacted with dithioacetals to form an intermediate Ti-carbene species, which reacted with carbonyl groups to form the corresponding alkene. Under classical Takeda conditions,<sup>15</sup> Ti(II) was stabilised by triethyl phosphite; however, in our case, no phosphite was necessary. In addition, even a one-pot reaction with all reagents present from the start was successful. During the initial metal screening, we observed a surprising lanthanide effect: while La, Nd and Dy enabled the olefination reaction in moderate to good yields, no product was obtained with Yb and Sm, suggesting that the latter cannot afford Ti(II) species (Scheme 1b).<sup>14</sup>

We have now investigated this outcome in detail, conducting further reactivity studies and employing EPR spectroscopy, electrospray mass spectrometry (ESI-MS) and X-ray diffraction analysis on the *in situ* formed low-valent titanocene complexes, unveiling new insights into the reduction chemistry of lanthanide metals. This study provides, in fine, the possibility to choose between the formation of Ti(III) or Ti(II) complexes by selecting the right lanthanide metal.

## Results and discussion

### Reactivity studies

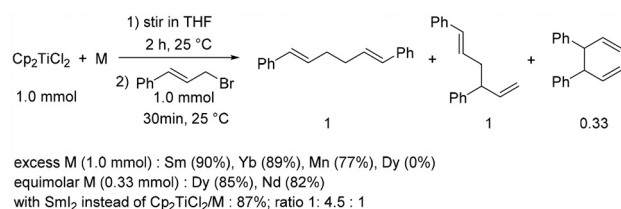
Reductive dimerization of alkynes is a well-known reaction with low-valent group 4 metallocenes (Ti and Zr).<sup>1b,5</sup> While this reaction is mostly restricted to internal alkynes, the previously reported bimetallic Cp<sub>2</sub>ZrCl<sub>2</sub>/La system also allowed the efficient coupling of terminal alkynes, which we have successfully applied for the synthesis of 2,4-disubstituted phospholes.<sup>16</sup> We therefore set out to investigate the reaction of 4-octyne with the Cp<sub>2</sub>TiCl<sub>2</sub>/Ln system. To our surprise, when using La metal as the reducing agent, we observed the for-



**Scheme 2** Reductive dimerization and trimerization of 4-octyne using Cp<sub>2</sub>TiCl<sub>2</sub>/Ln systems.

mation of not only the expected butadiene but also a hexa-substituted benzene derivative in a 1 : 1 ratio (Scheme 2). On the other hand, when using Ce or Dy, the major product was by far the butadiene with only trace or small amounts of benzene byproduct. Importantly, the use of Sm or Yb did not provide any coupling product, in agreement with the ineffective reduction to Ti(II) complexes, even upon heating at 50 °C for several hours. In the case of the previously reported Cp<sub>2</sub>ZrCl<sub>2</sub>/La system, trimerization was only observed for terminal alkynes.<sup>17</sup> A possible explanation for this surprising reaction behaviour of the Cp<sub>2</sub>TiCl<sub>2</sub>/La system could be derived from the results of the ESI-MS studies (see below).

As mentioned above, titanocene(III) species are often involved in radical reactions. We therefore screened Cp<sub>2</sub>TiCl<sub>2</sub>/Ln systems for the homocoupling of cinnamyl bromide, a reaction known to occur with Mn as the reducing agent.<sup>18</sup> In the case of Sm and Yb, the reaction always provided the expected radical-radical homocoupling products in similar ratios, comparable to Mn, even when a large excess of Ln metal was employed (Scheme 3). In the case of Dy, two different results were observed. When equimolar amounts of Cp<sub>2</sub>TiCl<sub>2</sub> and Dy were employed, the same homocoupling reaction was observed as with Yb and Sm. A similar result was obtained with equimolar amounts of Nd. However, with an excess of Dy no coupling reaction occurred, which is in agreement with the formation of a Ti(II) species, which does not undergo radical reactions. We previously showed by EPR studies that the amount of Dy was important to obtain selectively Ti(III) or Ti(II) species.<sup>14</sup> It should be noted that when the reaction was carried out with SmI<sub>2</sub> instead of the Cp<sub>2</sub>TiCl<sub>2</sub>/Ln system, the coupling products were obtained in a different ratio (1 : 4.5 : 1), pointing to the likely absence of a divalent Sm species in the Cp<sub>2</sub>TiCl<sub>2</sub>/Sm system.



