Articles

IAN Amines: Chiral C_2-Symmetric Zirconium(IV) Complexes from Readily Modified Axially Chiral C_1-Symmetric β-Diketimines

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A general synthesis of β-diketimines derived from *I*soquinoline and *A*mino*N*aphthalene components (IAN amines) is reported. Beginning from inexpensive 2-naphthol and isoquinoline, the sequence of reactions leading to R-IAN amines is convergent, short, and high-yielding. Several new derivatives are reported (e.g., R = Bn, ^{i}Pr, ^{t}Bu, Ph, 2,6-Me_2Ph, 2,6-$^i Pr_2$Ph, 2-Np). All of these were complexed to zirconium(IV) by transamination with $Zr(NMe_2)_4$, and in all cases 1:1 R-IAN:Zr complexes immediately formed at 25 °C. Except in cases of severe steric hindrance (^{i}Pr-IAN and 2,6-Me_2Ph), the corresponding 2:1 IAN:Zr complexes formed at temperatures ranging from 25 to 100 °C in toluene. A feature conserved among all 2:1 IAN:Zr complexes was a remarkable degree of diastereoselectivity favoring a C_2-symmetric bis(β-diketiminate) isomer bearing *cis*-NMe_2 and *cis*-pyridyl ligands. Although all complexations were performed from *rac*-IAN, the resulting complexes are composed solely of homochiral ligands. The configurational integrity of Me-IAN and its ability to transfer asymmetry upon metal coordination was demonstrated in the catalyzed enantioselective addition of diethylzinc to benzaldehyde. Given the topographical similarity between these and metallocene complexes, several derivatives were preliminarily evaluated in ethylene polymerization.

Introduction

Diastereoselective complexation of a ligand to a metal is a fundamental principle of coordination chemistry, yet few control elements have been elucidated for this phenomenon. Among these, the *trans*-influence/effect is certainly the most prominent.[1] Single isomer complexes of high symmetry are most often attained either through careful synthesis of a ligand designed specifically for a 1:1 ligand:metal complex and/or by employing a ligand with a higher symmetry element in the formation of 2:1 complexes. Although the former is by far the most common, the latter approach is now accepted to be quite effective, particularly with C_2-symmetric ligands. Rarely are examples characterized in which high-symmetry coordination complexes are formed from ligands of low symmetry,[2] and there are no examples where this behavior has been generalized.

Diastereoselection in metal coordination chemistry is also a central issue to the development of new polymerization catalysts and asymmetric reaction catalysts, where it is commonly postulated that a single diastereomeric ligand−metal−substrate complex is responsible when high levels of stereoselection (diastereo- or enantioselection) are observed.[3] Yet, this assumption is confirmed experimentally only a fraction of the time.[4,5] Notwithstanding, this is a reasonable proposition when ligands of high symmetry are implemented and 1:1 ligand-to-metal complexes are created. The use of chiral C_2-symmetric ligands[6] dramatically simplifies the number of diastereomeric metal complexes that can form in a catalytic system.[7,8]

We recently became interested in the isoquinoline-derived binaphthyl ligands **1**−**5**, for which amino derivatives **1** had not been reported.[9] Naphthyl isoquinoline derivatives **2**−**5**[10,11] have attracted attention primarily as ligands for late transition metal complexes. Their value is best demonstrated by the use of Brown's P,N-ligand "Quinap" (**4**)[12] in asymmetric hydrobora-

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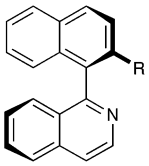
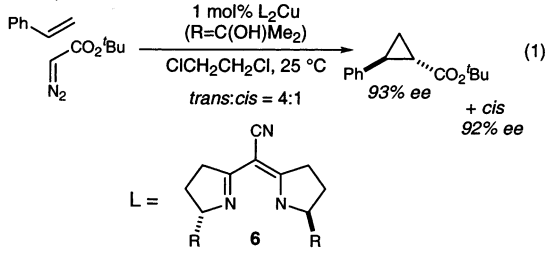


1, R = NR^1R^2 ***IAN amines***
2, R = OMe
3, R = SMe
4, R = PPh_2 ***Quinap***
5, R = CH_2OH

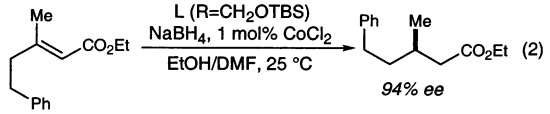
tion,[13] allylic alkylation,[14] Diels–Alder cycloaddition,[15] enolate arylation,[16] and Mannich additions.[17] In all of these examples, the 1:1 ligand–metal complexes have been the sole object of attention.

Amines **1** are bidentate *N*,*N* ligands formally of the β-diketimine class. In recent years, activity in the β-diketimine ligand area has intensified due to the search for alternatives to metallocene catalysts.[18] These studies of Group IV metal β-diketiminate complexes and their ability to polymerize α-olefins have elucidated some of the challenges that face this ligand motif.[19] Yet only one chiral, nonracemic β-diketiminate has been developed for a similarly small number of asymmetric reactions.[20] Pfaltz's seminal work demonstrated the utility of semicorrin-derived β-diketimine **6** in copper(I/II)-catalyzed cyclopropanation (eq 1)[21] and cobalt(II)-catalyzed conjugate reduction (eq 2),[22] suggesting fertile ground for future development.[23] More recently, Sibi developed the use of chiral β-bis*imidates* **7** in the enantioselective alkyl addition to enamidomalonates (eq 3).[24] Modest to high enantioselection is observed with absolute stereocontrol for either enantiomer when using homochiral ligands.

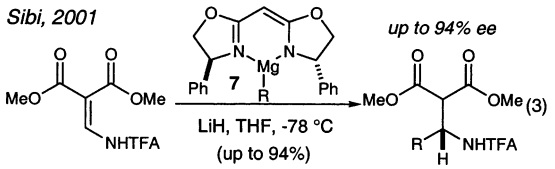
Pfaltz, 1986



Pfaltz, 1989



Sibi, 2001



The slow development of β-diketimine-based chiral reagents might be attributed to several limitations. Collins[25] and Lappert[26] noted the formation but fluxional nature (via Bailar twist) of simple 2:1 β-diketiminate:zirconium(IV) amido complexes (Figure 1). Additionally, alkyl migration to azomethine carbon (Floriani[27] and Jordan[28]) and intervention of an η^5 coordination mode have been noted.[25,29] It is significant to note that all chelate rings of β-diketimines studied prior to our work were largely planar. An emphasis has also been placed on symmetrical β-diketimines, although exceptions clearly exist (e.g. **9**). These limitations notwithstanding, the pioneering work of Smith,[30] Collins,[31] Jordan,[28] and Lappert,[26] among others,[32] has provided a basis for development of single site group IV metal catalysts supported by *achiral* β-diketimines.

Hence, we targeted ligands derived from *I*soquinoline and *A*mino*N*aphthalene (IAN amines) **1** as axially chiral

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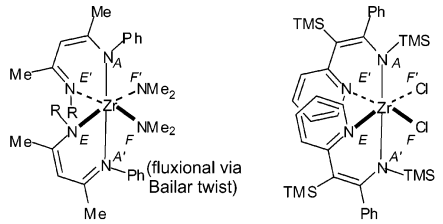


	8	9[a]
Zr-N/Cl(X) (Å)		
A/A'	2.266/2.262	2.141/2.141
E/E'	2.397/2.380	2.354
F/F'	2.078/2.074	2.434
N(A)ZrN(A')	162.9°	165.0°

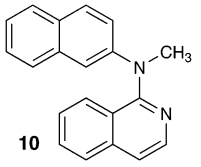
[a] Ligand is η^5-bound to zirconium (dihedral angle of N_{py}C-C-C = 125.8°).

Figure 1. Relevant 2:1 β-diketiminate zirconium(IV) complexes of Collins and Lappert.

β-diketimines that not only address these current limitations but might also provide unique stereodefined coordination complexes despite their lack of a higher symmetry element. From the outset several intriguing questions arose regarding the potential electronic dissymmetry (and therefore chelating ability) of the nitrogens due to the nonplanar biaryl rings, and the ability to modify the resulting complexes at the naphthylamine nitrogen substituent.

Results and Discussion

IAN Amine Synthesis. The utility of ligands in metal-based chemistry is often determined in part by the ease of synthesis. The IAN amine scaffold offers a convergent disconnection at the conjoining biaryl σ-bond. Furthermore, the nucleophilicity of the 2-aminonaphthalene synthon is suitably matched to the electrophilic 1-position of the isoquinoline subunit. However, a survey of conditions to activate the aniline precursor revealed that coupling via the nitrogen to deliver amidinate **10** was almost exclusively observed (Table

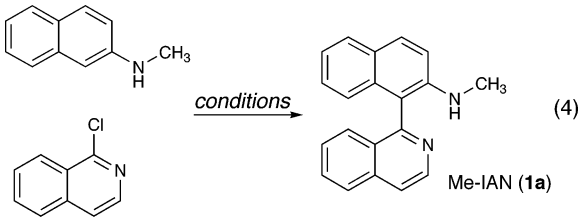


10

1). Metalated 2-(methylamino)naphthalene consistently furnished the *N*-coupled product irrespective of counterion (Table 1, entries 1 and 2). Only the bromomagnesium metalloenamine provided small amounts of the desired C−C coupling product.[33] Many Lewis acids behaved similarly, providing either **10** or starting material with a variety of promoter loadings (1−10 equiv), temperatures (25−130 °C), and solvents (THF, Et_2O, benzene, toluene, CH_2Cl_2). From these experiments, only scandium(III) triflate showed promising signs of the desired coupling (Table 1, entry 4).

