Syntheses of rac/meso-{PhP(3-t-Bu-C5H3)2}Zr(RN(CH2)3NR), structural analyses of rac-{PhP(3-t-Bu-C5H3)2}Zr{RN(CH2)3NR} (where R is SiMe3 or Ph), and meso to rac isomerization

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ABSTRACT

Syntheses of rac/meso-{PhP(3-t-Bu-C5H3)2}Zr{Me3SiN(CH2)3NSiMe3} (rac-3/meso-3) and rac/meso-{PhP(3-t-Bu-C5H3)2}Zr{PhN(CH2)3NPh} (rac-4/meso-4) were achieved by metallation of K2[PhP(3-t-Bu-C5H3)2]Cl/THF with Zr{RN(CH2)3NR}Cl/THF (where R = SiMe3 or Ph, respectively) using ethereal solvent. These isomeric pairs were characterized by 1H, 13C{1H}, and 31P{1H} NMR spectroscopy; rac-3 and rac-4 were also examined via single crystal X-ray crystallography. The structures of rac-3 and rac-4 are notable in the tendency of the cyclopentadienyl rings towards nη coordination. While isolated samples of rac-3/meso-3 and rac-4/meso-4 slowly isomerize in tetrahydrofuran-d8 to equilibrium ratios, the isomerization rate for 3 is more than 15-fold greater than that for 4. In addition, equilibrium ratios are rapidly reached when isolated samples of rac-3/meso-3 and rac-4/meso-4 are exposed to tetrahydroxalaminium chloride in tetrahydrofuran-d8. We propose that a nucleophile (either chloride or the phosphine interannular linker) brings about dissociation of one cyclopentadienyl ring, thus promoting the rac/meso isomerization mechanism.

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1. Introduction

A wide range of group 4 metalloccenes and metalloccene analogs have been synthesized and tested as precatalysts for polymerization of ethylene, propylene, and other α-olefins [1]. From this wealth of polymerization data, defined relationships between precatalyst symmetry and polymer tacticity have emerged [2]. Symmetry may be enforced by use of an interannular bridge, or linker, between the two cyclopentadienyl rings of these metalloccenes. Ansa-metalloccenes [3] differ electronically from their unlinked counterparts; these differences were recently scrutinized in the literature [4]. Choice of interannular linker and its effect on reactivity was a subject of a recent review [5].

Over the past eight years, Jordan and coworkers [6] have described the chelate-controlled synthesis of a wide range of ansa-zirconocenes (with substituted bis(cyclopentadienyl) or bis(indenyl) ligands incorporating a Me2Si or in one case, a CH2C5H2, interannular bridge). The importance of metallation agent and solvent selection was highlighted in Ref. [6c], where the chelate-controlled synthesis of meso- and rac-Me2Si(3-t-Bu-C5H3)2Zr{RN(CH2)3NR} (where R is Ph or SiMe3, respectively) was presented (Fig. 1). The chelating bis(amide) ligand accounts for the differing diastereomeric outcomes of these metallations. While the [Me2SiN-(CH2)3NSiMe3] ligand adopts a twist conformation, best suited to the rac-isomer, the [PhN(CH2)3NPh] ligand can, in some cases, adopt an envelope conformation to accommodate the steric requirements of the meso isomer; these diastereomeric preferences were the subject of a recent DFT study [6e]. Solvent choice is critical for isolation of a single diastereomer in these chelate-controlled metallations. For example, use of the mismatched metallation agent/solvent pair, Zr[PhN(CH2)3NPh]Cl2/THF, provides a rac/meso mixture of products [6f]. Jordan et al. propose that the solvent effect stems from differing solubility of the lithium chloride reaction byproduct; chloride ion catalyzes isomerization of the meso isomer to the more thermodynamically stable rac isomer.

We sought to employ Jordan’s methodology for the preparation of rac- and meso-ansa-zirconocenes with a phenyl-phosphine interannular bridge. Ligands such as ([Me2P(2-Me-4-fluorenyl)]2) [7] and [R2P(2-Me-4-t-Bu-C5H3)2] where R = Me or n-Bu [8] and group 4 metalloccenes with a phosphorus-containing ansa-bridge are the subject of two recent review articles [9,10]. A few of these group 4 ansa-metalloccenes have been tested as ethylene [11–13] and α-olefin polymerization precatalysts [14] (Fig. 2). Other group 4 metalloccene dichlorides with a phosphorus-containing ansa-bridge have been reported with no mention of their use as...
Fig. 1. Choice of metallation agent, Zr(RN(CH2)3NR)Cl2(THF)2 (where R is Ph or SiMe3), and reaction solvent (Et2O or THF) allows for isolation of either meso- or rac-Me2Si(3-t-Bu-C5H3)2Zr(RN(CH2)3NR) (where R is Ph or SiMe3, respectively) [6c].

Fig. 2. Group 4 ansa-metallocene ethylene and/or propylene polymerization precatalysts incorporating a phosphine-containing interannular bridge: [PhP(C5Me4)2]MX2 (where M = Zr or Hf) [12], rac/meso-[PhP(2-Me-4-Ph-indenyl)]ZrCl2, rac/meso-[t-PrP(2-Me-4-Ph-indenyl)]2ZrCl2 [14], [t-BuP(2-indenyl)]2ZrCl2 [13], rac-PPh(indenyl)2ZrCl2, PhP[(fluorenyl)(Cp)]ZrCl2 [14], and PhP(fluorenyl)2ZrCl2 [11,14].