**Scheme 3** Radical coupling of cinnamyl bromide using Cp<sub>2</sub>TiCl<sub>2</sub>/Ln systems.



## Electrospray-MS studies

ESI-MS has become an important tool for the elucidation of reaction mechanisms and the characterization of reactive organometallic complexes.<sup>19</sup> This is due to the rather mild experimental conditions and the compatibility with air-sensitive compounds *via* introduction under an inert atmosphere. We have studied four reduction processes of  $\text{Cp}_2\text{TiCl}_2$  with Sm, Yb, Dy and La metals in THF at room temperature for 3 hours. Samples of these solutions were taken directly from the Schlenk tube under argon and injected without further dilution. The ESI-MS spectra were recorded in positive and negative modes. As expected, in the case of Sm and Yb, the major signal could be attributed in the negative mode to the  $[\text{LnCl}_4]^-$  anionic species. However, upon closer inspection, signals corresponding to bimetallic  $\{[\text{Cp}_2\text{TiCl}][\text{LnCl}_3]\text{Cl}\}^-$  type complexes were also detected in both cases ( $m/z = 506.8$  for Sm and 528.8 for Yb), albeit in low intensities. The isotope distribution is in perfect agreement between calculated and observed values (Fig. 1 and ESI†). This is a first indication of the formation of a  $[\text{Ti(III)/Ln(III)}]$  type bimetallic complex, which will be further corroborated by XRD studies (see below).

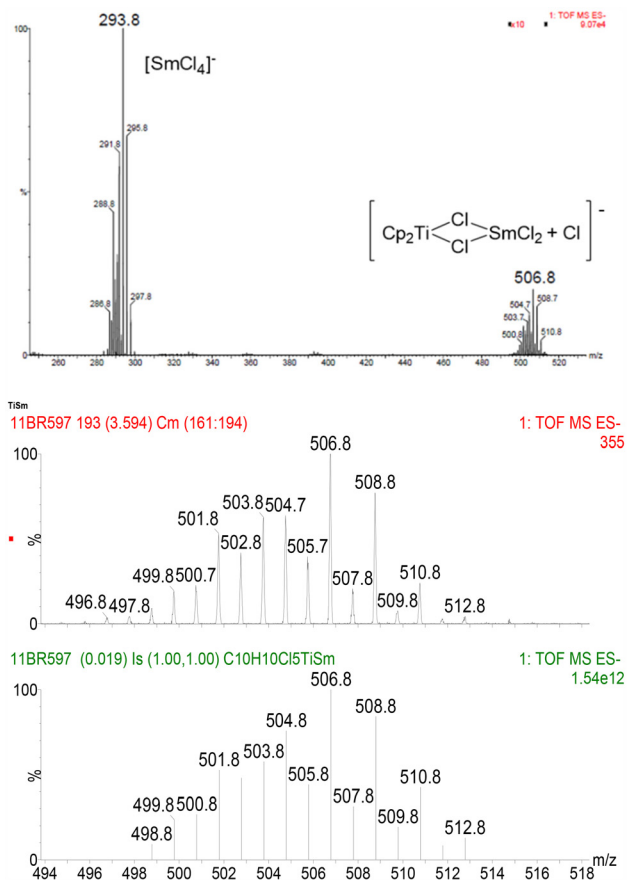


Fig. 1 ESI-MS spectrum (negative mode) for the reduction of  $\text{Cp}_2\text{TiCl}_2$  with Sm in THF (above); observed (middle) vs. calculated (bottom) isotope distribution of the bimetallic complex.

In the case of Dy,  $[\text{DyCl}_4]^-$  was detected as the major species in the negative mode, whereas in the positive mode titanocene-derivatives could be observed, including  $[\text{Cp}_2\text{Ti}]^+$  at  $m/z = 178.0$  (from the oxidation of divalent  $[\text{Cp}_2\text{Ti}]$  in the spectrometer), and  $[\text{Cp}_2\text{TiO}_2]^+$  at  $m/z = 209.9$  (from trace amounts of oxygen) (see the ESI†). The former was previously observed from  $[\text{Cp}_2\text{TiMe}_2]$  under EI-MS conditions.<sup>20</sup> On the other hand, for other supposedly  $[\text{Cp}_2\text{Ti}]$  species in the literature, the corresponding bimetallic fulvalene titanium hydride complex was observed by mass spectrometry,<sup>21</sup> which is not present in our case (no peak at  $m/z = 354$  or 356). From these experiments, the formation of stable divalent  $[\text{Cp}_2\text{Ti}][\text{DyCl}_3]$  type complexes in solution can be deduced.

When La metal was used for the reduction of titanocene dichloride, a very intriguing observation was made in the ESI-MS spectrum in the negative mode. In addition to the major signal corresponding to  $[\text{LaCl}_4]^-$ , several other products corresponding to  $[\text{CpLaCl}_3]^-$ ,  $[\text{Cp}_2\text{LaCl}_2]^-$  and  $[\text{Cp}_3\text{LaCl}]^-$  were observed (Fig. 2). Such byproducts resulting from Cp abstraction from the Ti centre were not observed for the other lanthanides or observed only in trace amounts. This phenomenon, which has been sporadically reported in the literature,<sup>22</sup> may explain why in the case of La the formation of trimerization occurs (Scheme 2). It is well established now that  $[\text{TiX}_2]$

