



Cite this: *RSC Adv.*, 2016, 6, 70581

Triamidoamine-supported zirconium: hydrogen activation, Lewis acidity, and *rac*-lactide polymerization†

Sarah E. Leshinski,^a Craig A. Wheaton,^b Hongsui Sun,^b Andrew J. Roering,^{‡a} Joseph M. Tanski,^c Daniel J. Fox,^d Paul G. Hayes^{*b} and Rory Waterman^{*a}

Received 15th June 2016

Accepted 19th July 2016

DOI: 10.1039/c6ra15617g

www.rsc.org/advances

Investigation of a triamidoamine-supported zirconium hydride intermediate, important to a range of catalytic reactions, revealed the potential Lewis acidity of $[\kappa^5\text{-}N,N,N,N,C\text{-}(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_2\text{NCH}_2\text{CH}_2\text{NSiMe}_2\text{CH}_2]\text{Zr}$ (**1**). A preliminary study of **1** as a precursor for the polymerization of *rac*-lactide showed modest activity but indicated that five-coordinate zirconium complexes with tetra-N donor ligands may be an avenue for further development in group 4 metal lactide polymerization catalysis.

Introduction

The transfer of hydrogen is an essential step impacting a range of catalytic reactions from commodity (*e.g.*, hydrogenation) to specialty chemical synthesis, with broad impact on energy and environmental issues.^{1,2} It has been observed that hydrogen transfer from triamidoamine-supported zirconium compounds frequently arises from C–H bond activation of a trimethylsilyl substituent. Such cyclometalation reactions are a pivotal step in transformations catalyzed by $(\text{N}_3\text{N})\text{ZrX}$ derivatives including dehydrocoupling, hydrogenation, and heterofunctionalization reactions.^{3–10} The commonly observed product, $[\kappa^5\text{-}N,N,N,N,C\text{-}(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_2\text{NCH}_2\text{CH}_2\text{NSiMe}_2\text{CH}_2]\text{Zr}$ (**1**), is therefore a key intermediate in these catalytic reactions. In hydrophosphination, for instance, cyclometalation has been proposed to be the product-elimination step.⁷ In dehydrocoupling catalysis, H_2 loss is proposed from a putative hydride intermediate, $(\text{N}_3\text{N})\text{ZrH}$ (**2**), *via* cyclometalation and formation of **1**.¹⁰ Computational analysis of **2** with respect to related derivatives (*e.g.*, $(\text{N}_3\text{N})\text{ZrMe}$) has been reported. Based on that analysis, the Zr–H bond dissociation energy of **2** is greater than that calculated for $(\text{N}_3\text{N})\text{ZrMe}$.⁹

Hydride compounds of group 4 metals supported by triamidoamine ligands are rare and unstable. Schrock and coworkers previously reported the observation of a titanium(IV) hydride complex, $(\text{N}_3\text{N})\text{TiH}$, with a hydride resonance at δ 8.29 in the ^1H NMR spectrum.¹¹ However, the complex was not isolable due to a cyclometalation process involving a trimethylsilyl substituent. In analogous zirconium chemistry, Scott and coworkers reported that a benzyl complex, $(\text{N}_3\text{N}')\text{Zr}(\text{CH}_2\text{Ph})$ ($\text{N}_3\text{N}'=\text{N}(\text{CH}_2\text{CH}_2\text{NSiMe}_2^t\text{Bu})_3$), reacts with H_2 or by sublimation to afford the cyclometalated product $[\kappa^5\text{-}(\text{Me}_2^t\text{BuSiNCH}_2\text{CH}_2)_2\text{NCH}_2\text{CH}_2\text{NSi}^t\text{BuMeCH}_2]\text{Zr}$,¹² which was the inspiration for the preparation of **1**.⁹ Notably, the expected hydride intermediate was not observed in those studies. In a later effort to avert cyclometalation, Scott and coworkers replaced the trialkylsilyl ligand substituents with aryl groups, which did not afford the targeted family of tetradentate compounds.¹³ Interestingly, four coordinate tris(amido) hydride derivatives of group 4 metals are isolable.¹⁴

Efforts to better understand compounds **1** and **2** provided evidence of potential Lewis acidity of **1**. In an attempt to leverage this behavior, **1** was tested as a pre-catalyst for the polymerization of *rac*-lactide. These initial studies revealed moderate activity for *rac*-lactide polymerization. More important, these results demonstrate that lower coordination number triamidoamine-supported zirconium compounds may be a viable catalyst type for lactide polymerizations.

