A Remarkably Facile Zirconium(IV) → Aluminum(III) *β*-Diketiminate Transmetalation That Also Results in a More Active Olefin Polymerization Catalyst upon Activation

Sarah B. Cortright,[†] Joseph N. Coalter III,[‡] Maren Pink,[†] and
Jeffrey N. Johnston*,[†]

*Department of Chemistry, Indiana University, Bloomington, Indiana 47405-7102, and
The Dow Chemical Company, 3200 Kanawha Terrace, South Charleston, West Virginia 25303*

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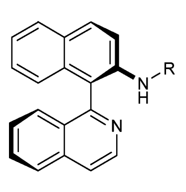
Summary: (R-IAN)$_2$ZrX$_2$ complexes, where X = NMe$_2$, Cl, have recently emerged as effective olefin polymerization precatalysts bearing chiral ligands formally of the β-diketimine class. An attempt to exchange dimethylamido ligands for alkyl (methyl) using the Jordan protocol resulted in a surprisingly facile transmetalation of the bidentate Me-IAN ligands from zirconium(IV) to aluminum(III). An initial study of the process and the finding that the (R-IAN)AlMe$_2$ complexes that result are more potent precatalysts themselves provide a case study within the rapidly growing area of catalysis based on β-diketiminate metal complexes.

The development of *β*-diketimines as supporting ligands for metal-centered reactions constitutes one of the most active research areas in recent years. This phenomenon has been largely driven by their promise as complements, if not surrogates, for metallocene catalysts[1] and their use as electron-rich bidentate ligands that can be rendered substantially more hindered than their 1,3-dicarbonyl counterparts.[2] Through the efforts of numerous investigators, general guidelines have been drawn for the formation of group IV metal *β*-diketiminate complexes and their ability to polymerize α-olefins.[3–6] Moreover, the challenges that face this ligand motif and their solutions have brought an increased diversity to the field of Ziegler–Natta polymerization.[7–10]

IAN amines **1** (amine ligands formed from isoquinoline and 2-aminonaphthalene subunits) are bidentate N,N ligands formally of the *β*-diketimine class but are more appropriately identified as *β*-amido Schiff bases on the basis of their binding characteristics.[11] As part of a general program to develop the asymmetric catalysis of chiral *β*-diketimine-supported metal complexes,[12] we have studied their unique coordination chemistry and have systematically evaluated the activity of these complexes in ethylene polymerization as a function of catalyst structure and the ancillary ligand removed to form the putative cationic polymerization catalyst.[13,14] Accordingly, the low solubility of (R-IAN)$_2$ZrX$_2$ dihalides (X = Cl, I) led us to attempt synthesis of their dialkyl derivatives. Whereas exposure of R-IAN amines of various structure (R = Me, Ph) to ZrBn$_4$ readily provided the 1:1 complexes (R-IAN)ZrBn$_3$, the corresponding 2:1 complexes (R-IAN)$_2$ZrBn$_2$ of potential C_2 symmetry were not forthcoming by this approach.



Me-IAN 1a, R = Me
Bn-IAN 1b, R = Bn
Ph-IAN 1c, R = Ph

We therefore turned to the Jordan amido/alkyl exchange protocol using AlMe$_3$, a technique primarily

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[*] To whom correspondence should be addressed. E-mail: jnjohnst@indiana.edu.

[†] Indiana University.

[‡] The Dow Chemical Company.

(1) Review of *β*-diketimine coordination chemistry: Bourget-Merle, L.; Lappert, M. F.; Severn, J. R. *Chem. Rev.* **2002**, *102,* 3031.

(2) (a) Kakaliou, L.; Scanlon, W. J. IV; Qian, B.; Baek, S. W.; Smith, M. R., III; Motry, D. H. *Inorg. Chem.* **1999**, *38*, 5964. (b) Basuli, F.; Bailey, B. C.; Brown, D.; Tomaszewski, J.; Huffman, J. C.; Baik, M.-H.; Mindiola, D. J. *J. Am. Chem. Soc.* **2004**, *126*, 10506. (c) Eckert, N. A.; Smith, J. M.; Lachicotte, R. J.; Holland, P. L. *Inorg. Chem.* **2004**, *43*, 3306.

(3) Rahim, M.; Taylor, N. J.; Xin, S.; Collins, S. *Organometallics* **1998**, *17*, 1315.

(4) Deelman, B.; Hitchcock, P. B.; Lappert, M. F.; Leung, W.; Lee, H.; Mak, T. C. W. *Organometallics* **1999**, *18*, 1444.

(5) Giannini, L.; Solari, E.; De Angelis, S.; Ward, T. R.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1995**, *117*, 5801.

(6) Martin, A.; Uhrhammer, R.; Gardner, T. G.; Jordan, R. F.; Rogers, R. D. *Organometallics* **1998**, *17*, 382.

