Triamidoamine-supported zirconium: Hydrogen activation, Lewis acidity, and: Rac-lactide polymerization

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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 \([N,N]ZrX\) derivatives including dehydrocoupling, hydrogenation, and heterofunctionalization reactions.\(^3-7\) The commonly observed product, \([\kappa^5-N,N,N,N,C-(Me_3SiNCH_2CH_2)_2NCH_2CH_2NSiMe_2CH_2]Zr\) (1), is therefore a key intermediate in these catalytic reactions. In hydropophosphination, 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, \([N,N]ZrH\) (2), via cyclometalation and formation of 1.\(^8\) Computational analysis of 2 with respect to related derivatives (e.g., \([N,N]ZrMe\)) has been reported. Based on that analysis, the Zr–H bond dissociation energy of 2 is greater than that calculated for \([N,N]ZrMe\).\(^9\)

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, \([N,N]TiH\), with a hydride resonance at \(\delta 8.29\) in the \(^1H\) NMR spectrum.\(^10\) 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, \([N,N']Zr(CH_2Ph)\) \((N,N'\equiv(N(CH_2CH_2NSiMe_2Bu)_3)\), reacts with \(H_2\) or by sublimation to afford the cyclometalated product \([\kappa^5-(Me_3BuSiNCH_2CH_2)_2NCH_2CH_2NSiMe_2CH_2]Zr\) (1), 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 tetradeutate compounds.\(^11\) Interestingly, four coordinate tris(amide) hydride derivatives of group 4 metals are isolable.\(^12\)

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 \([N,N]ZrH\) (2) and 1 (in an approximate 1:2 ratio, eqn (1)). As an average of three trials, an equilibrium constant, \(K_{eq} = 0.54(2)\), for the formation of 2 was measured by integration of \(^1H\) NMR
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 (N3N)TiH at δ 8.29 and that for
Cp*Zr(H)2 at δ 7.46.11,12 A NOE experiment revealed magneti-
zation 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-d6
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 stan-
dard. 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 (N3N)/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 H2 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 H2 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
1 with molecular hydrogen rather than sacrificial donors like
amine boranes.16

An example, nitriles engage in 1,2-insertion reactions too rapidly
to provide evidence of pre-coordination.19 Accordingly, less reac-
tive 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 zirco-

Fig. 1 1D NOE spectrum of (N3N)ZrH (2) illustrating magnetization transfer to dihydrogen (scale = −1 to 11 ppm).

Fig. 2 Molecular structure of [κ5-N,N,N,N,C-(Me3SiNCH2CH2)3-
NCH2CH2–NSiMe2CH2]Zr(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: Zr–C(7)
2.3373(18), Zr–C(7)–Si(1) 1.8505(2), N(1)–Si(1) 1.7137(15), Zr–N(11) 2.1008(15),
Zr–N(2) 2.1244(15), Zr–N(3) 2.1348(15), Zr–N(4) 2.4571(14), Zr–O(1)
2.3478(14) Å, N(1)–Zr–N(2) 108.93(6), N(1)–Zr–N(3) 104.52(6), N(2)–
Zr–N(3) 122.03(6), N(1)–Zr–C(7) 71.98(6), N(2)–Zr–C(7) 114.05(7),
N(3)–Zr–C(7) 120.76(6), N(1)–Zr–O(1) 152.79(5), N(2)–Zr–O(1)
86.83(5), N(3)–Zr–O(1) 83.98(6), C(7)–Zr–O(1) 81.43(6), C(7)–Zr–N(4)
142.83(6), O(1)–Zr–N(4) 135.71(5)°.
s 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 [N,N]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 amidines 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, it is 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-d₈ 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 In[laclactide] 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 \( M_w \) 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 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.26-29 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.

Table 1. Molecular weight data for PLA samples prepared using different concentrations of 1 as initiator.

| [LA]₀/[1] | [Cat] | Time (h) | Calc. \( M_w \) (×10⁶) | \( M_w \) (×10⁶) | PDI |
|----------|-------|---------|----------------------|----------------|-----|
| 25       | 0.020 | 14      | 3.4                  | 97.1           | 245.1 | 2.53 |
| 25       | 0.020 | 24      | 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 \([\text{LA}]_0 = 0.5 \text{ M}, \text{toluene, 70 °C.}\)b Calculated using the formula \( M_w = ([\text{LA}]_0/[1]) \times 144.13 \times \text{conversion.}\)

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-d₆ or toluene-d₈ 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

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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, \[k^5\{N, N, N, C-(Me_3SiNCH_2CH_2)_2NCH_2CH_2NSiMe_2CH_2\}Zr(THF) \] (1-THF), was prepared according to the published procedure.\(^a\) All other reagents were used as received.

Reactions of 1

**Observation of (N,N)ZrH (2).** A PTFE-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 H\(_2\) (~3 atm). The reaction proceeded for one hour and the NMR tube was recharged with H\(_2\). The hydride was observed in 35% conversion as compared to starting 1 by integration in reactions with added ferrocene.\(^1\)\(H\) (500.1 MHz): \(\delta\) 10.59 (s, 1H, \(H_2\)), 3.60 (t, 6H, \(CH_2\)), 2.22 (t, 6H, \(CH_2\)), 0.31 (s, 36H, \(CH_2\)), \(^13\)C\(^{1H}\) (125.8 MHz): \(\delta\) 62.8 (s, \(CH_2\)), 47.5 (s, \(CH_2\)), 0.5 (s, \(CH_3\)). 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 D\(_2\).** A PTFE-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 \(D_2\) using standard Schlenk techniques. The reaction proceeded for 4 days and additional \(D_2\) was added to the tube once daily to yield the deuterated product in 83% conversion from 1 to 1-\(d_2\) as calculated by use of ferrocene as an internal standard.\(^1\)\(H\) (500.1 MHz): \(\delta\) 3.57 (t, 2H, \(CH_2\)), 3.21 (m, \(CH_2\)), 3.13 (m, 4H, \(CH_2\)) , 2.32 (m, 6H, \(CH_2\)), 2.21 (t, \(CH_2\)) 0.20–0.42 (s, 5H, \(CH_3\)).

**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-shimmered spectrometer while data collected.

**Polymerization reactions**

**Kinetic measurements.** In a glovebox, an NMR tube was loaded with an appropriate amount of initiator \((e.g. 2.2 \text{ mg for [La]0[1]} = 100)\) 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-shimmered 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 \((e.g. 4.3 \text{ mg of [La]0[1]} = 100)\). Toluene (1 mL) was added to the vial and the resulting solution was stirred for an 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 \(CH_2Cl_2\) 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\(_\lambda\), \(\lambda = 0.71073\) 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 \(F^2\) with SHELXTL (version 6.14).\(^38\) Non-hydrogen atoms were refined anisotropically. Hydrogen atoms on carbon were included in calculated positions and were refined using a riding model. EXTL refined to zero and was removed from the refinement. Crystal data and refinement details are presented in Table 2.

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