Results and discussion

Reactions with hydrogen and Lewis bases

Reaction of **1** with approximately 3 atm of hydrogen in benzene-*d*₆ solution resulted in the equilibrium formation of $(\text{N}_3\text{N})\text{ZrH}$ (**2**) and **1** (in an approximate 1 : 2 ratio, eqn (1)). As an average of three trials, an equilibrium constant, $K_{\text{eq}} = 0.54(2)$, for the formation of **2** was measured by integration of ^1H NMR

^aDepartment of Chemistry, University of Vermont, Cook Physical Sciences Building, Burlington, VT 05405, USA. E-mail: rory.waterman@uvm.edu; Fax: +1-802-656-8705; Tel: +1-802-656-0278

^bDepartment of Chemistry and Biochemistry, University of Lethbridge, 4401 University Drive, Lethbridge, AB, Canada T1K 3M4. E-mail: p.hayes@uleth.ca

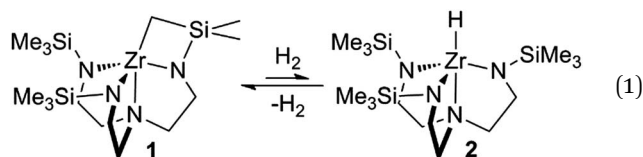
^cDepartment of Chemistry, Vassar College, Poughkeepsie, NY 12604, USA

^dDepartment of Chemistry, Boston College, Chestnut Hill, MA 02467-3860, USA

† Electronic supplementary information (ESI) available: Plots and spectra from polymerization reactions and X-ray data. CCDC 1471864. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6ra15617g

‡ Current address: Department of Chemistry, SUNY Cortland, Cortland, NY 13045, USA.

resonances against an internal standard of ferrocene. The most telling feature of **2** is the hydride resonance at δ 10.59 in the ^1H NMR spectrum, which is downfield of the resonance observed by Schrock and coworkers for $(\text{N}_3\text{N})\text{TiH}$ at δ 8.29 and that for $\text{Cp}^*_2\text{Zr}(\text{H})_2$ at δ 7.46.^{11,15} An NOE experiment revealed magnetization transfer between the hydride resonance and that of hydrogen gas, illustrating the equilibrium formation of **2** and confirming the hydride resonance originates from hydrogen addition (Fig. 1). The small equilibrium formation of **2** is likely a contributing reason for the limited hydrogenation reactivity of **1** with molecular hydrogen rather than sacrificial donors like amine boranes.¹⁶



Deuteration of the trimethylsilyl substituents of **1** was successfully accomplished by repeatedly flushing a benzene- d_6 solution of **1** with deuterium gas. The reaction was monitored over 4 days, and 83% of methyl proton intensity was lost from **1**, as measured by ^1H NMR spectroscopy *versus* an internal standard. This value represents exchange of approximately 22 of the 27 hydrogen atoms. Further exposure to deuterium gas did not result in additional exchange. H/D exchange of this kind is known for $(\text{N}_3\text{N}')\text{Zr}$ compounds, as reported by Scott.¹²

Mechanistic insight into bond-activations involving complex **1** was sought by reaction with *para*-hydrogen.^{17,18} However, treatment of **1** with *para*-enriched hydrogen gas did not result in an enhanced polarization. This negative result may indicate that H_2 activation is not a concerted process, but rather, involves one or more of a variety of other possibilities that thwart polarization. One of the most intriguing possibilities is rapid and reversible pre-coordination of H_2 at a vacant orbital on zirconium prior to activation and ring opening. Such metal interaction may catalyze the redistribution of the *para*-enriched hydrogen sample back to a typical distribution of *ortho* and *para* H_2 .¹⁷ Hence, an effort to substantiate or disprove coordination to **1** without ring opening was undertaken.