Fig. 3. Meso/rac isomer pairs of bis(phosphoryl)zirconocenes described by Hollis [22] and Fu [23], titanocenes described by Hollis [22], hafnocenes described by Fu [23], and bis(phosphino-η1-indenyl)iron(II) complexes described by Curnow [24].

polyolefin precatalysts, including [PhP(fluorenyl)]2HfCl2 [11], [Ph(E)P(C5Me4)]2MX2 (where M = Zr or Hf; E = O, S, or Se) [12], [PhP(2-indenyl)]2ZrCl2 [13], [PhP(C5Me4)2]TiCl4 [15], [RP(C5H4)2]2ZrCl2 (where R = Me, Et, i-Pr, or t-Bu) [16], [PhP(C5Me4)2]ZrCl2 [17], [(Me2P(C5Me4)2)]MCl2 (where M = Zr or Hf) [18], and rac/meso-[R7P(2-Me-4-t-Bu-C5H4)2]ZrCl2 (where R = Me or n-Bu) [19]. Also, phosphorus has been used as a component of multi-atom interannular bridges for ansa-zirconocenes, such as [(Me2P(C5H4))(Cl2B(C5H4))]ZrCl2, [(EtP(2-Me-indenyl)][Cl2B(2-methylindenyl)])ZrCl2 [20], and [PhP(CH2CH2-η5-C5H4Me3)2]ZrCl2 [21].

We were drawn to the phosphine interannular linker due to its pyramidal nature and ability to enforce two different steric environments at the rear of the metallocene wedge. This feeds into one long-term goal of our research program; namely, the design and testing of complexes to probe the steric requirements for regiocontrol in α-olefin polymerization. It follows that the ability to isolate a single diastereomeric zirconocane (rac or meso) is critical for meaningful polymerization trials in this vein.

The inclusion of phosphorus in our ligand array introduces the potential for phosphorus-mediated meso- to rac-isomerization in addition to the possibility of chloride catalyzed rac/meso isomerization as described by Jordan (vide supra) [6f]. Hollis [22] and Fu [23] have implicated the role of phosphorus in a ring slip-inversion-ring slip mechanism of isomerization for bis(phosphoryl)tinanium, zirconium and hafnium(IV) complexes (Fig. 3). Curnow [24] proposes the following stepwise mechanism for rac/meso isomerization of bis(phosphino-η1-indenyl)iron(II) complexes (Fig. 3): tetrahydrofuran-assisted indenyl ring slip, phosphorus coordination, indenide dissociation, indenide recoordination, phosphorus decoordination, and ring slip. Herein, we will describe the synthesis and characterization of rac/meso-PPh(3-t-Bu-C5H3)2-Zr[RN(CH2)3NR] (where R = SiMe3 or Ph) and will present our observations of meso to rac isomerization in these systems. Pure rac-PPh(3-t-Bu-C5H3)2Zr[RN(CH2)3NR] (where R = SiMe3 or Ph) can be isolated (either via controlled isomerization or preferential crystallization); these complexes will be employed in future work directed towards α-olefin polymerization.

2. Results and discussion

Synthesis of our target ligand, K2[PhP(3-t-Bu-C5H3)2] · 1.3 THF (2), was achieved via standard methods as described in Scheme 1. Treatment of a solution of Li(3-t-Bu-C5H3)2 (tetrahydrofuran/pentane, 3:1, v/v) with a tetrahydrofuran solution of dichlorophosphine provided neutral compound, PhP(3-t-Bu-C5H3)2 (1) as a mixture of double bond isomers [25]. Characterization via multinuclear NMR spectroscopy (1H, 13C, and 31P) verified the presence of these isomers; due to overlapping NMR signals throughout all three spectra, individual isomer identities were not assigned. Compound 1 can be doubly deprotonated by addition of 2 equiv. of either potassium bis(trimethylsilyl)amide or potassium tert-butox-
ide to yield K$_2$[PhP(3-t-Bu-C$_5$H$_3$)$_2$]. 1.3 THF (2) as a white powder. We found preparation and isolation of a dipotassio salt preferable to a dilithio salt due to persistent impurities observed upon isolation of the dilithio salt; the analogous preparation of a disodium salt was not attempted. $^1$H NMR analysis of 2 reveals the presence of nonstoichiometric protio THF (1.3 equiv.); poor solubility of 2 in THF has precluded preparative scale recrystallizations for elemental analysis purposes.

Preparative scale metallation of K$_2$[PhP(3-t-Bu-C$_5$H$_3$)$_2$]. 1.3 THF (2) with Zr[Me$_3$SiN(CH$_2$)$_3$NSiMe$_3$]Cl$_2$(THF)$_2$ in tetrahydrofuran solvent over the course of 28 h provides both rac- and meso-PhP(3-t-Bu-C$_5$H$_3$)$_2$Zr[Me$_3$SiN(CH$_2$)$_3$NSiMe$_3$] (rac-3/meso-3) as a pale yellow microcrystalline solid in a 2:1 isomeric ratio (Eq. (1)). The pyramidal geometry at phosphorus is evidenced by the number of nonstoichiometric protio THF (1.3 equiv.); poor solubility of 2 in THF has precluded preparative scale recrystallizations for elemental analysis purposes.

**Scheme 1.** Reagents and conditions: (i) chlorodiphenylphosphine, THF/pentane, –78 °C → 22 °C, 18 h; (ii) 2 equiv. potassium tert-butoxide, THF, 0 °C → 22 °C, 72 h.