Interestingly, aluminum Lewis acids were uniquely capable of effecting the coupling with formation of the

Table 1. Development of a Direct Coupling Route to IAN Amine Ligands (Eq 4)



		% yield[a]	
entry	conditions	**10**	**1a**
1	KHMDS, THF, 0−50 °C	64	0
2	LHMDS, THF, 0−50 °C	60	0
3	EtMgBr, THF, 0−70 °C	11	9
4	$Sc(OTf)_3$, C_6H_6, 80 °C	15	15
5	$EtAlCl_2$, tol, 100 °C	0	5
6	Et_2AlCl, tol, 100 °C	0	76
7	Me_3Al, tol, 100 °C	0	83

[a] Isolated yield after chromatography.

carbon−carbon bond *to the exclusion* of coupling through nitrogen (Table 1, entries 5−7). Our study included trimethylaluminum (TMA) and the mixed chloroalkylaluminum Lewis acids. TMA furnished the desired Me-IAN (**1a**) in high yield (83%) and selectivity (>95:5 **1a**:**10**), and with the lowest reaction time among any of the aluminum Lewis acids (Table 1, entry 7).

This optimized coupling protocol then became the basis for a general synthesis of the R-IAN amines studied (Table 2). Bucherer reaction of aqueous methylamine with 2-naphthol provided a convenient, scalable route to 2-(methylamino)naphthalene.[34] This approach also worked well for other derivatives. Yet the need to use an excess of the amine not only becomes wasteful but is also impractical as it necessitates removal of the amine during workup. The solution to this is the conversion of 2-naphthol to its trifluoromethane sulfonate derivative[35] and treatment with 1.5 equiv of the amine and the appropriate palladium catalyst.[36] *tert*-Butylamine was most effectively coupled by using a Buchwald protocol (Table 2, entry 4).[37] Naphthylamines **12** were then readily coupled to chloroisoquinoline[12,38] (**13**) with the assistance of trimethylaluminum. This protocol is the method of choice to access all secondary IAN amines, nearly all of which are light yellow crystalline solids (Table 2).

Me-IAN. Me-IAN (**1a**) readily crystallized from a variety of solvents. Slow diffusion involving an ethyl acetate−hexanes solvent system yielded orange crystals suitable for structural elucidation. The structure was deduced to be two independent but chemically equivalent molecules (**1a**, **1a′**) in the asymmetric unit (Figure 2), and hydrogen atoms were located.[39] Despite the fact that *rac*-Me-IAN was used in the crystallization, *these*

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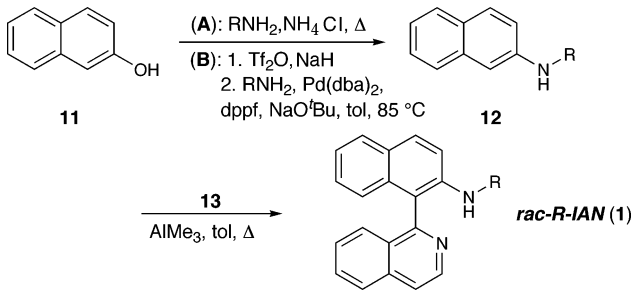
Table 2. Preparation of R-IAN Amines



		naphthylamine			coupling		
entry	R	method	product	yield[a] (%)	product	mp (°C)	yield[a] (%)
1	Me	A	**12a**	75	**1a**	159−160	83
2	Bn	A	**12b**	54	**1b**	107.5−108.5	80
3	^{i}Pr	A	**12c**	88	**1c**	oil	92
4	^{t}Bu	B[c]	**12d**	87	**1d**	oil	71
5	Ph	—[b]	**12e**	—[b]	**1e**	163−164	84
6	2,6-Me_2Ph	B	**12f**	53	**1f**	186.5−187.5	87
7	2,4,6-Me_3Ph	B	**12g**	60	**1g**	157−158	86
8	3,5-Me_2Ph	B	**12h**	61	**1h**	174.5−175.5	79
9	2,6-$^{i}Pr_2$Ph	B	**12i**	53	**1i**	171.5−172.5	52
10	2-Np	B	**12j**	65	**1j**	168−170	77

[a] Isolated yield. [b] Commercially available. [c] Formed from 2-bromonaphthalene and *tert*-butylamine, but with BINAP instead of dppf.

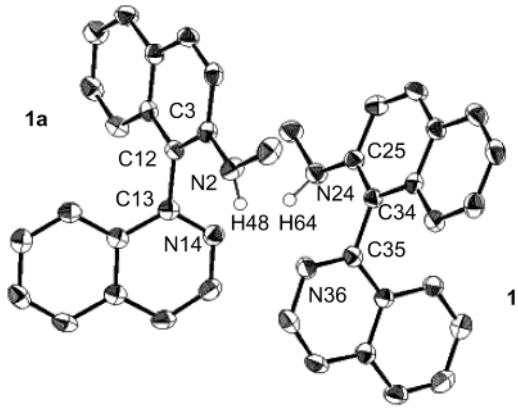


Figure 2. Two independent molecules of Me-IAN (**1a** and **1a′**) as they exist in the unit cell. The thermal ellipsoids are drawn at the 50% probability level and most hydrogen atoms are removed for clarity. See the Supporting Information for complete details.

Table 3. Selected Bond Distances and Angles for Me-IAN (1a)

distances (Å)		angles (deg)	
N(14)−H(48)	2.53(3)	N(2)−H(48)−N(14)	123.2
N(14)−H(64)	2.05(3)	N(2)−H(48)−N(36)	143.4
N(36)−H(48)	2.25(3)	N(14)−H(64)−N(24)	157.0
N(36)−H(64)	2.83(3)	N(24)−H(64)−N(36)	119.8
N(2)−H(48)	0.93(3)		
N(24)−H(64)	0.94(3)		

two forms exhibited the same absolute configuration and differed primarily by the dihedral angle between the binaphthyl ring systems (68° and 83°).

The s-cis biaryl conformation and lack of an intramolecular hydrogen bond between the amine N−H and the pyridine nitrogen are the most significant features of the solid-state structure. The intramolecular distances (for **1a**/**1a′**) between the pyridine nitrogen atom and the amine hydrogen are 2.53/2.83 Å, and the N−H−N bond angles are 123.2°/119.8° (Table 3). Intermolecular hydrogen bonding is weak but perhaps a significant effect between the two forms in the unit cell, with intermolecular N- -H−N distances and angles characterized by 2.25/2.05 Å and 143.4/157.0°, respectively.

These characteristics are rather typical of this representative IAN amine, since all solvates (CH_2Cl_2, C_6D_6) that we have isolated to-date display similar bonding constraints and features. As the remaining structural information reveals, these characteristics are also conserved upon metal coordination.[40]

(Bn-IAN)$_2$Zr(NMe$_2$)$_2$. The more sterically demanding *rac*-Bn-IAN (**1b**) was combined with $Zr(NMe_2)_4$ in a 1:1 ratio in d_8-toluene at room temperature. ^{1}H NMR analysis (Figure 3) revealed that 1:1 complex formation (**14b**; deep red color in solution) was immediate. Dimethylamine, presumably bound, is evident by a sharp resonance at δ 2.15 that is absent after vacuum removal of solvent. Also significant are upfield shifts of the isoquinoline *ortho*-CH from δ 8.71 to 8.33, as well as many of the aromatic ring hydrogens more distant from the site of coordination indicating a significant change in the binaphthyl dihedral angle.

Addition of a second equivalent of *rac*-Bn-IAN allows observation of both complexed and free ligand simultaneously without exchange by ^{1}H NMR at room temperature. It is not until the application of heat (80 °C) that formation of the (Bn-IAN)$_2$Zr(NMe$_2$)$_2$ complex (**16b**) is observed by amine metathesis.[41] Complete consumption of free ligand, concomitant with the formation of a single new product occurs after 12 h (Figure 3). Significantly, a single new complex (>15:1) is observed throughout the warming process, indicating a highly stereoselective reaction. The new species is characterized by further shifts upfield of most resonances, including the iso-

(39) In this and all subsequent crystal structures, the asymmetric unit cell is always paired with its mirror image. That is, the single crystals are (presumably) optically inactive.

(40) Cortright, S. B.; Johnston, J. N. *Angew. Chem., Int. Ed. Engl.* **2002**, *41*, 345.

(41) Diamond, G. M.; Rodewald, S.; Jordan, R. F. *Organometallics* **1995**, *14*, 5.

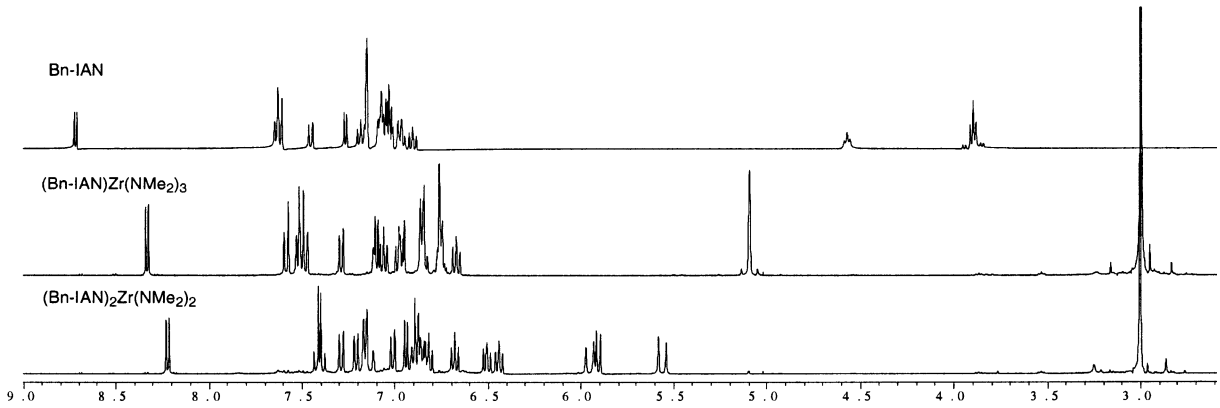


Figure 3. ^{1}H NMR (C_6D_6) of complexation of Bn-IAN (**1b**) to $Zr(NMe_2)_4$.