Many candidate substrates for coordination to **1** have been proven incompatible with the reactive metal-carbon bond. For

example, nitriles engage in 1,2-insertion reactions too rapidly to provide evidence of pre-coordination.¹⁹ Accordingly, less reactive ligands were sought. Only *via* X-ray crystallography was it unambiguously demonstrated that Lewis bases inert toward E-H bond activation and insertion could coordinate to zirconium. Recrystallization of **1** from concentrated THF solution at -30°C afforded X-ray quality crystals of **1**·THF (Fig. 2).

The molecular structure of **1**·THF features a highly distorted trigonal prismatic geometry with a weak axial amine interaction to zirconium, $\text{Zr}-\text{N}(4) = 2.4571(14)$ Å, analogous to the $(\text{N}_3\text{N}')\text{ZrCH}_2\text{Ph}$ complex by Scott and coworkers featuring $\text{Zr}-\text{N}_{\text{axial}} = 2.548(4)$ Å,¹² as well as the larger family of $(\text{N}_3\text{N})\text{ZrX}$ and $(\text{N}_3\text{N})\text{ZrX}(\text{L})$ compounds that have been structurally characterized.^{5-9,19-22} The most notable structural feature of **1**·THF is the metallacycle, which is highly similar to that in $[\kappa^5-(\text{Me}_2^t\text{BuSiNCH}_2\text{CH}_2)_2\text{NCH}_2\text{CH}_2\text{NSi}^t\text{BuMeCH}_2]\text{Zr}$ (**3**).¹² For example, **1**·THF has $\text{Zr}-\text{C}(7) = 2.337(2)$ Å and $\text{N}(1)-\text{Zr}-\text{C}(7) = 71.98(6)^\circ$, which compare favorably to the metallacycle of **3**, $\text{Zr}-\text{C} = 2.613(11)$ Å and $\text{N}-\text{Zr}-\text{C} = 67.8(2)^\circ$, where the shorter bond length and more open angle are a result of the additional ligand in **1**·THF. Indeed, the $\text{Zr}-\text{C}$ distance in **1**·THF is similar to $\text{Zr}-\text{C}$ bonds (2.324(3) and 2.309(3) Å) in six-coordinate $\text{Zr}[\text{CH}_2\text{SiMe}_2\text{N}(\text{SiMe}_3)]_2(\text{dmpe})$ ($\text{dmpe} = 1,2$ -bis(dimethylphosphino)ethane).²³

The THF of **1**·THF is a weakly coordinated ligand as suggested by the long $\text{Zr}-\text{O}$ contact ($\text{Zr}-\text{O}(1) = 2.3478(14)$ Å) and the observed reaction chemistry. For example, extended periods of reduced pressure quantitatively removed THF from **1**·THF in the solid state, but crystallinity of those samples was lost. NMR