Preparative scale metallation of K$_2$[PhP(3-t-Bu-C$_5$H$_3$)$_2$]. 1.3 THF (2) with Zr[Me$_3$SiN(CH$_2$)$_3$NSiMe$_3$]Cl$_2$(THF)$_2$ in tetrahydrofuran solvent over the course of 28 h provides both rac- and meso-PhP(3-t-Bu-C$_5$H$_3$)$_2$Zr[Me$_3$SiN(CH$_2$)$_3$NSiMe$_3$] (rac-3/meso-3) as a pale yellow microcrystalline solid in a 2:1 isomeric ratio (Eq. (1)). The pyramidal geometry at phosphorus is evidenced by the number of nonstoichiometric protio THF (1.3 equiv.); poor solubility of 2 in THF has precluded preparative scale recrystallizations for elemental analysis purposes.

Preparative scale metallation of K$_2$[PhP(3-t-Bu-C$_5$H$_3$)$_2$]. 1.3 THF (2) with Zr[Me$_3$SiN(CH$_2$)$_3$NSiMe$_3$]Cl$_2$(THF)$_2$ in tetrahydrofuran solvent over the course of 28 h provides both rac- and meso-PhP(3-t-Bu-C$_5$H$_3$)$_2$Zr[Me$_3$SiN(CH$_2$)$_3$NSiMe$_3$] (rac-3/meso-3) as a pale yellow microcrystalline solid in a 2:1 isomeric ratio (Eq. (1)). The pyramidal geometry at phosphorus is evidenced by the number of nonstoichiometric protio THF (1.3 equiv.); poor solubility of 2 in THF has precluded preparative scale recrystallizations for elemental analysis purposes.

Preparative scale metallation of K$_2$[PhP(3-t-Bu-C$_5$H$_3$)$_2$]. 1.3 THF (2) with Zr[Me$_3$SiN(CH$_2$)$_3$NSiMe$_3$]Cl$_2$(THF)$_2$ in tetrahydrofuran solvent over the course of 28 h provides both rac- and meso-PhP(3-t-Bu-C$_5$H$_3$)$_2$Zr[Me$_3$SiN(CH$_2$)$_3$NSiMe$_3$] (rac-3/meso-3) as a pale yellow microcrystalline solid in a 2:1 isomeric ratio (Eq. (1)). The pyramidal geometry at phosphorus is evidenced by the number of nonstoichiometric protio THF (1.3 equiv.); poor solubility of 2 in THF has precluded preparative scale recrystallizations for elemental analysis purposes.

Preparative scale metallation of K$_2$[PhP(3-t-Bu-C$_5$H$_3$)$_2$]. 1.3 THF (2) with Zr[Me$_3$SiN(CH$_2$)$_3$NSiMe$_3$]Cl$_2$(THF)$_2$ in tetrahydrofuran solvent over the course of 28 h provides both rac- and meso-PhP(3-t-Bu-C$_5$H$_3$)$_2$Zr[Me$_3$SiN(CH$_2$)$_3$NSiMe$_3$] (rac-3/meso-3) as a pale yellow microcrystalline solid in a 2:1 isomeric ratio (Eq. (1)). The pyramidal geometry at phosphorus is evidenced by the number of nonstoichiometric protio THF (1.3 equiv.); poor solubility of 2 in THF has precluded preparative scale recrystallizations for elemental analysis purposes.
The data from a representative reaction trial (with excess $\text{Zr}\{\text{Me}_3\text{SiN(CH}_2)_3\text{NSiMe}_3\}\text{Cl}_2(\text{THF})_2$ present) is given in Fig. 6. To further probe the role of phosphine in the isomerization mechanism, triphenylphosphine (1 equiv.) was added to one of our metallation trials. However, triphenylphosphine thwarts the desired metallation reaction; rac-3 and meso-3 were not observed.

The metallation described in Eq. (1) was also tracked at low temperature (−30°C) in tetrahydrofuran-$d_8$ solvent. Immediately, upon thawing a frozen sample of 2 and $\text{Zr}\{\text{Me}_3\text{SiN(CH}_2)_3\text{NSiMe}_3\}\text{Cl}_2(\text{THF})_2$ in tetrahydrofuran-$d_8$ solvent, new signals appear in both the $^1$H and $^{31}$P NMR spectra corresponding to unidentified intermediate(s) (the number and chemical shift range of the $^{31}$P signals suggest the intermediate(s) have structural similarity to 1), and after 45 min at −30°C, broad signals appear for rac-3 and meso-3 (in an approximate 3:2 ratio). Upon warming to 0°C, these signals continue to slowly increase in intensity; further warming to 25°C leads to complete consumption of starting materials while maintaining the initially observed rac/meso isomer ratio. Over the course of days at 22°C, the amount of rac isomer increases at the expense of meso isomer.

We decided to test whether or not the $\text{Zr}\{\text{PhN(CH}_2)_3\text{NPh}\}\text{Cl}_2(\text{THF})_2$/diethyl ether combination would allow for the preparative scale isolation of pure meso-4 (Eq. (2)). Metallation of $\text{K}_2[\text{PhP(3-t-Bu-C}_5\text{H}_3)_2]:1.3\text{ THF}$ (2) with $\text{Zr}\{\text{PhN(CH}_2)_3\text{NPh}\}\text{Cl}_2(\text{THF})_2$ in diethyl ether at 0°C over the course of 2 hours provides both rac- and meso-$\text{PhP(3-t-Bu-C}_5\text{H}_3)_2\text{Zr}[\text{PhN(CH}_2)_3\text{NPh}]$ (rac-4/meso-4) as an orange-red microcrystalline solid in a 0.36:1.0 isomeric ratio (Eq. (2)). Again, the pyramidal geometry at phosphorus is evidenced by the number of inequivalent $^1$H NMR resonances in this rac/meso mixture; COSY and HETCOR methods were used to assist with NMR peak assign-
also detected with a $^{31}$P NMR chemical shift of $\text{Zr}\{\text{Me}_3\text{SiN(CH}_2)_3\text{NSiMe}_3\}\text{Cl}_2(\text{THF})_2$ (time = 0) and subsequent conversion of the upper curve); $\text{[Ph(O)P(C}_5\text{Me}_4)_2\]ZrCl}_2$ has a $^{31}$P NMR signal at +17.9 ppm in benzene-