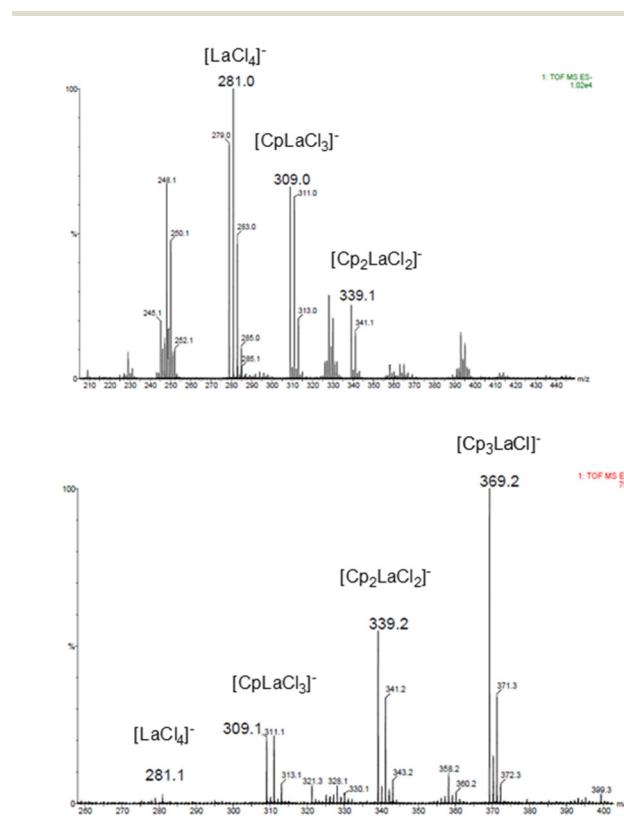


Fig. 2 ESI-MS spectrum (negative mode) for the reduction of  $\text{Cp}_2\text{TiCl}_2$  with La in THF, showing the formation of  $[\text{LaCl}_4]^-$ ,  $[\text{CpLaCl}_3]^-$ ,  $[\text{Cp}_2\text{LaCl}_2]^-$  and  $[\text{Cp}_3\text{LaCl}]^-$  species: after several minutes (top) and after 1.5 hours (bottom).



species can trigger the trimerization of alkynes,<sup>23</sup> whereas  $[\text{Cp}_2\text{Ti}]$  does not.

### EPR studies

The paramagnetism of  $\text{Ti(III)}$  precludes further characterisation by NMR spectroscopy studies; however, EPR spectroscopy has been extensively employed for such complexes.<sup>24</sup> The reduction of  $\text{Cp}_2\text{TiCl}_2$  was conducted in THF with an excess of Yb or Sm at room temperature and the resulting solutions were measured, after dilution, by EPR with the X-band at 150 K. In both cases, a signal centred at 3400 G, which can be attributed to a trivalent  $[\text{Cp}_2\text{TiCl}]$ -type complex, was observed (see the ESI†). The  $g_{\text{iso}}$  value of 1.976 derived from the spectra is identical to the data from the literature for  $[\text{Cp}_2\text{TiCl}(\text{THF})]$ .<sup>24b</sup> We previously reported a similar signal for the reduction with 0.33 equivalent of Dy metal. However, when an excess of Dy metal was employed, the EPR signal disappeared, in agreement with the reduction to titanocene(II).<sup>14</sup> In the case of Yb and Sm, the signal did not disappear in the presence of excess metal. It should be noted that most trivalent lanthanides (except Gd) cannot be detected in EPR spectroscopy above 15 K due to line-broadening.<sup>25</sup>

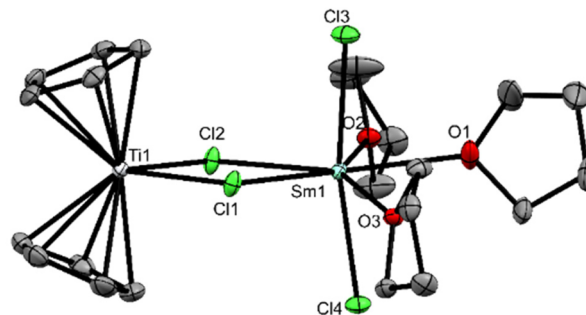
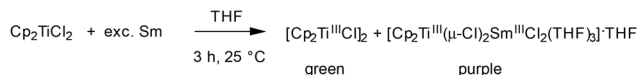
### XRD structure of $[\text{Cp}_2\text{Ti}(\mu\text{-Cl})_2\text{SmCl}_2(\text{THF})_3]\cdot\text{THF}$

As described above, the quest for identifying unambiguously the reaction product of the reduction of  $\text{Cp}_2\text{TiCl}_2$  with Sm in THF has been going on for 30 years.<sup>12a</sup> Our ESI-MS experiments have already pointed towards a bimetallic  $\text{Ti(III)}\text{-Sm(III)}$  species. This has now been confirmed by XRD studies on an isolated complex. From a concentrated THF solution, a mixture of two types of crystals was obtained after standing for several weeks, which were separated manually under a microscope for XRD determination: a green complex identified as the known titanocene dimer  $[\text{Cp}_2\text{TiCl}]_2$ , confirmed by the determination of its unit cell<sup>26</sup> and a purple bimetallic complex identified as  $[\text{Cp}_2\text{Ti}(\mu\text{-Cl})_2\text{SmCl}_2(\text{THF})_3]\cdot\text{THF}$  (Scheme 4).