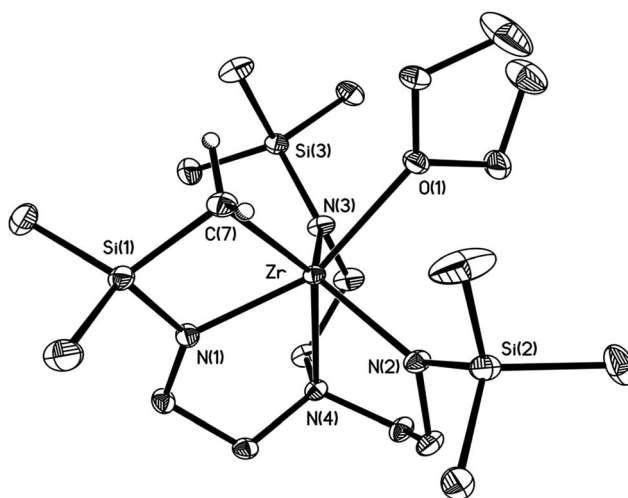


Fig. 2 Molecular structure of $[\kappa^5-N,N,N,N,C-(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_2\text{-NCH}_2\text{CH}_2\text{-NSiMe}_2\text{CH}_2]\text{Zr}(\text{THF})$ (**1**·THF). Thermal ellipsoids are drawn at the 35% level for optimal viewing. Hydrogen atoms except those on C(7) are omitted for clarity. Selected metrical parameters: $\text{Zr}-\text{C}(7)$ 2.3373(18), $\text{C}(7)-\text{Si}(1)$ 1.850(2), $\text{N}(1)-\text{Si}(1)$ 1.7137(15), $\text{Zr}-\text{N}(1)$ 2.1008(15), $\text{Zr}-\text{N}(2)$ 2.1244(15), $\text{Zr}-\text{N}(3)$ 2.1348(15), $\text{Zr}-\text{N}(4)$ 2.4571(14), $\text{Zr}-\text{O}(1)$ 2.3478(14) Å; $\text{N}(1)-\text{Zr}-\text{N}(2)$ 108.93(6), $\text{N}(1)-\text{Zr}-\text{N}(3)$ 104.52(6), $\text{N}(2)-\text{Zr}-\text{N}(3)$ 122.03(6), $\text{N}(1)-\text{Zr}-\text{C}(7)$ 71.98(6), $\text{N}(2)-\text{Zr}-\text{C}(7)$ 114.05(7), $\text{N}(3)-\text{Zr}-\text{C}(7)$ 120.76(6), $\text{N}(1)-\text{Zr}-\text{O}(1)$ 152.79(5), $\text{N}(2)-\text{Zr}-\text{O}(1)$ 86.83(5), $\text{N}(3)-\text{Zr}-\text{O}(1)$ 83.98(6), $\text{C}(7)-\text{Zr}-\text{O}(1)$ 81.43(6), $\text{C}(7)-\text{Zr}-\text{N}(4)$ 142.83(6), $\text{O}(1)-\text{Zr}-\text{N}(4)$ 135.71(5)°.

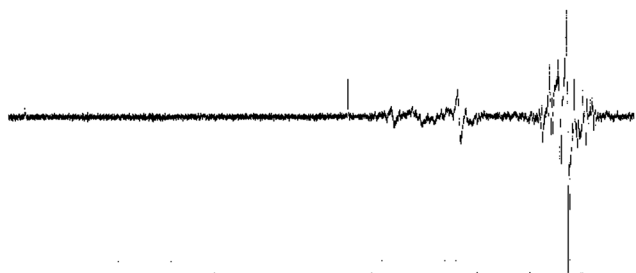


Fig. 1 1D NOE spectrum of $(\text{N}_3\text{N})\text{ZrH}$ (**2**) illustrating magnetization transfer to dihydrogen (scale = -1 to 11 ppm).

spectra of complex **1** in the presence of THF, as well as spectra of isolated samples of **1**·THF provided little evidence of Lewis base coordination in the solution state because the spectra are identical except for the presence of THF. Effort to establish purity by combustion analysis on isolated, dried samples of **1**·THF afforded data consistent with **1** (e.g., found: C, 39.82; H, 8.55; N, 12.10). Regardless, the structure of **1**·THF demonstrates coordination at zirconium without ring opening is indeed possible, and suggests that such latent Lewis acidity may reveal new reactivity for the (N₃N)Zr fragment.

rac-Lactide polymerization

Lactide polymerization was chosen as a test reaction that might take advantage of the Lewis acidity of **1** because Lewis acids are known to polymerize lactide. Interest in biodegradable polymers from renewable precursors such as lactic acid has been tremendous,²⁴ which has fueled global efforts to discover and understand catalysts for these reactions.²⁵ There has been significant attention on group 4 metal compounds in these efforts for their unique reactivity and the relative abundance of metals like titanium and zirconium.^{26,27} Zirconium compounds supported by triamidoamine ligands have been studied as lactide polymerization catalysts and demonstrated good activities with low PDI values.^{28,29} For other systems, silyl-substituted amides have not proven an optimal ancillary substituent in this catalysis.²⁶ This observation prompted the omission of an alcohol cocatalyst that might cleave N–Si bonds in this study, and excess alcohol decomposes **1**.⁹ Indeed, is it known that excess alcohol will decompose **1** and related derivatives.