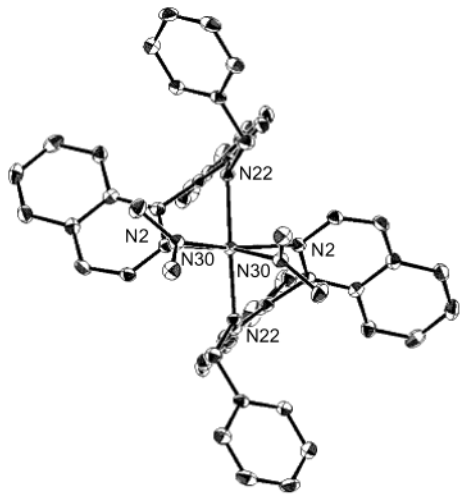
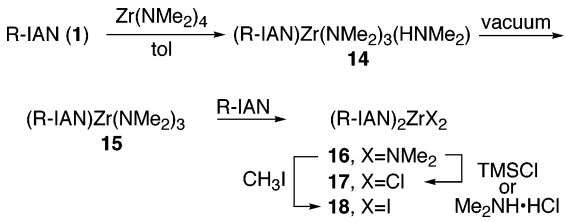


Figure 4. X-ray crystal structure of $(Bn\text{-}IAN)_2Zr(NMe_2)_2$ (**16b**). The thermal ellipsoids are drawn at the 50% probability level with hydrogen atoms removed for clarity. See the Supporting Information for complete details.

Scheme 1



quinoline *ortho*-CH from 8.33 to 8.22 ppm.[42] Whereas the degree of selectivity can be adequately ascertained by NMR spectroscopy, the preferred relative stereochemistry of the favored complex can only be deduced by using X-ray crystallography. Orange crystals of the putative 2:1 complex were obtained by slow evaporation of toluene, and the structure was solved as depicted in Figure 4.

The Bn-IAN ligands in **16b** are clearly homochiral, and the enantiomeric $(Bn\text{-}IAN)_2Zr(NMe_2)_2$ is present in the unit cell (not shown) and oriented with the binaphthyl rings of each complex pointing toward the other. The binaphthyl dihedral angle of both bound Bn-IAN ligands is 62°. This value is significantly depressed from the 68° minimum observed among the various uncomplexed forms of the ligand (*vide supra*). Yet, the angle is quite large if one considers the possibility to form a nearly planar six-membered-ring chelate.

Table 4. Selected Bond Distances and Angles for $(Bn\text{-}IAN)_2Zr(NMe_2)_2$ (16b)

distances (Å)		angles (deg)	
Zr−N(2)	2.428(3)	N(2)−Zr−N(2)	100.78(15)
Zr−N(22)	2.173(3)	N(2)−Zr−N(22)	77.12(11)
Zr−N(30)	2.083(3)	N(2)−Zr−N(22)	80.56(11)
		N(2)−Zr−N(30)	170.92(11)
		N(22)−Zr−N(22)	144.68(16)
		N(30)−Zr−N(30)	90.28(17)

The aminonaphthalene nitrogen of each ligand occupies the axial coordination site, each with a Zr−N bond distance of 2.17 Å (Table 4). This distance is only slightly longer (0.03 Å) than the analogous bond to the trimethylsilylamido ligand in **9**, but substantially shorter (0.09 Å) than the arylamido ligand in **8**. These distances are contrasted by the distance of 2.43 Å to each isoquinoline nitrogen in the square plane, which is elongated by 0.04 Å relative to **8**. Not unexpectedly, the dimethylamido nitrogens are in close range (2.08 Å) to the zirconium center within the distorted square plane. By using the isoquinoline nitrogens and zirconium to arbitrarily assign three of the five points of the square plane, the dimethylamido ligands are canted by 10°.

The aminonaphthalene nitrogen is significantly pyramidalized, with the sum of bond angles at nitrogen equalling 354°. This degree of pyramidalization is only marginally greater than that observed in $(Me\text{-}IAN)_2Zr(NMe_2)_2$ in which the sum of bond angles at the apical nitrogen equals 357°. Bonding between the isoquinoline nitrogen and zirconium is slightly compromised by distortion of the isoquinoline plane relative to zirconium. The zirconium atom formally sits 27° out of the isoquinoline plane in which the nitrogen lone pair resides. This is most likely the result of the chelating ligand's demand to optimize bonding of both nitrogens to zirconium simultaneously. This effect also seems to work synergistically with the electronic demands of the dimethylamido ligands. That is, the pyridine ligands occupy the square plane as the more appropriate weak ligand *trans* to the strongly donating dimethylamido ligands. This underscores an important feature of the IAN amine design. Unlike all other β-diketimines, including "β-anilido imines" congeners reported more recently,[43] the nonplanarity of the binaphthyl rings at-

(42) Zirconium amido complexes **14**−**18** immediately decompose to free ligand (**1**) upon contact with water.

tenuates the extent of electron delocalization when the parent amine is deprotonated. As a result, the chelating β-diketimine framework is substantially differentiated electronically and perhaps *better described as a β-amido Schiff base*. It is significant to note that the thermodynamic affinity for a proton is nearly equal for the two nitrogens when in neutral form ($5 < pK_a < 6$).[44]

(Ph-IAN)$_2$Zr(NMe$_2$)$_2$. Coupling of commercially available *N*-(2-naphthyl)aniline to chloroisoquinoline furnished Ph-IAN (**1e**) in 84% yield (Table 2, entry 5). The resulting light yellow crystalline solid was combined with Zr(NMe$_2$)$_4$ in a 1:1 ratio in d_8-toluene as before, completely producing the 1:1 complex (**14e**) and 1 equiv of dimethylamine (presumably bound) within 5 min. The dimethylamine was removed by application of a vacuum, followed by reconstitution in d_8-toluene and addition of a second equivalent of Ph-IAN. Unlike both Me-IAN and Bn-IAN complexation with zirconium(IV), the 2:1 complex (Ph-IAN)$_2$Zr(NMe$_2$)$_2$ (**16e**) did not require heating and slowly formed at room temperature over the course of 12 h. The process is complete within 6 h when the temperature is raised to 60 °C. On the basis of a reduced pK_a for the aminonaphthalene nitrogen (pK_a(Ph$_2$NH) = 25.0, DMSO)[45] and the diminished steric hindrance at a nitrogen bearing two sp^2-hybridized carbons, the faster 2:1 complex formation from Ph-IAN might not be surprising. Significantly, a single complex emerged from this reaction as the major product, consistent with the behavior of both Me- and Bn-IAN. Of all the cases examined, complexation of Ph-IAN was the only case in which formation of a second identifiable isomeric complex was observed (~15%).

Pale orange single crystals were grown from the crude reaction mixture by slow evaporation from toluene. The structure was subsequently determined by X-ray diffraction and is depicted in Figure 5. The ligands are again homochiral and arranged in identical relative fashion about the distorted octahedron of zirconium. Moreover, the 2:1 complex is C_2-symmetric as in the analogous complexes of Me- and Bn-IAN. The binaphthyl dihedral angle of the bound Ph-IAN ligand is 63°, nearly identical with that of the analogous Bn-IAN complex.

Zr−N bond distances of 2.438 and 2.458 Å (Table 5) for the isoquinoline nitrogens are also within 0.01 Å of the distance observed in the Bn-IAN complex **16b**. However, subtle elongation of the aminonaphthalene nitrogen−zirconium bonds is observed, characterized by distances of 2.190 and 2.205 Å. These distances are substantially shorter than the analogous bonds to the arylamido ligand in **8** (2.26 Å), thereby indicating localization of electrons on the naphthylamido nitrogen in **16b**. Distances of 2.081 and 2.073 Å from zirconium to the dimethylamido nitrogens are unremarkable. Consistent with observations in both (Me-IAN)$_2$Zr-

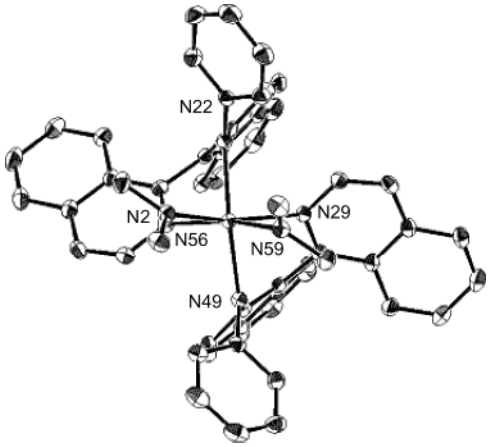


Figure 5. X-ray crystal structure of (Ph-IAN)$_2$Zr(NMe$_2$)$_2$ (**16e**). The thermal ellipsoids are drawn at the 50% probability level with hydrogen atoms removed for clarity. See the Supporting Information for complete details.

Table 5. Selected Bond Distances and Angles for (Ph-IAN)$_2$Zr(NMe$_2$)$_2$ (16e)

distances (Å)		angles (deg)	
Zr−N(2)	2.4384(23)	N(2)−Zr−N(22)	77.20(8)
Zr−N(22)	2.2049(22)	N(2)−Zr−N(29)	96.10(7)
Zr−N(29)	2.4577(22)	N(2)−Zr−N(49)	79.99(8)
Zr−N(49)	2.1903(22)	N(2)−Zr−N(59)	171.78(8)
Zr−N(56)	2.0730(23)	N(22)−Zr−N(29)	78.29(8)
Zr−N(59)	2.0809(23)	N(22)−Zr−N(49)	144.65(8)
		N(29)−Zr−N(49)	77.69(8)
		N(29)−Zr−N(56)	170.78(8)
		N(56)−Zr−N(59)	93.84(9)

(NMe$_2$)$_2$ (**16a**) and (Bn-IAN)$_2$Zr(NMe$_2$)$_2$ (**16b**), the dimethylamido ligands are canted approximately 12° out of the ideal square plane, again defined by the isoquinoline nitrogens and zirconium. The sum of bond angles at the aminonaphthalene nitrogen is now 359°, indicating all but complete planarity of this chelating atom. And again, the zirconium atom formally sits 32° above the isoquinoline plane.

(2-Np-IAN)$_2$Zr(NMe$_2$)$_2$. 2-Naphthyl-IAN (2-Np-IAN, **1j**) was made via palladium-catalyzed amination of 2-naphthol triflate with 2-aminonaphthalene (Table 2, Method B) and subsequent coupling to chloroisoquinoline (50% overall yield). The complexation behavior of 2-Np-IAN was nearly indistinguishable from that of Ph-IAN, rapidly providing the 1:1 complex (**14j**) at room temperature, followed by slower formation of the 2:1 complex (**16j**) once additional ligand had been added. Qualitatively, the rate of complexation of a second ligand equivalent was also nearly identical in rate to the Ph-IAN case. Spectroscopic features of the reaction were also similar to all ligands studied previously, forming a major diastereomer (>10:1 by ^{1}H NMR) in the crude reaction mixture, from which red single crystals were grown and analyzed by X-ray diffraction (Figure 6).