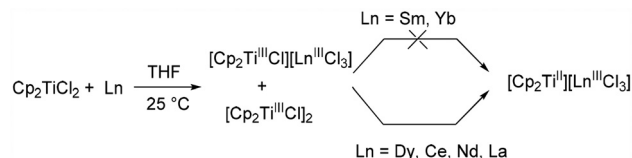
In this bimetallic structure, the Sm ion is seven-coordinate in a distorted pentagonal bipyramidal coordination environment with the terminal chloride ligands in the apical positions. The structure has many similarities to a previously described di-samarium(III) complex  $[\text{CpSmCl}(\mu\text{-Cl})_2\text{SmCl}_2(\text{THF})_3]$  with respect to bond distances and coordination,<sup>27</sup> and it also compares well with the heterotrimetallic complexes  $[(\text{Cp}_2\text{TiCl})_2\text{MCl}_2]$  (with  $\text{M} = \text{Zn}, \text{Mn},$  and  $\text{Ni}$ ).<sup>28</sup>

## Discussion

The reduction of titanocene dichloride has intrigued chemists for over fifty years. In this contribution, we have shown by various experimental and analytical techniques that depending on the choice of lanthanide metal as the reducing agent, different outcomes are possible (Scheme 5). The two elements Sm and Yb lead to trivalent  $[\text{Cp}_2\text{TiCl}]$  species, according to radical coupling experiments, and ESI-MS, EPR and XRD analyses. Why these two metals are not capable of reducing the intermediate  $[\text{Cp}_2\text{TiCl}]$  species further to the divalent complex



**Scheme 4** Synthesis and XRD structure of bimetallic  $[\text{Cp}_2\text{Ti}(\mu\text{-Cl})_2\text{SmCl}_2(\text{THF})_3]\cdot\text{THF}$ . ORTEP plot with 50% probability ellipsoids. Hydrogen atoms and lattice solvent are omitted for clarity. Selected bond lengths (Å) and angles ( $^\circ$ ):  $\text{Ti1}-\text{Cl1}$  2.5401(8);  $\text{Ti1}-\text{Cl2}$  2.5441(8);  $\text{Sm1}-\text{O1}$  2.4151(17);  $\text{Sm1}-\text{O3}$  2.4547(16);  $\text{Sm1}-\text{O2}$  2.4840(19);  $\text{Sm1}-\text{Cl1}$  2.7705(6);  $\text{Sm1}-\text{Cl2}$  2.7618(6);  $\text{Sm1}-\text{Cl3}$  2.6427(7);  $\text{Sm1}-\text{Cl4}$  2.6586(6);  $\text{Cl3}-\text{Sm1}-\text{Cl4}$  168.49(2);  $\text{Cl2}-\text{Sm1}-\text{Cl1}$  73.915(19);  $\text{O1}-\text{Sm1}-\text{O2}$  70.49(6);  $\text{Cl1}-\text{Ti1}-\text{Cl2}$  81.72(2); and  $\text{Ti1}-\text{Cl2}-\text{Sm1}$  102.24(2).



**Scheme 5** Reduction of  $\text{Cp}_2\text{TiCl}_2$  by lanthanides.

$[\text{Cp}_2\text{Ti}]$  has not been elucidated so far. The standard redox potentials of these metals ( $E^\circ(\text{Sm}^{3+}/\text{Sm}^0) = -2.30$  V and  $E^\circ(\text{Yb}^{3+}/\text{Yb}^0) = -2.19$  V) were reported to be in the same range as those of other lanthanide metals, e.g.  $E^\circ(\text{Dy}^{3+}/\text{Dy}^0) = -2.29$  V.<sup>29</sup> Furthermore, if direct oxidation of the lanthanide metal to divalent Ln intermediates occurred, the potentials would be even more negative ( $E^\circ(\text{Sm}^{2+}/\text{Sm}^0) = -2.68$  V and  $E^\circ(\text{Yb}^{2+}/\text{Yb}^0) = -2.76$  V)<sup>29</sup> and more favorable to access  $[\text{Cp}_2\text{Ti}^{\text{II}}]$ . Consequently, at this stage, we cannot rule out that other factors or other reaction pathways influence the further reduction of  $[\text{Cp}_2\text{TiCl}]$  to divalent titanocene species.

In contrast to Sm and Yb, other lanthanide metals, such as Dy, Ce, and Nd, which also proceed *via* the  $[\text{Cp}_2\text{TiCl}]$  species as shown by the radical coupling experiment and EPR analysis, provide a relatively stable divalent titanocene complex, with a suggested composition of  $[\text{Cp}_2\text{Ti}][\text{LnCl}_3]$ , based on ESI-MS and reactivity studies (alkyne coupling and carbonyl olefination). Intriguingly, La metal, the largest and often the most reactive lanthanide metal, reduces titanocene dichloride to divalent species but also exchanges not only chloride but also Cp ligands with the titanium ion. The resulting low-valent titanium species have been shown to facilitate the trimerization of internal alkynes.