Preliminary investigations of **1** for the ring-opening polymerization (ROP) of *rac*-lactide were undertaken on an NMR scale in toluene-*d*₈ solution at 70 °C. Using an initial concentration of 0.5 M *rac*-lactide and either 1% or 4% loading of **1**, conversion to polylactide (PLA) was determined by integration of the lactide methine resonance in the ¹H NMR spectra. Under these conditions linear relationships between ln[lactide] and time (pseudo first-order kinetics) were established revealing observed rate constants of $k_{\text{obs}} = 1.61 \times 10^{-5} \text{ s}^{-1}$ and $k_{\text{obs}} = 3.43 \times 10^{-5} \text{ s}^{-1}$ for 100 and 25 equiv. of lactide, respectively. Compared to related zirconium and other group 4 metal initiators, **1** shows only modest activity.²⁶ Importantly, however, these activities were obtained in the absence of a cocatalyst, such as isopropanol or benzyl alcohol.

Polymer samples isolated from ROP experiments were analyzed by gel-permeation chromatography (Table 1). These materials exhibited broad molecular weight distributions (PDI: 1.50–2.53) and substantially larger M_n than calculated. Though the mechanism of polymerization remains unclear, the poor molecular weight control may be due to multiple active species and/or initiator degradation during the polymerization process. Likewise, slow initiation relative to propagation is also consistent with large PDI values and longer than anticipated polymer chains.

These observations confirm that five-coordinate zirconium compounds supported by triamidoamine ligands can effectively initiate the polymerization of *rac*-lactide. This observation

Table 1 Molecular weight data for PLA samples prepared using different concentrations of **1** as initiator^a

[LA] ₀ [1]	[Cat]	Time (h)	Calc. M_n^b ($\times 10^3$)	M_n ($\times 10^3$)	M_w ($\times 10^3$)	PDI
25	0.020	14	3.4	97.1	245.1	2.53
25	0.020	14	3.4	66.5	113.4	1.70
50	0.010	24	6.6	56.5	91.3	1.62
50	0.010	24	6.6	32.7	68.1	2.08
100	0.005	24	11.6	41.3	62.0	1.50
100	0.005	24	11.6	27.3	47.4	1.74
100	0.005	24	11.6	20.5	35.7	1.74
100	0.005	24	11.6	34.3	20.3	1.69

^a [LA]₀ = 0.5 M, toluene, 70 °C. ^b Calculated using the formula $M_n = ([\text{LA}]_0/[\mathbf{1}]) \times 144.13 \times \text{conversion}$.

compliments extensive lactide polymerization studies reported by Mountford that demonstrate the triamidoamine framework is an effective support for group 4 metal catalysts in lactide polymerization.^{28,29} It is, however, important to note that those studies involved zirconium compounds of sulfonyl-substituted derivatives, which are eight-coordinate.²⁸ Interestingly, Mountford's system exhibits substantially narrower PDI values than those of **1**, despite comparable activities for the two systems.

Conclusions

The triamidoamine-supported zirconium hydride **2** is observable under H₂ pressure in an equilibrium with cyclometalated compound **1**. This highly reversible reactivity with hydrogen allows for extensive deuteration of the trimethylsilyl substituents of **1** under D₂ gas. In an effort to assess the relative Lewis acidity of **1**, an ether adduct **1**·THF was crystallographically characterized. Seeking to exploit this Lewis acidity, **1** was tested as an initiator for the ring-opening polymerization of *rac*-lactide. Compound **1** demonstrated comparable activity to related zirconium pre-catalysts from other researchers, but it provides less molecular-weight control than those systems. Most important, the *rac*-lactide polymerization activity demonstrated by **1** establishes that five-coordinate tetra-N donor group 4 compounds are a potentially viable class of initiators for further study.