Although the inner coordination sphere is again C_2-symmetric, the orientations of the naphthyl substituents are not equivalent, rendering the overall complex pseudo-C_2-symmetric. Binaphthyl dihedral angles of 58° and 64° are observed in this homochiral complex. Isoquinoline nitrogen−zirconium bond distances of 2.434 and 2.485 Å (Table 6) are quite similar to those of the analogous Ph-IAN complex, as are the naphthylamine−zirconium distances of 2.232 and 2.192 Å. Again,

(43) (a) Weymann, C.; Danopoulos, A. A.; Wilkinson, G. *Polyhedron* **1996**, *15*, 3605. (b) Porter, R. M.; Winston, S.; Danopoulos, A. A.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **2002**, 3290. (c) Hayes, P. G.; Welch, G. C.; Emslie, D. J. H.; Noack, C. L.; Piers, W. E.; Parvez, M. *Organometallics* **2003**, *22*, 1577.

(44) pK_a values for pyridinium tosylate and dimethylanilinium tosylate are 5.21 and 5.20, respectively. March, J. *Advanced Organic Chemistry*, 3rd. ed.; Wiley: New York, 1985. Unpublished results of W. P. Jencks.

(45) Bordwell, F. G.; Branca, J. C.; Hughes, D. L.; Olmstead, W. N. *J. Org. Chem.* **1980**, *45*, 3305.

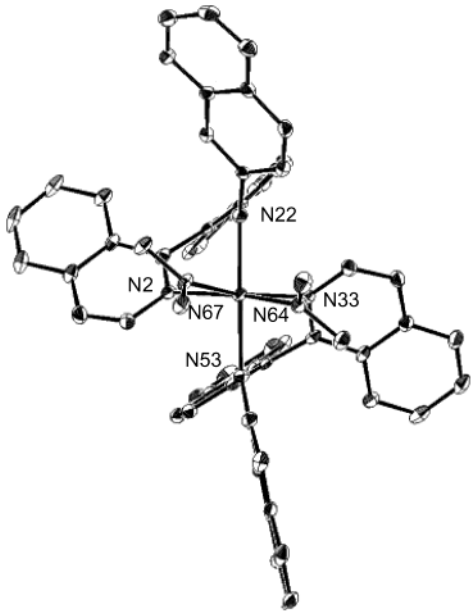


Figure 6. X-ray crystal structure of (2-Np-IAN)$_2$Zr(NMe$_2$)$_2$ (**16j**). The thermal ellipsoids are drawn at the 50% probability level with hydrogen atoms removed for clarity. See the Supporting Information for complete details.

Table 6. Selected Bond Distances and Angles for (2-Np-IAN)$_2$Zr(NMe$_2$)$_2$ (16j)

distances (Å)		angles (deg)	
Zr−N(2)	2.434(3)	N(2)−Zr−N(22)	77.02(9)
Zr−N(22)	2.192(3)	N(2)−Zr−N(33)	95.86(9)
Zr−N(33)	2.485(3)	N(2)−Zr−N(53)	81.59(9)
Zr−N(53)	2.232(2)	N(2)−Zr−N(64)	174.04(9)
Zr−N(64)	2.075(3)	N(22)−Zr−N(33)	78.59(9)
Zr−N(67)	2.086(3)	N(22)−Zr−N(53)	145.29(11)
		N(33)−Zr−N(53)	76.77(9)
		N(33)−Zr−N(67)	171.64(9)
		N(64)−Zr−N(67)	93.66(11)

distances of 2.086 and 2.075 Å from zirconium to the dimethylamido nitrogens are unremarkable. The dimethylamido ligands are canted approximately 10° out of the ideal square plane and the naphthylamine nitrogen is now completely planar. The zirconium atom resides at an angle of 22° relative to the isoquinoline plane.

A significant difference between the 2:1 complex of 2-Np-IAN and those above is the loss of ideal C_2-symmetry, at least in the solid state. The 2,2′-substitution of the naphthyl rings does not present any identifiable intermolecular steric repulsion, yet the additional fused benzene ring relative to the Ph-IAN complex carves out significantly greater coordination space near the dimethylamido ligands. In support of this notion, the naphthyl rings clearly prefer the extended conformation about the N−2′-Np σ bond. However, there is significant flexibility in this degree of conformational freedom, since the dihedral angle defined by the two naphthylamine planes varies from 70° to 87°.

(Bn-IAN)$_2$ZrI$_2$. Conversion of bis(dimethyl)amido complexes **16** to dichloride derivatives **17** normally provides a precatalyst more readily activated in single-site polymerizations. However, dichlorides **17** are only sparingly soluble in most nonpolar solvents. Therefore, diiodide derivatives **18** were targeted as potentially more soluble alternatives. Treatment of (Bn-IAN)$_2$Zr-(NMe$_2$)$_2$ (**16b**) with 2 equiv of methyl iodide in dilute benzene at room temperature resulted in complete consumption of the bis(dimethylamido) complex and precipitation of red single crystals that were subsequently examined by X-ray crystallography (Figure 7).[46]

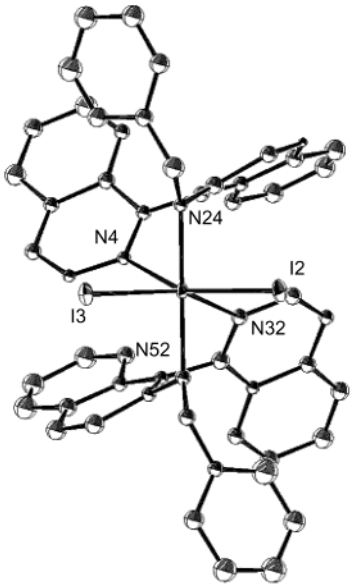


Figure 7. X-ray crystal structure of (Bn-IAN)$_2$ZrI$_2$ (**18b**). Atoms are drawn as arbitrary spheres and hydrogen atoms are removed for clarity. See the Supporting Infomation for complete details.

Table 7. Selected Bond Distances and Angles for (Bn-IAN)$_2$ZrI$_2$ (18b)

distances (Å)		angles (deg)	
Zr−N(4)	2.291(11)	N(4)−Zr−N(24)	80.1(4)
Zr−N(24)	2.094(9)	N(4)−Zr−N(32)	83.7(3)
Zr−N(32)	2.289(10)	N(4)−Zr−N(52)	115.0(3)
Zr−N(52)	2.088(9)	N(24)−Zr−N(32)	116.5(3)
Zr−I(2)	2.8864(15)	N(24)−Zr−N(52)	160.8(4)
Zr−I(3)	2.8630(17)	N(32)−Zr−N(52)	78.4(3)
		I(2)−Zr−N(32)	156.1(2)
		I(3)−Zr−N(4)	157.4(2)
		I(2)−Zr−I(3)	104.83(5)

In contrast to the conservation of most structural features when converting (Me-IAN)$_2$Zr(NMe$_2$)$_2$ (**16a**) to (Me-IAN)$_2$ZrCl$_2$ (**17a**),[40] the replacement of the dimethylamido ligands in **16b** by iodide to produce **18b** results in greater distortion of the octahedral coordination geometry. The geometry at zirconium is best described as trigonal antiprismatic.

The degree of pyramidalization at the aminonaphthalene nitrogen is identical with that of the bis(dimethylamido) derivative, and the binaphthyl dihedral angle is within the range observed for the complexes described above (63° and 59°). Hence, the distortion results from a combination of bonding changes: (a) shortening at the aminonaphthalene Zr−N bond to 2.088 and 2.094 Å (Table 7), (b) contraction at the isoquinoline Zr−N bond to 2.289 and 2.291 Å, and (c) elongation of the bonds from zirconium to the ancillary ligands (I$^-$) with distances of 2.863 and 2.886 Å. Perhaps the most important feature that can be concluded from

(46) Crystals were invariably twinned, but the Gemini programs (Bruker) readily resolved the twinning. Ligand exchange method: Johnson, A. R.; Wanandi, P. W.; Cummins, C. C.; Davis, W. M. *Organometallics* **1994**, *13*, 2907.

comparison of the bis(dimethylamido) and iodide complexes is the flexibility of the Bn-IAN ligand to geometrically and electronically accommodate a change from strong (hard) to weak (soft) ancillary ligands without affecting the overall C_2-symmetry. Unfortunately, diiodide **18b** was no more soluble than its dichloride counterpart (**17b**).

General Observations. The synthesis and coordination chemistry of IAN amines is essentially uncomplicated by the variable hapticity and azomethine reactivity noted for the β-diketimines of Floriani and Jordan. Unintended chemical modification of the β-diketimine at the β-carbon of the diketimine backbone is also notably absent. The steric demand of β-diketimines **1** is a factor distinguishing this ligand from both cyclopentadienyl and amidinate classes. It is equally straightforward to complex cyclopentadiene ligands or their isoelectronic counterparts[47] in a controlled manner to access 1:1 (half sandwich)[48] and 2:1 ligand:metal (sandwich) complexes. The amidinate literature is also replete with examples of 1:1 to even 3:1 amidinate:metal complexes,[49] again underscoring the sterically unimposing nature of these ligands.

β-Diketimines of the IAN amine class impart substantially greater steric bias that retards the rate at which a second ligand can bind. This effect is observed clearly in the alkyl-IAN series in which Me- and Bn-IAN 2:1 complexes (**16a**, **16b**) readily form, but ^{i}Pr- and ^{t}Bu-IAN provide only 1:1 complexes (**14c**, **14d**) resistant to further IAN ligand binding. Similarly, although aromatic-IANs form their respective 2:1 complexes more rapidly than the alkyl-IANs, 2,6-disubstituted aryl-IANs (**1f**, **1g**, **1i**) form only 1:1 complexes with Zr(IV). 3,5-Disubstituted aryl-IANs (e.g. **1h**) readily form 2:1 complexes (**16h**). While the steric nature of the naphthylamine nitrogen limits the formation of some 2:1 complexes, it clearly exerts a beneficial stereodifferentiation effect.