## Experimental

### General

All reactions were conducted under an atmosphere of argon using standard Schlenk techniques and an argon-filled Jacomex BS531-type dry box. Tetrahydrofuran was collected under argon from a PURSOLV MD-3 (Innovative Technologies Inc.) solvent purification unit. Titanocene dichloride, iodine and manganese were purchased from Strem Chemicals. 4-Octyne, cinnamylbromide and diethylether were purchased from Aldrich and used as received. Neodymium, samarium, europium, dysprosium and ytterbium ingots were purchased from Aldrich or Strem and, prior to use, were freshly filed in a drybox under argon.  $\text{SmI}_2$  was prepared *in situ* by reacting elemental samarium with iodine in THF.

### ESI-MS

All experiments (MS and HRMS) were performed on a hybrid tandem quadrupole/time-of-flight (Q-TOF) instrument, equipped with a pneumatically assisted electrospray (Z-spray) ion source (Micromass, Manchester, UK) operated in positive mode. The electrospray potential was set to 3 kV in positive ion mode and the extraction cone voltage was usually varied between 30 and 60 V, with an injection flow rate of  $5 \mu\text{L min}^{-1}$ .

### EPR

EPR spectra were recorded using a Bruker ESP300e spectrometer (X-band) equipped with a Bruker E035M gaussmeter and an HP 5350B microwave frequency counter. Samples were prepared at a concentration of  $2 \text{ mmol L}^{-1}$  in THF frozen solutions (150 K, Bruker ER4111VY variable-temperature unit). The best resolution was obtained at  $T = 150 \text{ K}$  by using a modulation amplitude of 16.789 G, a time constant of 81.92 ms, a conventional time of 20.48 ms and a sweep time of 20.972 s.

### XRD

A single crystal coated with viscous hydrocarbon oil was mounted on a cryoloop. Single crystal X-ray diffraction was performed on a Bruker D8 Venture diffractometer. The D8 Venture was equipped with a Cu microsource ( $K_{\alpha 1}$  radiation  $\lambda = 1.54056 \text{ \AA}$ ) and a PHOTON100 CMOS detector. Data were collected at  $-173.15 \text{ }^\circ\text{C}$  (100 K). Data collection and integration were performed using Bruker Apex2 software.<sup>30</sup> The structures were solved using SHELXS-97 and refined by full-matrix least-squares on all F2 data using SHELXL-97.<sup>31</sup> All hydrogen atoms were placed in calculated positions using the riding model.

### Alkyne coupling

A Schlenk tube was loaded with dichlorotitanocene (1.0 mmol), lanthanide (1.5 mmol (excess)) and THF (5 mL) under an argon atmosphere. The resulting mixture was stirred vigorously at room temperature until a deep green color appeared. 4-Octyne (2.0 mmol) was added to the mixture and the solution was vigorously stirred for 4 hours at room temperature. The reaction was then quenched by the addition of a hydrochloric acid solution (1 M). An extraction with diethyl-

ether ( $3 \times 25 \text{ mL}$ ) was performed and the organic phases were collected, washed with brine, dried over magnesium sulfate, and filtered over cotton. The solvent was concentrated under vacuum and the crude mixture was purified by column chromatography with petroleum ether as the eluent, leading to 1,2,3,4-tetrapropylbutadiene (colorless oil) and 1,2,3,4,5,6-hexapropylbenzene (white solid). The NMR data were in agreement with the literature.<sup>16a,32</sup>

### Radical coupling

A Schlenk tube was loaded with dichlorotitanocene (1.0 mmol), lanthanide (0.33 mmol (equimolar) or 1.0 mmol (excess)) and THF (5 mL) under an argon atmosphere. The resulting mixture was stirred vigorously at room temperature for 2 h, leading to a deep green solution. Cinnamylbromide (1.0 mmol) was solubilized in THF (2 mL) and then introduced into the mixture. The solution was vigorously stirred for 30 minutes at room temperature and the reaction was quenched by the addition of a hydrochloric acid solution (1 M). The aqueous phase was extracted with diethylether ( $3 \times 25 \text{ mL}$ ). The organic phases were collected, washed with brine, dried over magnesium sulfate, and filtered over cotton. The solvent was concentrated under vacuum and the crude was purified by column chromatography with petroleum ether as the eluent, leading to a mixture of three dienes as a colorless oil. The NMR data were in agreement with the literature.<sup>18</sup>

## Conclusions

The reduction of titanocene dichloride by different lanthanide metals has been investigated revealing a substantial lanthanide effect. While with Sm and Yb, the reduction stopped at trivalent titanocene species, with Dy, Ce and Nd, the formation of divalent titanocenes was evidenced. In the case of La, an additional feature is the abstraction of the Cp ligand from the titanium centre during the reduction process. Further studies on selective synthetic applications are currently underway.