Experimental section

General considerations

Manipulations were performed under a nitrogen atmosphere with dry, oxygen-free solvents using a glove box or standard Schlenk techniques. NMR solvents were degassed and dried by conventional procedures. NMR spectra were recorded with a Varian 500 MHz or a Bruker Avance II NMR spectrometer in benzene-*d*₆ or toluene-*d*₈ solution and are reported with reference to the residual solvent resonance. Samples of *para*-enriched hydrogen were prepared from commercial H₂ using reported methods.^{17,18} GPC analyses were performed on a Waters 2695 equipped with a Waters 410 refractive index

detector and a Wyatt light scattering detector. Solutions of the polymer samples were prepared in THF to a concentration of approximately 10 mg mL⁻¹. All samples were filtered (0.2 μm) prior to performing the analysis, and were run at a temperature of 40 °C. Light scattering data were processed using $dn/dc = 0.0483$ which was measured using a PLA sample prepared with **1** as initiator. The cyclometalated compound, [κ^5 -N,N,N,N,C-(Me₃SiNCH₂CH₂)₂NCH₂CH₂NSiMe₂CH₂]Zr (**1**), was prepared according to the published procedure.⁹ All other reagents were used as received.

Reactions of **1**

Observation of (N₃N)ZrH (2**).** A PFTE-valved NMR tube was charged with **1** (0.010 g, 0.022 mmol) and benzene-*d*₆ (500 μL). The tube was degassed *via* freeze-pump-thaw cycles and backfilled with excess H₂ (~3 atm). The reaction proceeded for one hour and the NMR tube was recharged with H₂. The hydride was observed in 35% conversion as compared to starting **1** by integration in reactions with added ferrocene. ¹H (500.1 MHz): δ 10.59 (s, 1H, H), 3.60 (t, 6H, CH₂), 2.22 (t, 6H, CH₂), 0.31 (s, 36H, CH₃). ¹³C{¹H} (125.8 MHz): δ 62.8 (s, CH₂), 47.5 (s, CH₂), 0.5 (s, CH₃). The ¹H NMR NOE experiment was carried out using the standard Varian pulse sequence.

Crystallization of **1 as **1**·THF.** Samples of **1** (*ca.* 20 mg) were dissolved in minimal THF and filtered. Those solutions were cooled to -30 °C for several days until colorless crystals formed. NMR spectra of crystalline products were identical to **1** with added THF.

Reaction of **1 with D₂.** A PFTE-valved NMR tube was charged with **1** (0.010 g, 0.022 mmol) and benzene-*d*₆ (500 μL). The tube was charged with excess D₂ using standard Schlenk techniques. The reaction proceeded for 4 days and additional D₂ was added to the tube once daily to yield the deuterated product in 83% conversion from **1** to **1**-d_{*n*}, as calculated by use of ferrocene as an internal standard. ¹H (500.1 MHz): δ 3.57 (t, 2H, CH₂), 3.21 (m, CH₂), 3.13 (m, 4H, CH₂), 2.32 (m, 6H, CH₂), 2.21 (t, CH₂) 0.20–0.42 (s, 5H, CH₃).

***para*-Hydrogen experiments.** Degassed, frozen solutions of **1** in benzene-*d*₆ solution in a J-Young type NMR tube were subject to an atmosphere of *para*-enriched hydrogen gas. The NMR tube was sealed and the sample allowed to thaw in a pre-shimmed spectrometer while data collected.

Polymerization reactions

Kinetic measurements. In a glovebox, an NMR tube was loaded with an appropriate amount of initiator (*e.g.* 2.2 mg for [LA]/[**1**] = 100) and 72.1 mg of *rac*-lactide, to which 0.50 mL of toluene-*d*₈ was then added. The tube was immediately sealed with a rubber septum, removed from the glove box, and inserted into the temperature stabilized (70 °C) and pre-shimmed NMR instrument.

Polymer preparations. In a glove box with an ambient temperature of approximately 26 °C, a scintillation vial was loaded with 144.1 mg of *rac*-lactide and an appropriate amount of initiator (*e.g.* 4.3 mg of **1** for [LA]/[**1**] = 100). Toluene (1 mL) was added to the vial and the resulting solution was stirred for an

Table 2 Crystal data and structure refinement parameters for [κ^5 -N,N,N,N,C-(Me₃SiNCH₂CH₂)₂NCH₂CH₂NSiMe₂CH₂]Zr(THF) (**1**·THF)