tents. The deshielded $^{31}$P NMR chemical shifts for $\text{meso-4}$ and $\text{rac-4}$ (-38.7 (meso) and -35.8 (rac) in benzene-$d_6$ solvent) are similar to those reported for $\text{meso-3}$/$\text{rac-3}$. Another species was also detected with a $^{31}$P NMR chemical shift of -24.6 ppm, a single $t$-butyl methyl $^1$H NMR signal, and another $^1$H NMR signals that overlap with those of $\text{meso-4}$/rac-4. The chemical shift difference of this species relative to $\text{rac-4}$/meso-4 is not pronounced enough to suggest oxidation of the phosphine linker (for example, $\text{[Ph(O)P(C}_5\text{Me}_4)_2\]ZrCl}_2$ has a $^{31}$P NMR signal at +17.9 ppm in benzene-$d_6$ solvent [12]). It is conceivable that this species is the other potential meso isomer of 4, with the phosphorus-phenyl substituent on the same side of the zirconocene as the $t$-butyl substituents (not pictured in Eq. (2)), though our experiments to date have not allowed us to obtain samples sufficiently enriched in this species to carry out complete NMR characterization.

Similar to the $\text{rac-3}$/meso-3 mixture, the rac isomer preferentially crystallizes from solutions of $\text{rac-4}$/meso-4 in various solvents. A concentrated benzene-$d_6$ solution was prepared using a recrystallized sample of $\text{rac-4}$/meso-4 (1.0:0.1 isometric ratio). Upon standing for 5 weeks at 22 °C, single crystals suitable for X-ray diffraction were obtained (Fig. 7).

One unusual feature of this structure is that the $\{\text{PhN(CH}_2)_3\text{NPh}\}$ chelate adopts a conformation intermediate between the idealized twist and envelope forms. Ref. [6e] reports the following trends in displacement of atoms from the N(1)–Zr–N(2) plane for idealized twist and envelope conformers of the $\{\text{PhN(CH}_2)_3\text{NPh}\}$ chelate: twist (+, +, 0, -, +) and envelope (-, +, 0, 0, 0), (where + is above; 0 is in; - is below the N(1)–Zr–N(2) plane). The displacement of atoms in our system (-, -, +, +, +) is intermediate between these two idealized conformers, with the following deviations in Å of C atoms from the N(1)–Zr–N(2) plane: C(34) –0.43, C(27) –0.41, C(26) +0.51, C(25) –0.94, C(28) +0.78. Similar to $\text{rac-3}$, the cyclopentadienyl rings of $\text{rac-4}$ tend towards $\eta^-$-coordination, evidenced by the 2.4958–2.7317 Å range of Zr–C(cyclopentadienyl) bond lengths. The centroid–Zr–centroid angle ($\gamma$ = 120.6°), interplanar ring angle ($\phi$ = 70.5°), Cp(normal)–Cp(normal) dihedral angle ($\beta$ = 109.5°), and tilt angle ($\tau$ = 5.6°) for $\text{rac-4}$ have less tendency towards the characteristic angles of a doubly-linked zirconocene as compared to those for $\text{rac-3}$. However, the N(1)–Zr–N(2) angle of 89.45(6)° is small in comparison to that of $\text{rac-3}$ (93.95(9)°), $\text{meso-Me}_3\text{Si(3-}$-$\text{Bu-C}_5\text{H}_3)\text{Zr[PhN(CH}_2)_3\text{NPh}\}$ (95.34(10)°) [6c] and $\text{rac-Me}_3\text{Si[3-}$-$\text{Bu-C}_5\text{H}_3\]Zr[Me$_2$Si(CH$_2$)$_3$NSiMe$_3$] (92.63(8)°) [6c].

We followed the course of this metallation reaction at low temperature (0 °C) using $^{31}$P NMR spectroscopy (with an unlocked Bu$_4$NCl immediately converts the sample to 100% $\text{rac-3}$/THF-$d_8$) in diethyl ether solvent. All of these experiments were carried out in the dark to rule out the possibility of photochemically promoted isomerization. In each case, the $\text{rac}$/meso ratio was monitored using $^{31}$P NMR spectroscopy, with frequent data sampling for the first 12 h, and daily monitoring until an equilibrium state was reached.

As described in Fig. 8, the $\text{rac-3}$/meso-3 ratio was monitored with no additive, with 2 equiv. KCl, and with 2 equiv. Bu$_4$NCl additive present. While the presence of KCl causes an initial drop in the percentage of meso-3, over time the rate of decay mimics that observed in the absence of KCl. It should be noted that solid KCl is apparent at the bottom of the NMR tube both before and after NMR monitoring; we assume that the KCl is at best sparingly soluble under reaction conditions. Both samples are completely converted to 100% $\text{rac-3}$ over the course of 2 d at 60 °C. In contrast, addition of Bu$_4$NCl immediately converts the sample to 100% $\text{rac-3}$. Also, a color change is immediately observed in the presence of Bu$_4$NCl (yellow → orange solution). We invoke solubility and ion pairing effects to account for the differing kinetics of rac to meso isomerization in the presence of KCl and Bu$_4$NCl.
In contrast, addition of KCl immediately converts the sample to a 1.0:0.16 ratio of meso to rac isomerization in THF-C4 (orange-red solution). This appears to be the equilibrium ratio. A subtle color change is immediately observed in the presence of KCl (sparingly soluble); run ii (squares), 2 equiv. KCl (sparingly soluble); run iii (triangles), 2 equiv. nBu4NCl.