Diastereoselection. Perhaps the most notable feature of the IAN amines described here is the electronic differentiation offered by the nonplanar β-diketiminate ligand. The ramifications of this were observed in all of the solid state structures: the isoquinoline nitrogens paired consistently with dimethylamido ligands in the square plane while the naphthylamido ligands of intermediate donor ability consistently occupy apical positions. This electronic differentiation of donor ability is likely the single most important factor contributing to the high levels of stereoselection.

The stereochemical analysis for formation of 6-coordinate complexes from *rac*-C_1-symmetric R-IAN amines is decidedly more complex than most prior examples in the literature. It is therefore worthwhile to identify the design principles that underlay highly stereoselective complexations such as these to generalize this behavior. Figure 8 describes the possibilities for conversion of racemic R-IAN to complexes of the molecular formula

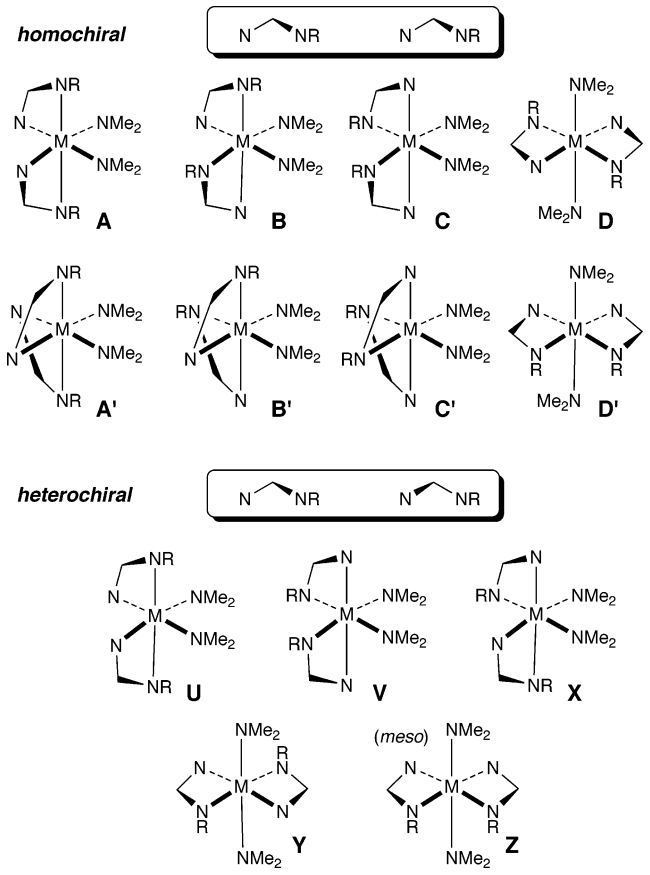


Figure 8. Possible 2:1 diastereomeric complexes formed from a Chiral C_1-symmetric ligand and octahedral coordination geometry.

$(R\text{-IAN})_2Zr(NMe_2)_2$. The use of racemic ligand results in the possible formation of eight homochiral complexes (**A**/**A**′−**D**/**D**′) and five heterochiral complexes (**U**−**Z**), with only one lacking an enantiomeric counterpart (**Z**).

The belief that these processes are kinetically controlled (and perhaps thermodynamically as well) is based on two observations. First, identical diastereocontrol is observed when complexing Me-IAN by either thermal (80 °C) amine metathesis with $Zr(NMe_2)_4$ or low-temperature (0 °C) deprotonation/addition to $ZrCl_4$.[40] Additionally, all spectroscopic data of the 2:1 complexes reported here suggest that the Bailar twist is not operable in these cases, a likely consequence of the nonplanarity of these β-diketimines. Such an interconversion would require correlated motion in which the biaryl σ-bond is epimerized in *both* ligands as the pyridine nitrogens formally exchange positions in the square plane.[50] We recently determined the barrier to atropisomerization in a series of IAN amines by measuring the kinetics for thermal isomerization of the free amines IAN, Me-IAN, and Me_2-IAN.[51] The free energy for the racemization process for these three examples ranged from 29.8 to 31.3 kcal/mol, indicating not only indefinite configurational integrity at room temperature (an approximate half-life of 6 days at 70 °C) but also a relative insensitivity of the atropisomerization barrier to the size of the naphthylamine substituent.

(47) Tanski, J. M.; Parkin, G. *Organometallics* **2002**, *21*, 587.

(48) (a) Keaton, R. J.; Jayaratne, K. C.; Henningsen, D. A.; Koterwas, L. A.; Sita, L. R. *J. Am. Chem. Soc.* **2001**, *123*, 6197. (b) Keaton, R. J.; Jayaratne, K. C.; Fettinger, J. C.; Sita, L. R. *J. Am. Chem. Soc.* **2000**, *122*, 12909. (c) Jayaratne, K. C.; Keaton, R. J.; Henningsen, D. A.; Sita, L. R. *J. Am. Chem. Soc.* **2000**, *122*, 10490.

(49) (a) Barker, J.; Kilner, M. *Coord. Chem. Rev.* **1994**, *133*, 219. (b) Averbuj, C.; Tish, E.; Eisen, M. S *J. Am. Chem. Soc.* **1998**, *120*, 8640.

(50) For a discussion of correlated motion of aromatic rings, see: Eliel, E. L.; Willen, S. H. *Stereochemistry of Carbon Compounds*; Wiley: New York, 1994; pp 1160−1163.

(51) Cortright, S. B.; Yoder, R. A.; Johnston, J. N. *Heterocycles* **2004**, *62*, 223.

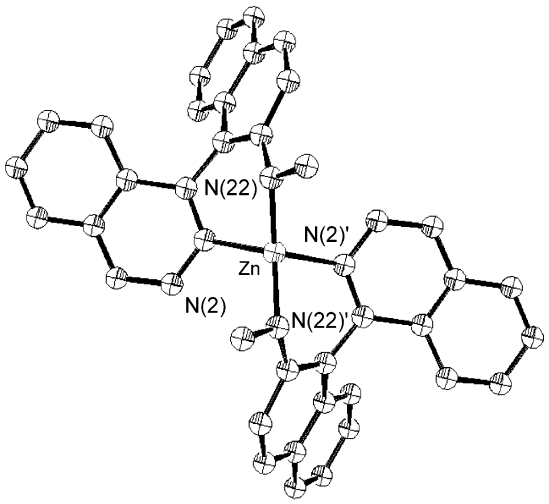


Figure 9. X-ray crystal structure of $(Me\text{-}IAN)_2Zn$ (**19**). The thermal ellipsoids are drawn at the 50% probabiity level with hydrogen atoms removed for clarity. See the Supporting Information for complete details.

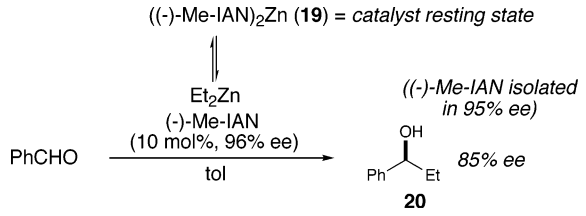
Table 8. Bond Distance and Angles for $(Me\text{-}IAN)_2Zn$ (19)

distances (Å)		angles (deg)	
Zn−N(2)	2.041(6)	N(2)−Zn−N(22)	94.48(25)
Zn−N(22)	1.929(6)	N(2)−Zn−N(22′	113.83(26)
		N(2)−Zn−N(2)′	113.8(4)
		N(22)−Zn−N(2)	127.6(5)

The ability of Me-IAN to complex a metal without atropisomerization was demonstrated most clearly by the finding that (−)-Me-IAN catalyzes diethyl zinc addition to benzaldehyde to give **20** in 85% ee at 25 °C.[52] Moreover, the C_2-symmetric 2:1 Me-IAN−Zn(II) complex **19** analogous to $(Me\text{-}IAN)_2Zr(NMe_2)_2$ could be formed by stirring Me-IAN with diethylzinc at room temperature, followed by crystallization from toluene. The X-ray crystal structure and associated bond distances and angles are shown in Figure 9 and Table 8, respectively. This complex serves as the resting state in the diethyl zinc addition as evidenced by its formation in the absence of benzaldehyde, its rapid decomposition concomitant with formation of enantioenriched carbinol **20** upon benzaldehyde addition, and its reformation (with excess diethyl zinc present) following benzaldehyde consumption. All of these events are conveniently observed by ^1H NMR spectroscopy. (−)-Me-IAN Isolated from this crude reaction mixture exhibited less than 1% ee loss.

Why is the level of diastereocontrol so high? That the complexation selectivity can be first rationalized with kinetic control is supported by the finding that (+)-Me-IAN can be deprotonated and added to $ZrCl_4$ at 0 °C to form $((+)\text{-}Me\text{-}IAN)_2ZrCl_2$. Hydrolytic decomposition of this complex allowed (+)-Me-IAN to be reisolated with <3% ee loss. In most examples described above, the relative donating ability of the coordinating groups correlates well, considering $Me_2N > ArNR > N_{py}$. The optimal pairing of strong and weak donors is uniquely achieved by **A** and **A′** among the homochiral complex possibilities, and **U** in the heterochiral series.

Scheme 2. Demonstration of (−)-Me-IAN Configurational Integrity during 2:1 Metal Complexation



To discriminate among these three diastereomers that bear isoquinoline nitrogens in the square plane and naphthylamido nitrogens in the apical positions (**A**, **A′**, **U**), a closer look at the interligand interactions is necessary. A telling feature of the crystal structures of 2:1 IAN:Zr(IV) complexes reported here is the near-parallel arrangement between the aminonaphthalene rings of each ligand. The angle between the planes defined by these naphthalene rings spans the range 0.8−11.1°. It is also significant to note that the distance between the planes not only is outside the constraints of π-stacking, but the naphthalene rings also overlap only minimally in the solid state. This sterically favorable parallel alignment, perhaps attained optimally by this diastereomeric complex, is the best explanation for why this complex is favored above all others. Unfortunately, attempts to use molecular mechanics calculations to arrive at convincing low-energy structures for these complexes were unsuccessful. The contention that **A** lacks the steric congestion of **A′** also implies that conversion of **A** to **A′** is endothermic regardless of mechanism (Bailar[53] or Ray-Dutt twist). This stands in stark contrast to the fluxional bis(β-diketiminate) zirconium dichloride complexes described by Collins.[25]

Polymerization. Chiral C_2-symmetric metallocene complexes have emerged over the past two decades as powerful olefin polymerization catalysts. The use of 2:1 R-IAN zirconium(IV) complexes as precatalysts in single site ethylene polymerization was therefore investigated to benchmark these unusual bis(β-diketimine) complexes. The complexes that were evaluated fell into two groups based on solubility. The bis(dimethylamido) complexes of all ligands were soluble in a variety of solvents, whereas the dihalide complexes were only sparingly soluble in most nonpolar solvents.