## Data availability

The data supporting this article have been included as part of the ESI.† Crystallographic data for  $[\text{Cp}_2\text{Ti}(\mu\text{-Cl})_2\text{SmCl}_2(\text{THF})_3]$  have been deposited at the CCDC under 2369904 and can be obtained from <https://www.ccdc.cam.ac.uk/>.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

Financial support from the CNRS, the Université de Reims Champagne-Ardenne and the Université de Montpellier is



acknowledged. G. B. thanks the Region Grand Est for a PhD scholarship. We thank Dr G. Dantelle for helpful discussions on EPR spectroscopy.

## References

- (a) F. Sato, H. Urabe and S. Okamoto, *Chem. Rev.*, 2000, **100**, 2835; (b) *Titanium and Zirconium in Organic Synthesis*, ed. I. Marek, Wiley-VCH, Weinheim, 2002; (c) P. J. Chirik, *Organometallics*, 2010, **29**, 1500; (d) M. Manßen and L. L. Schafer, *Chem. Soc. Rev.*, 2020, **49**, 6947; (e) S. Fortier and A. Gomez-Torres, *Chem. Commun.*, 2021, **57**, 10292; (f) X. Wu, Y. Chang and S. Lin, *Chem*, 2022, **8**, 1805; (g) U. N. Oloyede and R. A. Flowers, *Dalton Trans.*, 2024, **53**, 2413.
- Reviews: (a) A. R. Martínez, L. P. Morales, E. D. Ojeda, M. C. Rodríguez and I. Rodríguez-García, *J. Org. Chem.*, 2021, **86**, 1311; (b) T. Hilche, S. L. Younas, A. Gansäuer and J. Streuff, *ChemCatChem*, 2022, **14**, e202200530 Original research papers: (c) P. K. Mandal, G. Maiti and S. C. Roy, *J. Org. Chem.*, 1998, **63**, 2829; (d) H. R. Diéguez, A. López, V. Domingo, J. F. Arteaga, J. A. Dobado, M. M. Herrador, J. F. Quílez del Moral and A. F. Barrero, *J. Am. Chem. Soc.*, 2010, **132**, 254; (e) I. Sancho-Sanz, D. Miguel, A. Millán, R. E. Estévez, J. L. Oller-López, E. Álvarez-Manzaneda, R. Robles, J. M. Cuerva and J. Justicia, *J. Org. Chem.*, 2011, **76**, 732; (f) A. Gansäuer, M. Behlendorf, D. von Laufenberg, A. Fleckhaus, C. Kube, D. V. Sadasivam and R. A. Flowers II, *Angew. Chem., Int. Ed.*, 2012, **51**, 4739; (g) S. Begum and T. K. Chakraborty, *J. Org. Chem.*, 2021, **86**, 11812; (h) J. Ni, X. Xia, W.-F. Zheng and Z. Wang, *J. Am. Chem. Soc.*, 2022, **144**, 7889; (i) T. Saito, H. Nishiyama, H. Tanahashi, K. Kawakita, H. Tsurugi and K. Mashima, *J. Am. Chem. Soc.*, 2014, **136**, 5161; (j) G. Frey, J. N. Hausmann and J. Streuff, *Chem. – Eur. J.*, 2015, **21**, 5693; (k) D. S. G. Henriques, K. Zimmer, S. Klare, A. Meyer, E. Rojo-Wiechel, M. Bauer, R. Sure, S. Grimme, O. Schiemann, R. A. Flowers and A. Gansäuer, *Angew. Chem., Int. Ed.*, 2016, **55**, 7671.
- (a) I. M. M. Fusing, D. Pletcher and R. J. Whitby, *J. Organomet. Chem.*, 1994, **470**, 119–125; (b) R. J. Enemærke, J. Larsen, T. Skrydstrup and K. Daasbjerg, *J. Am. Chem. Soc.*, 2004, **126**, 7853; (c) A. Gansäuer, C. Kube, K. Daasbjerg, R. Sure, S. Grimme, G. D. Fianu, D. V. Sadasivam and R. A. Flowers II, *J. Am. Chem. Soc.*, 2014, **136**, 1663.
- (a) Z. Zhang, R. B. Richrath and A. Gansäuer, *ACS Catal.*, 2019, **9**, 3208; (b) A. Gualandi, F. Calogero, M. Mazzarini, S. Guazzi, A. Fermi, G. Bergamini and P. G. Cozzi, *ACS Catal.*, 2020, **10**, 3857; (c) Z. Zhang, D. Slak, T. Krebs, M. Leuschner, N. Schmickler, E. Kuchuk, J. Schmidt, L. I. Domenianni, J. B. Kleine Büning, S. Grimme, P. Vöhringer and A. Gansäuer, *J. Am. Chem. Soc.*, 2023, **145**, 26667; (d) Z. Zhang, T. Hilche, D. Slak, N. R. Rietdijk, U. N. Oloyede, R. A. Flowers and A. Gansäuer, *Angew. Chem., Int. Ed.*, 2020, **59**, 9355.