Similar experiments using rac-meso are depicted in Fig. 9. In this case, the meso isomer is the major isomer at the start of the experiments (1.0:0.24 meso-rac). Here we observed similar behavior in the both the presence and absence of KCl with negligible isomerization over the course of 12 h at 60 °C. In fact, a full week at 60 °C is required to obtain a 1.0:1.0 ratio of rac-meso. In contrast, addition of nBu4NCl immediately converts the sample to a 1.0:0.16 ratio of rac-meso, and this ratio is maintained over the course of days at 60 °C. This appears to be the equilibrium ratio. A plot of [−ln((Xrac − Xmeso)/(Xmeso − Xrac))] versus time (in s), where X is the mole fraction of meso isomer, affords kobs from the slope. The kobs value for meso to rac isomerization (kobs = 1.2 × 10^{-6} s^{-1}) is more than 15 fold smaller than that for meso to rac isomerization (kobs = 2.0 × 10^{-5} s^{-1}). Both of these kobs values are small in comparison to those reported by Hollis [22], Fu [23], and Curnow [24] for other metallocenes that incorporate phosphorus in their ligand arrays, albeit not as a component of an interannular linker. Indeed, the kobs value for meso to rac isomerization in THF-C4 at 60 °C has the same order of magnitude as Curnow’s kobs value (1.59(3) × 10^{-5} s^{-1}) for meso to rac isomerization of bis[1-diphenylphosphino-η^3-indenyl]iron(II) in THF-C4 at 23 °C [24b].

A priori, we expected chloride catalyzed rac to meso isomerization to occur for our rac/meso-3 and rac/meso-4 mixtures, as described by Jordan for related dimethylsilyl linked zirconocenes [6f]. Therefore, in the presence of chloride additive, we postulate that one operating mechanism for equilibration of our rac/meso mixtures involves displacement of one cyclopentadienyl ligand by chloride, P–C bond rotation, chloride loss, and cyclopentadienyl ligand recoordination, analogous to Jordan’s proposed mechanism (Scheme 2, where Nu is chloride). However, the fact that we observe rac to meso isomerization in the absence of an additive raises the possibility of a second potential mechanism. We propose another nucleophile catalyzed mechanism, with the phosphine interannular linker acting as a nucleophile instead of chloride. Specifically, this second mechanism involves intramolecular displacement of one cyclopentadienyl ligand by the phosphine interannular linker (along with coordination of tetrahydrofuran solvent), P–C bond rotation, phosphine and tetrahydrofuran loss, followed by cyclopentadienyl ligand recoordination (Scheme 2). We suggest that the second cyclopentadienyl ligand may undergo a ring slip (η^3 → η^1) to put the phosphine interannular linker in a more appropriate location (relative to zirconium) for intramolecular coordination. However, we realize it is difficult to rule out isomerization catalyzed by a negligible amount of adventitious chloride or water (a potential source of hydroxide) in our solutions of rac/meso-3 and rac/meso-4.

Regardless of the operating mechanism(s) of isomerization, the ability to isolate pure rac-3 and pure rac-4 via controlled isomerization of rac/meso mixtures (with no additive required) is valuable for our proposed future work in the realm of α-olefin polymerization (vide supra).

3. Summary

The syntheses of rac/meso-[PhP(3-t-Bu-C5H4)2]ZrSiMe3N-(CH2)3NSiMe3] (rac/meso-3, 2:1 ratio) and rac/meso-[PhP(3-t-Bu-C5H4)2]Zr(PhN(CH2)3NPh) (rac/meso-4, 0.36:1.0 ratio) underscore the influence of the interannular linker in the course of metallaclation when Jordan’s Zr[RN(CH2)5NR]Cl2(THF)2 (where R = SiMe3 or Ph, respectively) is used as a metallaclation agent. Both rac-3 and rac-4 display tendencies towards η^1-coordination of their cyclopentadienyl rings, as evidenced by X-ray crystallography. Since mixtures of rac/meso-3 and rac/meso-4 equilibrate both in the presence and absence of chloride additive, we suggest a general isomerization mechanism involving nucleophile catalyzed displacement of one cyclopentadienyl ligand (where Nu is chloride or the phosphine interannular linker). The ability to carry out controlled isomerization of rac/meso mixtures of 3 and 4 in the absence of additive is synthetically useful, irrespective of mechanism. Conversions of pure rac-3 and rac-4 to the corresponding zirconocene dichloride precatalyst and subsequent α-olefin polymerization studies are underway and will be reported in due course.

4. Experimental

4.1. General considerations

All chemical reactions were carried out under an atmosphere of argon using standard Schlenk techniques [28] unless otherwise noted. Argon gas was purified by passage over Drierite®. All chemicals were purchased from Aldrich and used as received unless otherwise noted. Dichlorophosphine was purchased from Strem. ZrCl3(THF)2[PhN(CH2)3NPh] [6b,6c,29], ZrCl3(THF)2[Me3...
Si(N(CH2)3NSiMe3) [30], and Li(t-Bu-C5H4) [27] were prepared according to literature methods. Benzene-d6 and tetrahydrofuran-d8 were purchased from Cambridge Isotope Laboratories and dried over molecular sieves (8–12 mesh, 4 Å, activated) before use. MBraun Manual Solvent Purification System (MB-SPS) was used to obtain the following anhydrous solvents: toluene, tetrahydrofuran, diethyl ether, pentane, and dichloromethane; solvents were submitted to three freeze-pump-thaw cycles before use [31]. Benzene was dried over sodium/benzophenone ketyl and stored under vacuum. Molecular sieves (8–12 Mesh, 4 Å) were purchased from J.T. Baker and activated before use. Potassium tert-butoxide was purchased from Aldrich and sublimed before use.