Dichloride **17a** could be prepared and precipitated in analytically pure form. Entries 1 and 2 (Table 9) represent trial conditions for ethylene polymerization with **17a** and MMAO as activator at 85 °C. Moderate activity was observed in these runs (1500−1600 g $(mmol/h/100\ psi)^{-1}$), translating to an efficiency of 15 kg of polyethylene/g of zirconium. To determine whether solubility and/or counterion affected the catalyst efficiency, the bis(dimethylamido) derivative was compared directly to the dichloride. In the event (Table 9, entry 3), precatalyst **16a** provided a higher, but comparable activity of 1727 g $(mmol/h/100\ psi)^{-1}$ and efficiency of 19 kg of polyethylene/g of zirconium. This

(52) The axially chiral bis(dimethylamino) binaphthylene derivative reported by Salvadori catalyzes the diethyl zinc addition in up to 64% ee: Rosini, C.; Franzini, L.; Iuliano, A.; Pini, D.; Salvadori, P. *Tetrahedron*: *Asymmetry* **1991**, *2*, 363. Reviews: (a) Pu, L.; Yu, H.-B. *Chem. Rev.* **2001**, *101*, 757. (b) Soai, K.; Niwa, S. *Chem. Rev.* **1992**, *92*, 833. (c) Noyori, R.; Kitamura, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 49.

(53) (a) Bailar, J. C. *J. Inorg. Nucl. Chem.* **1958**, *8*, 165. (b) Wentworth, R. A. D. *Coord. Chem. Rev.* **1972**, *9*, 171.

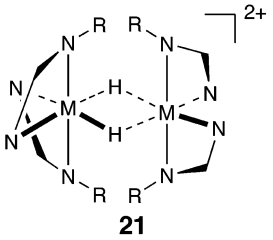
Table 9. Ethylene Polymerization by C_2-Symmetric Bis-β-diketimine (IAN Amine) Zirconium(IV) Complexes[a]

entry	precatalyst	cat. (μmol)	time (h)	activity[b]	eff (g PE/g Zr)
1	**17a**	2.6	0.67	1500	15000
2	**17a**	5.2	0.67	1600	16000
3	**16a**	2.2	0.5	1700	19000
4	**16e**	5	0.5	780	8600
5	**16b**	5	0.5	420	4600

[a] All runs were performed with 1 L batch reactors, using 1000 equiv of MMAO and ^{i}Bu$_3$Al scavenger (1000 μmol for entries 1 and 2, 200 μmol for entries 3−5) at 85 °C. Ethylene pressure is 135 psi for entries 1 and 2, and 200 psi for entries 3−5. Polymer molecular weights of 386 000/407 000 and PDI of 3.53/3.77 were obtained for entries 1/2. [b] g (mmol/h/100 psi)$^{-1}$.

data suggests that the bis(dimethylamido) leaving groups are readily activated by MAO and that no efficiency advantage is gained by transformation to poorly soluble dihalide derivatives. To our knowledge, no polymerization data for bis(β-diketimine) metal *amido* precatalysts has been previously reported for comparison.[54] Although a direct comparison is not possible, these precatalysts compare favorably to those evaluated by Collins (2461−3990 g (mmol/h/100 psi)$^{-1}$ at 70 °C)[31] and Lappert (9.5 g (mmol/h/100 psi)$^{-1}$ at 25 °C).[26,55]

The effect of the IAN amine substituent on catalyst activity was next examined. This structural feature was expected to have the greatest impact since it resides above/below the square plane in the putative active cationic zirconium complex. By varying the substituent along the series Me, Ph, and Bn, decreasing catalyst activity was observed (Table 9, entries 3−5). Such an effect is counterintuitive to the notion that a possible catalyst deactivation pathway is dimerization through hydride bridges to form **21** after β-hydride elimination



21

from the polymer and olefin decoordination, by analogy to neutral hydride-bridged metallocenes.[56,57] However, this polymerization data are only a preliminary indication of R-IAN-supported catalyst activity.

The flexibility of the IAN amine-supported zirconium complexes bodes well for their use in olefin polymerization, and our initial findings suggest that the soluble bis(dimethylamido) precatalysts **16** are readily activated with MAO and may serve as ideal developmental candidates.

Conclusion

We have described an improved IAN amine ligand synthesis that is general, high-yielding, and convergent. Despite their lack of symmetry, IAN amines **1** undergo highly stereoselective complexation with Zr(IV) chloride and tetrakis(dimethylamide) to give chiral C_2-symmetric 2:1 complexes. Assembly of the 2:1 ligand:Zr(IV) complexes from a racemic ligand source gave only homochiral complexes. This behavior is remarkable considering the possibility of 13 diastereomeric 2:1 ligand:metal complexes in this single reaction. Additionally, crystal structures of a series of 2:1 complexes demonstrate the generality of this phenomenon and provide insight into the design of ligands that stereoselectively complex to a metal coordination center. Finally, promising preliminary data regarding the use of these unusual zirconium amido complexes as precatalyts in olefin polymerization are provided. It is significant to note that ligand constraints result in complexes resembling constrained geometry metallocenes. The chiral C_2-symmetric topology characteristic of **16**−**18** bodes well for stereoselective olefin polymerization, by analogy to both *ansa*-metallocene catalysts[58] and the more recent PHI catalysts developed by Coates[59] and Fujita.[60]

The transfer of asymmetry from enantiopure IAN amine−metal complexes to organic substrates represents an exciting direction considering the longstanding success of chiral amines in asymmetric synthesis. The use of enantiopure IAN amines will generate enantiopure C_2-symmetric complexes, a motif common within asymmetric synthesis. Developments along these lines will be the subject of future reports.

Experimental Section[61]

Bn-IAN Amine (1b). 2-(*N*-Benzylamino)naphthalene (4.16 g, 17.8 mmol) and 1-chloroisoquinoline (2.93 g, 17.9 mmol) were dissolved in toluene (80 mL) and treated with $AlMe_3$ (32.0 mL, 2.0 M in hexanes) via syringe prior to heating at 110 °C for 3 d. The solution was cooled to room temperature, added to 6 M aq NaOH, and diluted with EtOAc and Rochelle's salt solution. The mixture was stirred for 1 h, the phases were separated, and the aqueous layer was further extracted with EtOAc. The combined organic layers were dried, filtered, and concentrated, and the residue was purified by flash chromatography (SiO_2, 20% ethyl acetate in hexanes) to give the desired amine as a tan powder (4.81 g, 75%). Alternately, the crude product may be purified by crystallization from a hot toluene solution with an equivalent volume of hexanes added. Mp 109−110 °C, R_f 0.28 (40% EtOAc/hexanes); IR (film) 3431, 3054, 1620 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, J = 5.6 Hz, 1H), 7.96 (d, J = 8.3 Hz, 1H), 7.83 (d, J = 9.0 Hz, 1H), 7.79 (d, J = 5.7 Hz, 1H), 7.76 (d, J = 8.6 Hz, 1H), 7.72 (dd, J = 8.1, 8.1 Hz, 1H), 7.60 (d, J = 8.3 Hz, 1H), 7.44 (dd, J = 8.1, 8.1 Hz, 1H), 7.25−7.13 (m, 8H), 6.82 (d, J = 8.3 Hz, 1H), 4.44 (s, 2H), 4.21 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0,

(54) An example of a zirconium complex with amine, amido, *and* chloro ligands has been reported for olefin polymerization: Fuhrmann, H.; Brenner, S.; Arndt, P.; Kempe, R. *Inorg. Chem.* **1996**, *35*, 6742.

(55) A very loose comparison may be made to the activity of Cp_2ZrCl_2/MMAO for ethylene polymerization − activity = 79000 g (mmol/h/100 psi)$^{-1}$ and efficiency = 64000 g PE/g Zr: Alonso-Moreno, C.; Antinolo, A.; Lopez-Solera, I.; Otero, A.; Prashar, S.; Rodriguez, A. M.; Villasenor, E. *J. Organomet. Chem.* **2002**, *656*, 129.

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(61) Complete experimental details can be found in the Supporting Information.

144.0, 143.6, 139.8, 134.0, 130.8, 130.3, 128.7 (3C), 128.2, 127.8 (3C), 127.3, 127.2, 127.1 (2C), 126.7, 124.1, 122.1, 120.7, 114.6, 45.0; HRMS (EI), exact mass calcd for $C_{26}H_{20}N_2$ $[M]^+$ 360.1626, found 360.1616. Anal. Calcd for $C_{26}H_{20}N_2$: C, 86.64; H, 5.59; N, 7.77. Found: C, 86.48; H, 5.63; N, 7.87.