- Reviews: (a) T. Takeda, *Chem. Rec.*, 2007, **7**, 24; (b) U. Rosenthal, *Organometallics*, 2020, **39**, 4403 Selected original papers: (c) S. A. Cohen and J. E. Bercaw, *Organometallics*, 1985, **4**, 1006; (d) H. G. Alt, K.-H. Schwind and M. D. Rausch, *J. Organomet. Chem.*, 1987, **321**, C9; (e) S. C. Berk, R. B. Grossman and S. L. Buchwald, *J. Am. Chem. Soc.*, 1994, **116**, 8593; (f) K. Sato, Y. Nishihara, S. Huo, Z. Xi and T. Takahashi, *J. Organomet. Chem.*, 2001, **633**, 18; (g) K. Kaleta, M. Ruhmann, O. Theilmann, T. Beweries, S. Roy, P. Arndt, A. Villinger, E. D. Jemmis, A. Schulz and U. Rosenthal, *J. Am. Chem. Soc.*, 2011, **133**, 5463; (h) M. Kessler, S. Hansen, C. Godemann, A. Spannenberg and T. Beweries, *Chem. – Eur. J.*, 2013, **19**, 6350; (i) A. A. Oluyadi, S. Ma and C. N. Muhoro, *Organometallics*, 2013, **32**, 70; (j) L. O. Khafizova, M. G. Shaibakova, N. A. Rikhter, T. V. Tyumkina and U. M. Dzhemilev, *Tetrahedron*, 2019, **75**, 906; (k) M. Reiß, F. Reiß, A. Spannenberg, P. Arndt and T. Beweries, *Organometallics*, 2018, **37**, 4415; (l) G. R. Kiel, A. E. Samkian, A. Nicolay, R. J. Witzke and T. D. Tilley, *J. Am. Chem. Soc.*, 2018, **140**, 2450; (m) J. Kim, D. T. Egger, C. W. Frye, E. P. Beaumier and I. A. Tonks, *Organometallics*, 2023, **42**, 1331.
- (a) N. El Murr and A. Chaloyard, *J. Organomet. Chem.*, 1982, **231**, 1; (b) B. H. Edwards, R. D. Rogers, D. J. Sikora, J. L. Atwood and M. D. Rausch, *J. Am. Chem. Soc.*, 1983, **105**, 416; (c) G. S. Girolami, G. Wilkinson, M. Thornton-Pett and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1984, 2347; (d) D. W. Stephan, *Organometallics*, 1992, **11**, 996.
- (a) P. B. Hitchcock, F. M. Kerton and G. A. Lawless, *J. Am. Chem. Soc.*, 1998, **120**, 10264; (b) M. D. Walter, C. D. Sofield and R. A. Andersen, *Organometallics*, 2008, **27**, 2959.
- Reviews: (a) G. Bousrez and F. Jaroschik, *Eur. J. Org. Chem.*, 2022, e202200202; (b) M. A. Halim, Z. Guo, V. L. Blair, G. B. Deacon and P. C. Junk, *J. Organomet. Chem.*, 2024, **1010**, 123094; (c) A. Mortis and R. Anwänder, *Eur. J. Inorg. Chem.*, 2024, **27**, e202400127.
- (a) T. Kumar, F. Massicot, D. Harakat, S. Chevreux, A. Martinez, K. Bordolinska, P. Preethalayam, R. Kokkuvayil Vasu, J.-B. Behr, J.-L. Vasse and F. Jaroschik, *Chem. – Eur. J.*, 2017, **23**, 16460; (b) X. Y. Cao, F. Huang and S. Zhang, *Synlett*, 2019, 1437; (c) S. Xiao, C. Liu, B. Song, L. Wang, Y. Qi and Y. Liu, *Chem. Commun.*, 2021, **57**, 6169.
- Z. Guo, R. Huo, Y. Q. Tan, V. Blair, G. B. Deacon and P. C. Junk, *Coord. Chem. Rev.*, 2020, **415**, 213232.
- B. K. Banik, *Eur. J. Org. Chem.*, 2002, 2431.
- (a) Y. Zhang, Y. Yu and W. Bao, *Synth. Commun.*, 1995, **25**, 1825; (b) Y. Huang and Y. Zhang, *Synth. Commun.*, 1996, **26**, 2911.
- L. Zhang, X. Yu, L. Zhang, X. Zhou and Y. Lin, *Org. Chem. Front.*, 2014, **1**, 929.
- G. Bousrez, I. Déchamps, J. L. Vasse and F. Jaroschik, *Dalton Trans.*, 2015, **44**, 9359.
- Y. Horikawa, M. Watanabe, T. Fujiwara and T. Takeda, *J. Am. Chem. Soc.*, 1997, **119**, 1127.