NMR spectra were recorded on a Varian Mercury spectrometer at 300 MHz (1H), 75 MHz (13C), and 121 MHz (31P) at 298 K. 1H and 13C chemical shifts are referenced relative to the NMR solvent (residual protio solvent peak(s)); 31P chemical shifts are referenced relative to phosphoric acid and triphenylphosphine oxide. The following abbreviations are used for NMR splitting patterns: pt (pseudo triplet) and br s (broad singlet).

Elemental analyses were performed at Atlantic Microlab, Inc. in Norcross, Georgia.

4.2. Preparation of PhP(3-t-Bu-C5H4)2 (1)

A 100-mL Schlenk flask was charged with Li(t-Bu-C5H4) (3.01 g, 23.5 mmol, 2.0 equiv.), tetrahydrofuran (20 mL), and pentane (7 mL). A 50-mL Schlenk flask was charged with PhPCl2 (1.60 mL, 11.8 mmol, 1.0 equiv.) and tetrahydrofuran (7 mL). The Li(t-Bu-C5H4) solution was cooled to −78 °C, followed by dropwise addition of the PhPCl2 solution via cannula transfer. The dry ice/acetone bath was left intact to allow the reaction mixture to slowly warm to 22 °C over the course of 18 h. Solvent was removed in vacuo and pentane (30 mL) was added inside the glove box to provide an orange-brown slurry. Vacuum filtration and pentane washes (5 × 8 mL) provided a brown filtrate, which was concentrated in vacuo to yield 1 as a light brown oil (3.73 g, 90.2% yield).

1H NMR (benzene-d6, 22 °C): δ 7.45–7.68 (m, C6H5), 6.98–7.14 (m, C6H5), 6.70 (m, C5H4), 6.31–6.39 (m, C5H4), 6.05 (m, C5H4), 5.99 (m, C5H4), 4.02 (m, allylic C5H4), 3.11 (m, allylic C5H4), 3.07 (br s, allylic C5H4), 3.06 (m, allylic C5H4), 3.01 (m, allylic C5H4), 2.98 (m, allylic C5H4), 2.78 (m, allylic C5H4), 1.09 (s, C(CH3)), 1.08 (s, C(CH3)), 1.07 (s, C(CH3)), 1.06 (s, C(CH3)), 1.04 (s, C(CH3)), 0.99 (s, C(CH3)), 0.98 (s, C(CH3)), 0.97 (s, C(CH3)), 0.96 (s, C(CH3)). 13C{1H} NMR (benzene-d6, 22 °C): δ 141.5–143.1, 132.8–133.6, 124.8–125.2, 44.1–44.3, 43.4–43.8, 41.8–42.0, 33.7, 32.4, 31.2, 31.1, 30.1. 31P{1H} NMR (benzene-d6, 22 °C): δ −18.7, −18.8, −19.1, −29.1, −29.2, −30.5, −30.6 (relative integrations for these peaks: 0.18, 0.08, 0.08, 1.00, 0.24, and 0.27, respectively).

4.3. Preparation of K2{PhP(3-t-Bu-C5H4)2} (2)

A 100-mL Schlenk flask was charged with PhP(3-t-Bu-C5H4)2 (3.73 g, 10.6 mmol, 1.0 equiv.) and tetrahydrofuran (25 mL), then cooled to 0 °C with stirring. In a separate Schlenk flask, potassium tert-butoxide (2.58 g, 23.0 mmol, 2.16 equiv.) was dissolved in tetrahydrofuran (15 mL), followed by dropwise transfer of this solution to the PhP(3-t-Bu-C5H4)2 solution, with stirring at 0 °C. The 0 °C ice-water bath was left intact to slowly warm to 22 °C; After 30 min of stirring at 0 °C, precipitate began to form, yielding a pale peach-colored slurry. After 72 h of stirring, the reaction mixture
was concentrated to dryness, followed by continued drying in vacuo
with heating to 50 °C for 3.5 h to remove residual solvent and
tert-butanol byproduct. Inside the glove box, tetrahydrofuran
(75 mL) was added to provide a pale peach-colored slurry. This
slurry was transferred to a jar and cooled to −35 °C for 1 week.
At this point, a white solid and red colored supernatant were pres-
ent. Vacuum filtration yielded a white solid, which was transferred
to a pear-shaped flask for drying in vacuo for 1 h. Compound 2 was
isolated as a white powder (4.27 g, 70.1% yield). \(^1\)H NMR analysis
revealed the presence of nonstoichiometric proto THF (1.3 equiv.);
this residual solvent was taken into account for percent yield cal-
culations. Satisfactory elemental analysis data has not been
obtained to date; poor solubility in THF has precluded preparative
scale recrystallizations for elemental analysis purposes. \(^1\)H NMR
(THF-d$_2$, 22 °C): δ 7.80 (pt, J = 6.8 Hz, 2H, ortho-C$_{H_2}$), 7.07 (pt,
J = 7.4 Hz, 2H, meta-C$_{H_2}$), 6.91 (pt, J = 6.9 Hz, 1H, para-C$_{H_2}$), 5.81
(br s, 4H, two overlapping signals, C$_{H_3}$), 5.57 (br s, 2H, C$_{H_2}$),
3.62 (t, C$_{H_2}$O), 1.78 (t, C$_{H_2}$O), 1.15 (s, 18H, C(CH$_3$)$_3$).