2-Np-IAN Amine (1j). 2,2′-Dinaphthylamine (108.6 mg, 403.2 μmol) and 1-chloroisoquinoline (66.5 mg, 406.5 μmol) were dissolved in toluene (4.0 mL) and treated with $AlMe_3$ (0.64 mL, 2.0 M in toluene) via syringe prior to heating at 110 °C for 24 h. The solution was cooled to room temperature, added to 6 M aq NaOH, and diluted with EtOAc and Rochelle's salt solution. The mixture was stirred for 30 min, the phases were separated, and the aqueous layer was further extracted with EtOAc. The combined organic layers were dried, filtered, and concentrated, and the residue was purified by flash chromatography (SiO_2, 10% ethyl acetate in hexanes) to give the desired amine as a tan powder (122.4 mg, 77%). Mp 168−170 °C; R_f 0.19 (20% EtOAc/hexanes); IR (film) 3404, 3053, 1619 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.79 (d, J = 5.6 Hz, 1H), 7.94−7.91 (m, 2H), 7.86 (d, J = 7.8 Hz, 1H), 7.81−7.79 (m, 2H), 7.69−7.64 (m, 4H), 7.59 (d, J = 8.3 Hz, 1H), 7.41−7.28 (m, 5H), 7.23−7.20 (m, 1H), 7.11 (dd, J = 8.9, 2.0 Hz, 1H), 6.95 (d, J = 8.6 Hz, 1H), 6.23 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 143.2, 140.8, 139.4, 137.0, 134.7, 134.1, 130.9, 129.9, 129.7, 129.5, 129.3, 128.8, 128.3, 128.0, 127.8, 127.6, 127.3, 126.9, 126.7, 126.6, 125.2, 123.9, 123.8, 122.6, 120.9, 120.7, 119.6, 112.9; HRMS (CI, CH_4), exact mass calcd for $C_{29}H_{19}N_2$ $[M - H]^+$ 395.1548, found 395.1558.

2-(*N*-Benzylamino)naphthalene (12b). 2-Naphthol (14.42 g, 100.0 mmol), ammonium chloride (11.86 g, 221.7 mmol), benzylamine (200 mL, 1.83 mol), and ethanol (20 mL) were combined. The solution was heated at 200 °C in a Parr reactor for 4 d. After being cooled to room temperature, excess benzylamine and ethanol were removed from the crude reaction mixture by distillation, leaving an oily residue. The residue was dissolved in EtOAc, washed with 6 M aq NaOH, dried, filtered, and concentrated, and the residue was purified by flash chromatography (SiO_2, 5% ethyl acetate in hexanes) to give the desired product as a tan powder (12.59 g, 54%). The product can also be purified by recrystallization from a hot toluene solution with an equivalent amount of hexanes. Mp 68−69 °C; R_f 0.51 (20% EtOAc/hexanes); IR (film) 3421, 3053, 1629 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.2 Hz, 1H), 7.72 (d, J = 8.9 Hz, 1H), 7.69 (d, J = 8.2 Hz, 1H), 7.50−7.37 (m, 6H), 7.29 (ddd, J = 8.0, 8.0, 1.2 Hz, 1H), 6.97 (dd, J = 8.8, 2.2 Hz, 1H), 6.92 (d, J = 1.6 Hz, 1H), 4.49 (s, 2H), 4.17 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.1, 139.5, 135.5, 129.3, 129.0 (2C), 128.0 (2C), 127.7, 126.7, 126.3, 122.4, 118.2, 104.9, 48.6; HRMS (CI, CH_4), exact mass calcd for $C_{17}H_{13}N$ $[M]^+$ 233.1204, found 233.1198. Anal. Calcd for $C_{17}H_{13}N$: C, 87.52; H, 6.48; N, 6.00. Found: C, 87.51; H, 6.55; N, 6.01.

Dinaphthalen-2-ylamine (12j). $Pd(dba)_2$ (191 mg, 332 μmol), dppf (533 mg, 961 μmol), and NaO^tBu (478 mg, 4.97 mmol) were loaded into a round-bottom flask in a glovebox and then transferred to a hood. Toluene (120 mL) was added to the mixture followed by 2-aminonaphthalene (712 mg, 4.97 mmol). 2-Naphthyl triflate (915 mg, 3.32 mmol) was dissolved in toluene and added before warming the reaction mixture to 85 °C for 65 h. The reaction mixture was cooled to room temperature and concentrated to an oil that was purified by flash chromatography (SiO_2, 5% ether in hexanes) to give the desired amine as a white solid (820 mg, 92%). Mp 172−174 °C; R_f 0.53 (20% EtOAc/hexanes); IR (film) 3414, 3392, 3048, 1628 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (m, 2H), 7.70 (d, J = 8.2 Hz, 1H), 7.56 (d, J = 2.0 Hz, 1H), 7.45 (m, 1H), 7.35 (m, 2H), 6.06 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.9, 134.9, 129.6, 129.5, 127.9, 126.8 (2C), 123.9, 120.5, 112.5; HRMS (CI, CH_4), exact mass calcd for $C_{20}H_{15}N$ $[M]^+$ 269.1204, found 269.1194.

(Bn-IAN)Zr(NMe$_2$)$_3$ (15b). Bn-IAN amine (20.0 mg, 55.5 μmol) and $Zr(NMe_2)_4$ (14.9 mg, 55.7 μmol) were weighed into a flame-dried vial in a glovebox. d_6-Benzene was then added and the clear orange solution was transferred to a J-Young tube. ^1H NMR, analyzed 5 min after mixing, revealed complete complexation. ^1H NMR (400 MHz, C_6D_6) δ 8.33 (d, J = 6.2 Hz, 1H), 7.58 (d, J = 9.1 Hz, 1H), 7.53−7.47 (m, 3H), 7.29 (d, J = 8.2 Hz, 1H), 7.10 (d, J = 6.2 Hz, 1H), 7.06 (dd, J = 8.1, 8.1 Hz, 1H), 7.00−6.95 (m, 2H), 6.86−6.82 (m, 3H), 6.76−6.74 (m, 3H), 6.67 (dd, J = 8.1, 8.1 Hz, 1H), 5.09 (s, 2H), 3.00 (s, 18H); ^{13}C NMR (100 MHz, C_6D_6) δ 158.7, 149.3, 142.7, 140.1, 136.7, 135.6, 131.9, 130.9, 130.4, 128.4, 128.1, 127.5 (2C), 127.3, 127.2, 126.6 (2C), 126.1, 125.6, 122.1, 119.7, 119.4, 117.1, 53.9, 43.0.

(2-Np-IAN)Zr(NMe$_2$)$_3$ (15j). 2-Np-IAN amine (8.6 mg, 21.7 μmol) and $Zr(NMe_2)_4$ (5.8 mg, 21.7 μmol) were combined in a flame-dried vial in the glovebox. d_6-Benzene was then added and the clear red-orange solution was transferred to a J-Young tube. ^1H NMR, analyzed 5 min after mixing, revealed complete complexation. ^1H NMR (400 MHz, C_6D_6) δ 8.26 (d, J = 6.2 Hz, 1H), 7.82 (d, J = 9.0 Hz, 1H), 7.72 (d, J = 8.5 Hz, 1H), 7.62 (d, J = 9.0 Hz, 1H), 7.60−7.55 (m, 4H), 7.48 (s, 1H), 7.46−7.45 (m, 1H), 7.26 (d, J = 8.2 Hz, 1H), 7.25−7.20 (m, 1H), 7.12−7.03 (m, 5H), 6.89 (ddd, J = 7.7, 7.7, 1.1 Hz, 1H), 6.79 (ddd, J = 7.7, 7.7, 1.1 Hz, 1H), 3.07 (s, 18H); ^{13}C NMR (100 MHz, C_6D_6) δ 157.6, 151.9, 145.4, 140.5, 136.8, 136.1, 134.7, 132.0, 131.2, 129.7, 129.5, 129.1, 128.5 (2C), 127.8, 127.7 (2C), 127.6, 126.8, 126.7, 126.6, 126.1, 126.0, 124.2, 124.0, 122.4, 122.3, 120.8, 113.8, 42.9.

(Bn-IAN)$_2$Zr(NMe$_2$)$_2$ (16b). Bn-IAN amine (110.6 mg, 306.8 μmol) and $Zr(NMe_2)_4$ (41.8 mg, 156.2 μmol) were weighed into a flame-dried vial in a glovebox. Benzene was then added and the clear, orange solution was transferred to a J-Young tube, which was sealed and heated at 90 °C for 17 h. The solvent was removed, leaving the product as a red-orange solid (236.4 mg, 86%). ^1H NMR (400 MHz, C_6D_6) δ 8.22 (d, J = 6.3 Hz, 2H), 7.43−7.38 (m, 4H), 7.29 (d, J = 8.7 Hz, 2H), 7.21 (d, J = 7.9 Hz, 2H), 7.16 (d, J = 7.3 Hz, 4H), 7.01 (d, J = 8.2 Hz, 2H), 6.94 (d, J = 6.3 Hz, 2H), 6.91−6.84 (m, 6H), 6.82 (dd, J = 7.9, 7.9 Hz, 2H), 6.68 (dd, J = 7.8, 7.8 Hz, 2H), 6.51 (dd, J = 8.1, 8.1 Hz, 2H), 6.44 (dd, J = 8.1, 8.1 Hz, 2H), 5.95 (d, J = 16.8 Hz, 2H), 5.90 (d, J = 8.5 Hz, 2H), 5.56 (d, J = 16.8 Hz, 2H), 3.00 (s, 12H); ^{13}C NMR (100 MHz, C_6D_6) δ 159.1, 152.4, 143.0 (2C), 139.9, 136.1, 134.8, 130.7, 130.3, 129.9, 128.2, 127.8, 127.4 (2C), 126.8, 126.5, 126.4, 126.3, 125.7, 125.6, 121.2, 119.1, 118.3, 52.3, 45.7.

(Ph-IAN)$_2$Zr(NMe$_2$)$_2$ (16e). Ph-IAN amine (1.259 g, 3.635 mmol) and $Zr(NMe_2)_4$ (0.499 mg, 1.868 mmol) were combined in a flame-dried vial in the glovebox. Benzene was added and the clear red solution was transferred to a J-Young tube, which was heated in an oil bath at 60 °C for 18 h. The solvent was removed, leaving a red powder. The solid was dissolved in warm toluene and then cooled to −25 °C to yield red crystals (1.393 g, 88%). ^1H NMR (400 MHz, C_6D_6) δ 8.77 (d, J = 6.2 Hz, 2H), 7.45−7.35 (m, 4H), 7.30−7.19 (m, 6H), 7.10−7.02 (m, 4H), 6.96 (d, J = 6.2 Hz, 2H), 6.91−6.80 (m, 6H), 6.71−6.63 (m, 4H), 6.52 (dd, J = 8.1, 8.1 Hz, 2H), 6.16 (dd, J = 8.1, 8.1 Hz, 2H), 5.51 (d, J = 8.6 Hz, 2H), 2.74 (s, 12H); ^{13}C NMR (100 MHz, C_6D_6) δ 159.2, 155.9, 153.0, 140.4, 136.1, 134.3, 130.7, 130.0, 128.9 (2C), 128.2, 127.9, 127.5, 127.1, 127.0, 126.5, 126.0, 125.7, 124.1 (2C), 122.7, 120.1, 119.1, 46.5.