- 16 (a) C. Denhez, S. Medegan, F. Helion, J.-L. Namy, J.-L. Vasse and J. Szymoniak, *Org. Lett.*, 2006, **8**, 2945; (b) G. Bousrez, F. Jaroschik, A. Martinez, D. Harakat, E. Nicolas, X. F. Le Goff and J. Szymoniak, *Dalton Trans.*, 2013, **42**, 10997.
- 17 A. Joosten, M. Soueidan, C. Denhez, D. Harakat, F. Hé lion, J.-L. Namy, J.-L. Vasse and J. Szymoniak, *Organometallics*, 2008, **27**, 4152.
- 18 (a) D. L. J. Clive, P. C. Anderson, N. Moss and A. Singh, *J. Org. Chem.*, 1982, **47**, 1641; (b) A. F. Barrero, M. M. Herrador, J. F. Quílez del Moral, P. Arteaga, J. F. Arteaga, H. R. Dieguez and E. M. Sanchez, *J. Org. Chem.*, 2007, **72**, 2988; (c) T. Strašák, F. Jaroschik, M. Malý, J. Čermák, J. Sýkora, R. Fajgar, J. Karban and D. Harakat, *Inorg. Chim. Acta*, 2014, **409**, 137.
- 19 Reviews: (a) *Reactive Intermediates: MS Investigations in Solution*, ed. L. S. Santos, Wiley-VCH, Weinheim, 2010; (b) J. Mehara and J. Roithová, *Chem. Sci.*, 2020, **11**, 11960  
Original research papers: (c) W. J. Evans, M. A. Johnston, C. H. Fujimoto and J. Greaves, *Organometallics*, 2000, **19**, 4258; (d) D. P. Daniels, G. B. Deacon, D. Harakat, F. Jaroschik and P. C. Junk, *Dalton Trans.*, 2012, **41**, 267; (e) H. Zhang, K. Yu, N. Li, J. He, H. You and J. Jiang, *J. Mass Spectrom.*, 2018, **53**, 511; (f) L. P. E. Yunker, Z. Ahmadi, J. R. Logan, W. Wu, T. Li, A. Martindale, A. G. Oliver and J. S. McIndoe, *Organometallics*, 2018, **37**, 4297; (g) M. Regnacq, D. Lesage, M. S. M. Holmsen, K. Miqueu, D. Bourissou and Y. Gimbert, *Dalton Trans.*, 2023, **52**, 13528.
- 20 M. Polášek and J. Kubišta, *J. Organomet. Chem.*, 2007, **692**, 4073.
- 21 H. Brintzinger and J. E. Bercaw, *J. Am. Chem. Soc.*, 1970, **92**, 6182.
- 22 (a) J. E. Bercaw, R. H. Marvich, L. G. Bell and H. H. Brintzinger, *J. Am. Chem. Soc.*, 1972, **94**, 1219; (b) V. Varga, K. Mach, J. Heyrovský, G. Schmid and U. Thewalt, *J. Organomet. Chem.*, 1994, **475**, 127.
- 23 (a) M. G. Shaibakova, L. O. Khafizova, N. M. Chobanov, R. R. Gubaidullin, N. Y. R. Popod'ko and U. M. Dzhemilev, *Tetrahedron Lett.*, 2014, **55**, 1326; (b) B. R. Reiner and I. A. Tonks, *Inorg. Chem.*, 2019, **58**, 10508; (c) S. Okamoto, T. Yamada, Y.-K. Tanabe and M. Sakai, *Organometallics*, 2018, **37**, 4431; (d) G. Siemiaszko and Y. Six, *New J. Chem.*, 2018, **42**, 20219; (e) S. Ohta, N. Miura, K. Saitoh, K. Itoh, S. Satoh, R. Miyamoto and M. Okazaki, *Organometallics*, 2021, **40**, 2826.
- 24 (a) J. G. Kenworthy, J. Myatt and M. C. R. Symons, *J. Chem. Soc. A*, 1971, 3428; (b) E. Samuel and J. Vedel, *Organometallics*, 1989, **8**, 237; (c) E. Samuel and J. Hénique, *J. Organomet. Chem.*, 1996, **512**, 183; (d) S. Van Doorslaer, J. J. Shane, S. Stoll, A. Schweiger, M. Kranenburg and R. J. Meier, *J. Organomet. Chem.*, 2001, **634**, 185.
- 25 A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions*, Clarendon Press, London, 1970.
- 26 F. Lacroix, C. E. Plecnik, S. Liu, F.-C. Liu, E. A. Meyers and S. G. Shore, *J. Organomet. Chem.*, 2003, **687**, 69.
- 27 G. Depaoli, P. Zanonato and G. Valle, *Inorg. Chim. Acta*, 1990, **170**, 109.
- 28 (a) D. G. Sekutowski and G. D. Stucky, *Inorg. Chem.*, 1975, **14**, 2192; (b) D. G. Sekutowski, R. Jungst and G. D. Stucky, *Inorg. Chem.*, 1978, **17**, 1848.
- 29 *CRC Handbook of Chemistry and Physics*, ed. D. R. Lide, CRC Press, Boca Raton, FL, 87th edn, 2006.
- 30 G. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112.
- 31 G. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, **71**, 3.
- 32 K. Yoshida, I. Morimoto, K. Mitsudo and H. Tanaka, *Tetrahedron*, 2008, **64**, 5800.