\(^{13}\)C{\(^1\)H} NMR (THF-d$_2$, 22 °C): δ 132.2 (J = 14.9 Hz, ortho-C$_{H_2}$),
126.8 (meta-C$_{H_2}$), 123.8 (para-C$_{H_2}$), 111.9 (J = 21.2 Hz, C$_{H_2}$),
108.3 (J = 23.5 Hz, C$_{H_2}$), 103.2 (J = 8.5 Hz, C$_{H_2}$), 67.3 (C$_{H_2}$O),
33.9 (C(CH$_3$)$_3$), four ipso carbon resonances not detected due to
poor solubility of 2. \(^{13}\)C{\(^1\)H} NMR (THF-d$_2$, 22 °C): δ −31.1.

4.4. Preparation of rac-meso-{PhP(3-t-Bu-
C$_{H_2}$)$_2$Zr(Me$_2$Si(CH$_3$)$_2$NSiMe$_3$) (rac-3/meso-3)

A 250-mL Schlenk flask was charged with K$_2$[PhP(3-t-Bu-
C$_{H_2}$)$_2$Zr], 1.3 THF (1.00 g, 1.93 mmol, 1.0 equiv.)
and ZrCl$_2$(THF)$_2$[Me$_2$Si(CH$_3$)$_2$NSiMe$_3$] (0.87 g, 1.93 mmol, 1.0 equiv.),
degassed, and cooled to −78 °C. Tetrahydrofuran (50 mL) was
added by vacuum transfer, yielding a pale yellow slurry. The
−78 °C dry ice/acetone bath was replaced by a 0 °C ice-water bath,
and the reaction mixture was allowed to slowly warm to 22 °C.
Upon warming, the reaction mixture took on a lemon-yellow color
and opaque appearance. After 27.5 h, the reaction mixture was
denatured to dryness, and then dried in vacuo for an additional
1.5 h. Inside the glove box, pentane (40 mL) was added and the
product mixture left to stir for 1 h. The product mixture was sub-
jected to vacuum filtration to yield a yellow filtrate. The filtrate
was then passed through a pad of celite, and finally though a dis-
posable pipet containing a Kimwipe plug. The resulting yellow fil-
trate was transferred to a jar and cooled to −37 °C
H$_2$, 7.18 (m, 2H, H$_2$), 6.98 (t, J = 6 Hz, 1H, H$_2$), 6.28 (t, J = 3 Hz, 1H, H$_2$),
5.62 (dt, J = 3 Hz, 3H, H$_2$), 6.42 (dt, J = 3 Hz, 3H, H$_2$), 6.31 (dt, J = 3 Hz, 3H, H$_2$), 5.87 (dt,
J = 3 Hz, 3H, H$_2$), 5.84 (dt, J = 3 Hz, 3H, H$_2$), 3.35 (dd, J = 15.7 Hz, 4.5 Hz, 1H, NC$_H$N),
3.23 (dd, J = 15.1 Hz, 4.9 Hz, 1H, NC$_H$N), 3.03 (dd, J = 15.7 Hz, 10.6 Hz, 4.8 Hz, 1H, NC$_H$N),
2.94 (ddd, J = 15.1 Hz, 10.9 Hz, 5.4 Hz, 1H, NC$_H$N), 1.21 (s, 9H, top ring C(CH$_3$)$_3$), 1.05 (s, 9H,
bottom ring C(CH$_3$)$_3$), 1.03 (m, 1H, NC$_H$NC$_H$NCH$_2$$_2$), 0.94 (m, 1H, NC$_H$NC$_H$NCH$_2$$_2$), 0.26 (s,
9H, bottom ring Si(CH$_3$)$_3$), 0.07 (s, 9H, bottom ring Si(CH$_3$)$_3$).

Note: NC$_H$N resonances at 3.35 ppm and 3.03 ppm are on the same car-
bon; NC$_H$N resonances at 2.32 ppm and 2.94 ppm are on the same car-
bons. \(^1\)H NMR (THF-d$_2$, 22 °C): δ 7.68 (pt, J = 6.8 Hz, 2H, H$_2$), 7.40
(pt, J = 6.8 Hz, 2H, H$_2$), 7.32 (m, 1H, H$_2$), 6.83 (t, J = 2.6 Hz, 1H, C$_{H_2}$), 6.49 (m, 1H, C$_{H_2}$), 6.23 (m, 2H, two overlapping resonances,
Cp–H–ring E), 6.44 (d, J = 8.2 Hz, 2H, H₆–ring C), 6.30 (m, 1H, Cp–H–ring D), 6.12 (m, 1H, Cp–H–ring D), 5.91 (m, 1H, Cp–H–ring E), 5.87 (m, 1H, Cp–H–ring E), 3.26–3.60 (overlapping m, 4H, NCH₂), 1.43–1.72 (overlapping m, 2H, NCH₂CH₂), 0.97 (s, 9H, C(CH₃)₃), 0.94 (s, 9H, C(CH₃)₃). ¹³C{¹H} NMR (benzene-d₆, 22°C): δ 162.0 (ipso-amino-phenyl), 160.4 (ipso-amino-phenyl), 143.2 (ipso-Bu-Cp, J = 9.7 Hz), 138.4 (ipso-Bu-Cp, J = 6.7 Hz). ipso-phosphino-phenyl resonance not detected, 131.2 (J = 14.2 Hz, C₆–ring A), 128.9 (J = 4.4 Hz, C₅–ring A), 128.7 (C₆–ring A), 128.2 (C₅–ring A), 128.1 (C₆–ring C), 123.6 (ring D), 121.8 (C₆–ring B), 120.2 (C₅–ring B), 119.8 (C₅–ring C), 119.4 (C₅–ring C), 116.3 (J = 38.8 Hz, ring D), 114.9 (J = 38.8 Hz, ring E), 112.8 (J = 9.7 Hz, ring E), 108.4 (J = 8.5 Hz, ring D), 105.8 (J = 8.5 Hz, ring E), 105.1 (J = 19.1 Hz, ring D), 101.0 (J = 19.1 Hz, ring E), 55.6 (NCH₂), 55.0 (NCH₂), C(CH₃)₃ resonances not detected, 31.5 (C(CH₃)₃), 31.2 (C(CH₃)₃), 26.3 (NCH₂CH₂).