(2-Np-IAN)$_2$Zr(NMe$_2$)$_2$ (16j). 2-Np-IAN amine (11.3 mg, 28.5 μmol) and $Zr(NMe_2)_4$ (3.9 mg, 14.6 μmol) were combined in a flame-dried vial in the glovebox. Benzene was added and the clear red solution was transferred to a J-Young tube, which was heated in an oil bath at 60 °C for 6 h. The solvent was removed, leaving the desired product as a red powder. ^1H NMR (400 MHz, C_6D_6) δ 8.89 (d, J = 6.2 Hz, 2H), 8.15 (br s, 2H), 7.86 (d, J = 8.1 Hz, 2H), 7.66 (d, J = 7.9 Hz, 2H), 7.63 (d, J = 8.7 Hz, 2H), 7.58−7.34 (m, 8H), 7.31 (dd, J = 7.5, 7.5 Hz, 2H), 7.20−7.05 (m, 6H), 7.01 (d, J = 6.0 Hz, 2H), 6.93 (dd, J = 7.5,

Table 10. Summary of X-ray Crystallographic Data

compd	Me-IAN amine	(Bn-IAN)$_2$Zr(NMe$_2$)$_2$	(Ph-IAN)$_2$Zr(NMe$_2$)$_2$	(2-Np-IAN)$_2$Zr(NMe$_2$)$_2$	(Bn-IAN)$_2$ZrI$_2$	(Me-IAN)$_2$Zn
cryst obtained from	ethyl acetate/hexanes	toluene	toluene	toluene	benzene	toluene
color	yellow-orange	orange	orange	red-orange	orange	red
formula	$C_{20}H_{16}N_2$	$C_{56}H_{50}N_6Zr\cdot C_7H_8$	$C_{54}H_{46}N_6Zr\cdot 2C_7H_8$	$C_{62}H_{50}N_6Zr\cdot 1.5C_7H_8$	$C_{52}H_{38}I_2N_4Zr\cdot C_6H_6$	$C_{40}H_{30}N_4Zn\cdot 2C_7H_8$
formula wt	284.35	990.42	1054.50	1108.50	1141.99	816.38
wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
cryst size (mm^3)	0.25 × 0.18 × 0.06	0.30 × 0.20 × 0.18	0.35 × 0.35 × 0.13	0.40 × 0.08 × 0.08	0.23 × 0.08 × 0.02	0.35 × 0.30 × 0.15
crystal system	monoclinic	orthorhombic	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	$Pbcn$	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$C2/c$
unit cell dimens						
a (Å)	15.1448(6)	9.4118(14)	9.4967(2)	10.6273(13)	13.218(3)	20.6759(17)
b (Å)	10.6146(4)	23.389(3)	26.4826(7)	25.610(3)	13.844(4)	7.0553(6)
c (Å)	18.1560(7)	22.874(2)	21.1702(5)	20.686(3)	14.138(3)	29.289(2)
α (deg)	90	90	90	90	64.015(6)	90
β (deg)	90.1409(11)	90	90.2338(11)	99.438(3)	83.626(8)	105.1882
γ (deg)	90	90	90	90	80.516(6)	90
V (Å^3)	2918.7(2)	5035.4(11)	5324.2(2)	5553.7(12)	2291.4(9)	4123.4(6)
Z	8	4	4	4	2	4
density, calcd (Mg/m^3)	1.294	1.306	1.316	1.326	1.655	1.315
abs coeff μ (mm^{-1})	0.0765	0.2658	0.2561	0.249	0.1632	0.6394
F (000)	1200	2072	2208	2316	1132	1712
T (K)	153(2)	117(2)	117(2)	117(2)	113(2)	115(2)
θ range (ϖ scans)	2.22−27.52	2.33−27.5	2.07−30.03	2.10−30.13	2.14−30.30	2.04124−27.5486
index ranges	$-19 \le h \le 19$	$-12 \le h \le 12$	$-13 \le h \le 13$	$-14 \le h \le 14$	$-18 \le h \le 18$	$-26 \le h \le 26$
	$-13 \le k \le 13$	$-30 \le k \le 30$	$-37 \le k \le 37$	$-34 \le k \le 35$	$-19 \le k \le 19$	$-9 \le k \le 9$
	$-23 \le l \le 23$	$-29 \le l \le 29$	$-29 \le l \le 29$	$-12 \le l \le 29$	$-19 \le l \le 19$	$-38 \le l \le 38$
no. reflns collected	38310	22312	15572	36750	39421	4761
no. independent reflns	6715	5791	8379	16172	12803	1633
no. of data/restr/parameters	3803/0/526	3083/0/431	8379/0/676	8437/0/949	4441/0/276	1633/0/253
refinement method	on F	on F	on F	on F^2	on F^2	on F
goodness-of-fit	0.6079	0.8991	0.5930	0.835	0.849	1.3585
R1/wR2 [$I > 2\sigma(I)$]	0.0439, 0.0311	0.0294, 0.0347	0.0305, 0.0306	0.0615, 0.1444	0.0739, 0.1276	0.0639, 0.0650
max/min peaks (e/Å^3)	0.21 and −0.25	0.40 and −0.47	0.28 and −0.51	1.36 and −1.15	1.21 and −1.23	0.52 and −0.57

7.5 Hz, 2H), 6.73 (dd, J = 7.5, 7.5 Hz, 2H), 6.63 (dd, J = 7.5, 7.5 Hz, 2H), 6.23 (dd, J = 7.5, 7.5 Hz, 2H), 5.60 (d, J = 8.5 Hz, 2H), 2.83 (s, 12H); ^{13}C NMR (100 MHz, C_6D_6) δ 159.3, 153.4, 152.6, 140.6, 136.3, 135.7 134.3, 130.8, 130.1, 130.0, 129.6, 128.6 (2C), 128.2, 127.9, 127.3 (2C), 127.2, 127.1, 127.0, 126.6, 126.2, 126.1, 125.7, 124.9, 123.1, 122.8, 119.3, 118.8, 46.7.

(−)-Me-IAN-Catalyzed Diethyl Zinc Addition to Benzaldehyde. (−)-Me-IAN amine (17.5 mg, 61.5 μmol, 96% ee) was dissolved in d_8-toluene (0.70 mL) and treated with diethylzinc (161.9 mg, 1.31 mmol), resulting in immediate formation of a clear red-orange solution. After 10.5 h at room temperature, ^{1}H NMR revealed complete ligand complexation, forming ((−)-Me-IAN)$_2$Zn. Benzaldehyde (63 μL, 0.620 mmol) was added and immediately the solution lightened to a pale orange-yellow. The solution had returned to red-orange after being stirred for 19 h, at which point it was cooled to 0 °C and MeOH was added. Dilution with water was followed by extraction with CH_2Cl_2. The combined organic layers were dried, filtered, and concentrated. Purification via flash chromatography (SiO_2, 5% Et_2O in hexanes) gave the product as a light yellow liquid (65.7 mg, 78%) and recovered (−)-Me-IAN (16.9 mg). HPLC analysis was used to determine the enantioenrichment of the product (OD column, 1.0 mL/min, 2% ^{i}PrOH in hexanes) at 85% ee (major peak = 13.7 min, minor peak = 16.3 min), and recovered (−)-Me-IAN amine (OD column, 1.0 mL/min, 10% ^{i}PrOH in hexanes) at 95% ee.

((+)-Me-IAN)$_2$ZrCl$_2$ ((+)-17a). **(+)**-Me-IAN amine (24.5 mg, 86.2 μmol, 99% ee) and $LiNMe_2$ (4.4 mg, 86.2 μmol) were combined in a vial and dissolved in toluene. The opaque purple solution was allowed to mix at room temperature for 30 min, after which the solvent and volatiles were removed by vacuum. The residue was redissolved in d_6-benzene and $ZrCl_4$ (10.0 mg, 42.9 μmol) was added. After 30 min at room temperature, a red solution and orange precipitate resulted. ^{1}H NMR revealed the desired complex present in ∼70% purity. To the reaction mixture was added H_2O. The mixture was extracted with CH_2Cl_2, and the organic layer was dried, concentrated, and purified by flash chromatography (SiO_2, 30% EtOAc in hexanes) to give recovered (+)-Me-IAN amine that was analyzed by HPLC (OD column, 1.0 mL/min, 10% ^{i}PrOH in hexanes) to reveal a 96% ee.

General Procedure for X-ray Analysis. X-ray diffraction data were collected on a Bruker diffractometer (SMART 6000CCD). Crystals were attached to a glass fiber with silicone grease and cooled to near lN_2 temperature for data collection. Data were corrected for Lorentz and polarization effects and equivalent reflections were averaged with use of the Bruker SAINT[62] software as well as utility programs from the XTEL library. The structures were solved with SHELXTL[63] and Fourier techniques. ORTEP drawings were constructed with ORTEP-III.[64]

General Polymerization Procedure. A mechanically stirred 1-L autoclave with an oven-dried stainless steal bottom was thoroughly purged with N_2 and charged with 400 g of hexanes. Via syringe under N_2 purge, triisobutylaluminum (200 or 1000 μmol) was added as a toluene solution to scavenge residual impurities. Over 20−30 min, the stirred mixture was brought to 85 °C, and the reactor was pressurized to 135 or 200 psi with ethylene. The activated precatalyst/MAO mixture (2−5 μmol of Zr; 1000 equiv of Al), stirred for 10−15 min, was injected into the reactor via a pressurized bomb followed by a few milliliters of a hexane "chaser" to ensure complete injection. The temperature was maintained at ∼85 °C during the 30 or 40 min run, using an external cooling jacket, and ethylene was fed on demand to maintain reactor pressure. The reactor was then vented, cooled, and opened to expose the polymer. The polyethylene yields were determined after drying in a vacuum oven overnight.

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Supporting Information Available: General experimental procedures and spectral data for all new compounds (PDF) and complete X-ray structural data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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