Formula	C ₁₉ H ₄₆ N ₄ OSi ₃ Zr
<i>M</i>	524.10
Crystal system	Monoclinic
Color	Colorless
<i>a</i> /Å	16.492(3)
<i>b</i> /Å	9.8668(2)
<i>c</i> /Å	17.009(3)
α /°	90
β /°	101.909(2)
γ /°	90
Unit cell vol./Å ³	2708.3(8)
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>Z</i>	4
θ range/°	1.26 to 30.47
μ /mm ⁻¹	0.555
<i>N</i>	37 174
<i>N</i> _{ind}	7736
<i>R</i> _{int}	0.0370
<i>R</i> ₁ ^a (<i>I</i> > 2σ(<i>I</i>))	0.0311
<i>wR</i> ₂ ^b (<i>I</i> > 2σ(<i>I</i>))	0.0801
$\Delta\rho_{\max}$; $\Delta\rho_{\min}$ /e Å ³	0.802, -0.642
GoF on <i>R</i> ₁	1.041

$$^a R_1 = |F_o| - |F_c|/|\Sigma|F_o. \quad ^b wR_2 = \{\Sigma[w(F_o^2 - F_c^2)]/\Sigma[w(F_o^2)]\}^{1/2}.$$

appropriate period of time at 70 °C. Afterwards, the vial was removed from the glove box and exposed to the atmosphere. Cold (-35 °C) wet methanol (10 mL) was added to the solution causing precipitation of the polymer. The vial was centrifuged and the solvent decanted. The isolated polymer was redissolved in 1 mL of CH₂Cl₂ and reprecipitated and isolated by the same procedure. The polymer sample was then dried *in vacuo* for no less than 24 h.

X-ray crystallography

X-ray diffraction data were collected on a Bruker APEX 2 CCD platform diffractometer (MoK α , $\lambda = 0.71073$ Å) at 125 K. A suitable crystal of **1**·THF, under paratone-*N* cryoprotectant oil, was mounted using a nylon loop. The structure **1**·THF was solved using direct methods and standard difference map techniques with refinement using full-matrix least squares procedures on F² with SHELXTL (version 6.14).³⁰ Non-hydrogen atoms were refined anisotropically. Hydrogen atoms on carbon were included in calculated positions and were refined using a riding model. EXTI refined to zero and was removed from the refinement. Crystal data and refinement details are presented in Table 2.

Acknowledgements

This work was support by the U. S. National Science Foundation (NSF, CHE-1265608 and CHE-1565658 to RW) and NSERC of Canada (PGH). X-ray crystallography facilities were provided by the NSF (CHE-0521237 to JMT).

Notes and references

- 1 H. Arakawa, M. Aresta, J. N. Armor, M. A. Barteau, E. J. Beckman, A. T. Bell, J. E. Bercaw, C. Creutz, E. Dinjus,