meso isomer: ¹¹H NMR (benzene-d₆): δ 7.72 (pt, J = 7 Hz, 2H, H₆–ring A), 7.20 (pt, J = 7 Hz, 2H, H₅–ring A), 7.0 (m, 1H, H₆–ring A), 6.4–7.8 (m, 10H, Ph(CH₂)₂NPh), 6.63 (m, 2H, Cp–H), 6.59 (d, J = 9.7 Hz, 2H, H₆–amino-phenyl), 6.59 (d, J = 9.7 Hz, 2H, H₅–amino-phenyl), 6.09 (m, 4H, Cp–H), 3.46 (t, J = 6 Hz, 2H, NCH₂CH₂), 1.58 (t, J = 5 Hz, 2H, NCH₂CH₂), 0.88 (s, 18H, C(CH₃)₃).

⁴¹Cl{¹H} NMR (benzene-d₆): δ 161.2, 144.9, 127–131 (overlapping resonances), 119.8, 113.0, 108.1, 53.9, 52.4, 33.1, 31.2, 29.1.

4.6. NMR monitoring of metallation to form rac-3/meso-3

Inside the glove box, a J. Young NMR tube was charged with ZnCl₂[TTF]₂[Me₆Si(CH₂)₃NSiMe₃] (26 mg, 57 μmol), and ferrocene (11 mg, 59 μmol). ¹¹H NMR internal standard. The upper portion (inside) of the NMR tube was wiped clean with a dry Kimwipe to remove residual solids and to allow the Telfon cap to make an air-tight seal. Using a Schlenk line, tetrahydrofuran-d₈ solvent (1.0 mL) was added via vacuum transfer at 273 K (see Section 2). The initial spectrum was recorded immediately (t = 0). Spectra were acquired every 10 min for 6 h, and then every 15 min for an additional 6 h. The NMR tube was removed from the instrument and placed in a 60°C constant temperature bath in the dark for continued heating. Subsequent spectra were acquired daily until the rac/meso equilibrium state was reached.

4.7. NMR monitoring of metallation to form rac-4/meso-4

Inside the glove box, a J. Young NMR tube was charged with ZnCl₂[TTF]₂[PhN(CH₂)₃NPh] (35 mg, 66 μmol). Using a Schlenk line, proto diethyl ether solvent (1.0 mL) was added via vacuum transfer at −196°C. While the sample was still frozen, the NMR tube was immediately inserted into a thermostated probe of a Varian Mercury 300 MHz NMR spectrometer at 333 K (see Section 2); overall, approximately 5 min elapsed between the addition of NMR solvent and insertion of the sample into the NMR probe. For ³¹P{¹H} NMR data acquisition, 128 transients were recorded for each experiment. The initial spectrum was recorded immediately (t = 0). Spectra were acquired every 10 min for 6 h, and then every 15 min for an additional 6 h. The NMR tube was removed from the instrument and placed in a 60°C constant temperature bath in the dark for continued heating. Subsequent spectra were acquired daily until rac/meso equilibrium state was reached.

4.8. NMR monitoring of isomerization in the absence or presence of salts

Inside the glove box, a small vial was charged with either meso-3/rac-3 (20 mg, 30 μmol, 0.46 (meso):1.00 (rac) ratio) or meso-4/
onto a glass fiber and cooled to the data collection temperature of 100 K. Data were collected on a Bruker-AXS Kappa APEX II CCD diffractometer with 1.54178 Å Cu Kα radiation. Unit cell parameters were obtained from 90 data frames, 0.5° φ, from three different sections of the Ewald sphere. For rac-3, the systematic absences in the diffraction data were consistent with the centrosymmetric monoclinic space group, C2/c. For rac-4, no higher symmetry than triclinic was evident from the diffraction data; solution in the centrosymmetric space group option P1 yielded chemically reasonable and computationally stable results of refinement. The data-set was treated with SADABS absorption corrections based on redundant and computationally stable results of refinement. The data-set was located in a general position yielding (for \( T_{\text{max}}/T_{\text{min}} = 1.22 \) (for rac-3) and \( T_{\text{max}}/T_{\text{min}} = 1.24 \) (for rac-4). A single molecule was located in a general position yielding \( Z = 8 \) and \( Z' = 1 \) for rac-3; \( Z = 2 \) and \( Z' = 1 \) for rac-4. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contribution. For rac-3, the largest difference peak and hole of 1.512 and –0.468 e/Å³ resulted from heavy atom noise around the zirconium atom.

**Supplementary material**

CCDC 697639 and 697640 contains the supplementary crystallographic data for rac-3 and rac-4. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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