- D. A. Dixon, K. Domen, D. L. DuBois, J. Eckert, E. Fujita, D. H. Gibson, W. A. Goddard, D. W. Goodman, J. Keller, G. J. Kubas, H. H. Kung, J. E. Lyons, L. E. Manzer, T. J. Marks, K. Morokuma, K. M. Nicholas, R. Periana, L. Que, J. Rostrup-Nielson, W. M. H. Sachtler, L. D. Schmidt, A. Sen, G. A. Somorjai, P. C. Stair, B. R. Stults and W. Tumas, *Chem. Rev.*, 2001, **101**, 953–996.
- 2 J. A. Gladysz, R. B. Bedford, M. Fujita, F. P. Gabbaï, K. I. Goldberg, P. L. Holland, J. L. Kiplinger, M. J. Krische, J. Louie, C. C. Lu, J. R. Norton, M. A. Petrukhina, T. Ren, S. S. Stahl, T. D. Tilley, C. E. Webster, M. C. White and G. T. Whiteker, *Organometallics*, 2014, **33**, 1505–1527.
- 3 M. B. Ghebreab, C. A. Bange and R. Waterman, *J. Am. Chem. Soc.*, 2014, **136**, 9240–9243.
- 4 M. B. Ghebreab, D. K. Newsham and R. Waterman, *Dalton Trans.*, 2011, **40**, 7683–7685.
- 5 M. B. Ghebreab, T. Shalumova, J. M. Tanski and R. Waterman, *Polyhedron*, 2010, **29**, 42–45.
- 6 A. J. Roering, J. J. Davidson, S. N. MacMillan, J. M. Tanski and R. Waterman, *Dalton Trans.*, 2008, 4488–4498.
- 7 A. J. Roering, S. E. Leshinski, S. M. Chan, T. Shalumova, S. N. MacMillan, J. M. Tanski and R. Waterman, *Organometallics*, 2010, **29**, 2557–2565.
- 8 A. J. Roering, S. N. MacMillan, J. M. Tanski and R. Waterman, *Inorg. Chem.*, 2007, **46**, 6855–6857.
- 9 A. J. Roering, A. F. Maddox, L. T. Elrod, S. M. Chan, M. B. Ghebreab, K. L. Donovan, J. J. Davidson, R. P. Hughes, T. Shalumova, S. N. MacMillan, J. M. Tanski and R. Waterman, *Organometallics*, 2009, **28**, 573–581.
- 10 R. Waterman, *Organometallics*, 2007, **26**, 2492–2494.
- 11 C. C. Cummins, R. R. Schrock and W. M. Davis, *Organometallics*, 1992, **11**, 1452–1454.
- 12 C. Morton, I. J. Munslow, C. J. Sanders, N. W. Alcock and P. Scott, *Organometallics*, 1999, **18**, 4608–4613.
- 13 C. Morton, K. M. Gillespie, C. J. Sanders and P. Scott, *J. Organomet. Chem.*, 2000, **606**, 141–146.
- 14 L. Turculet and T. D. Tilley, *Organometallics*, 2004, **23**, 1542–1553.
- 15 J. M. Manriquez, D. R. McAlister, R. D. Sanner and J. E. Bercaw, *J. Am. Chem. Soc.*, 1978, **100**, 2716–2724.
- 16 K. A. Erickson, J. P. W. Stelmach, N. T. Mucha and R. Waterman, *Organometallics*, 2015, **34**, 4693–4699.
- 17 R. Eisenberg, *Acc. Chem. Res.*, 1991, **24**, 110–116.
- 18 S. B. Duckett and R. E. Mewis, *Acc. Chem. Res.*, 2012, **45**, 1247–1257.
- 19 S. Leshinski, T. Shalumova, J. M. Tanski and R. Waterman, *Dalton Trans.*, 2010, **39**, 9073–9078.
- 20 A. F. Maddox, J. J. Davidson, T. Shalumova, J. M. Tanski and R. Waterman, *Inorg. Chem.*, 2013, **52**, 7811–7816.
- 21 A. F. Maddox, K. A. Erickson, J. M. Tanski and R. Waterman, *Chem. Commun.*, 2011, **47**, 11769–11771.
- 22 A. J. Roering, L. T. Elrod, J. K. Pagano, S. L. Guillot, S. M. Chan, J. M. Tanski and R. Waterman, *Dalton Trans.*, 2013, **42**, 1159–1167.
- 23 R. P. Planalp and R. A. Andersen, *Organometallics*, 1983, **2**, 1675–1680.
- 24 G.-Q. Chen and M. K. Patel, *Chem. Rev.*, 2011, **112**, 2082–2099.
- 25 O. Dechy-Cabaret, B. Martin-Vaca and D. Bourissou, *Chem. Rev.*, 2004, **104**, 6147–6176.
- 26 A. Sauer, A. Kapelski, C. Fliedel, S. Dagorne, M. Kol and J. Okuda, *Dalton Trans.*, 2013, **42**, 9007–9023.
- 27 G. B. Haxel, J. B. Hedrick, G. J. Orris, *Fact Sheet 087-02: Rare Earth Elements—Critical Resources for High Technology*, U. S. Department of the Interior, Washington, DC, 2005.
- 28 M. P. Blake, A. D. Schwarz and P. Mountford, *Organometallics*, 2011, **30**, 1202–1214.
- 29 A. D. Schwarz, A. L. Thompson and P. Mountford, *Inorg. Chem.*, 2009, **48**, 10442–10454.
- 30 G. M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112–122.