(7) Reviews: (a) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 428. (b) Piers, W. E.; Emslie, D. J. H. *Coord. Chem. Rev.* **2002**, *233*, 131.

(8) Qian, B.; Scanlon, W. J., IV; Smith, M. R., III; Motry, D. H. *Organometallics* **1999**, *18*, 1693.

(9) Vollmerhaus, R.; Rahim, M.; Tomaszewski, R.; Xin, S.; Taylor, N. J.; Collins, S. *Organometallics* **2000**, *19*, 2161.

(10) Jin, X.; Novak, B. M. *Macromolecules* **2000**, *33*, 6205.

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

(12) Enantioselective chiral *β*-diketimine-supported metal catalysis: (a) Leutenegger, U.; Madin, A.; Pfaltz, A. *Angew. Chem.* **1989**, *101*, 61. (b) Fritischi, H.; Leutenegger, U.; Pfaltz, A. *Angew. Chem.* **1986**, *98*, 1028. (c) Pfaltz, A. In *Enantioselective Catalysis With Chiral Cobalt And Copper Complexes*; Scheffold, R., Ed.; Modern Synthetic Methods Vol. 5; Springer-Verlag: Berlin, Heidelberg, 1989. (d) Fritischi, H.; Leutenegger, U.; Pfaltz, A. *Helv. Chim. Acta* **1988**, *71*, 1553. (e) Lo, M.-C. L.; Fu, G. C. *J. Am. Chem. Soc.* **2002**, *124*, 4572.

(13) (a) Cortright, S. B.; Huffman, J. C.; Yoder, R. A.; Coalter, J. N., III; Johnston, J. N. *Organometallics* **2004**, *23*, 2238. (b) Cortright, S. B.; Johnston, J. N. *Angew. Chem., Int. Ed.* **2002**, *41*, 345.

(14) For similar findings, see: Kettunen, M.; Vedder, C.; Schaper, F.; Leskelä, M.; Mutikainen, I.; Brintzinger, H.-H. *Organometallics* **2004**, *23*, 3800.

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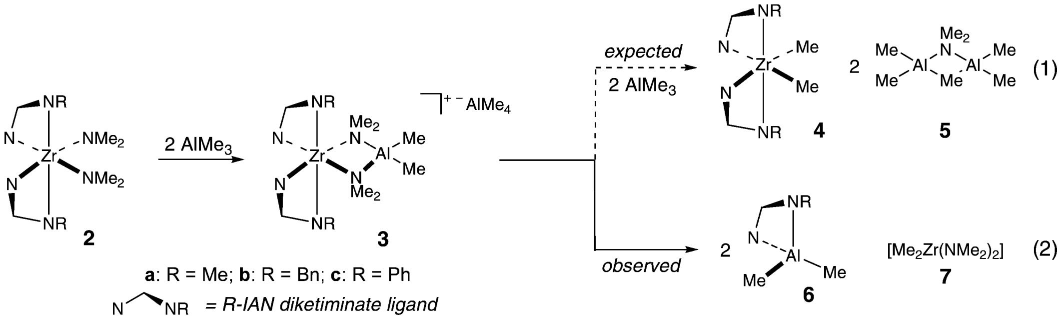
Scheme 1. Amide/Alkyl Exchange and Transmetalation Pathways from (R-IAN)$_2$Zr(NMe$_2$)$_2$



utilized with complexes of the metallocene type.[15,16] For complexes using bidentate nitrogen-based ligands, successful exchange reactions of this type have been documented for group IV metals.[17,18] Our attempt to directly convert **2a** to the dimethyl derivatives followed the typical protocol in which (Me-IAN)$_2$Zr(NMe$_2$)$_2$ (**2a**) in benzene was treated with 4 equiv of AlMe$_3$ (Scheme 1, eq 1). The deep red solution of **2a** immediately lightened to yellow and over a 30 min period darkened again to a deep red-violet. Removal of the volatile components by vacuum led to a red-black oil that was redissolved in d_6-benzene. The relative simplicity of the aromatic region of its ^{1}H NMR spectrum confirmed that a single ligand environment existed, indicating that either the C_2 symmetry had been preserved or a 1:1 ligand/metal complex was present. However, the methyl(metal) resonances appeared as two magnetically inequivalent singlets—an observation clearly inconsistent with the desired C_2-symmetric dimethyl product **4a**.

A second reaction between (Me-IAN)$_2$Zr(NMe$_2$)$_2$ (**2a**) and AlMe$_3$ in which the latter was limited to 2 equiv provided a similar result. After 90 min at 25 °C, the volatile components were again removed by vacuum to reveal only partial conversion to the previously observed product. Another aromatic product and several broad unidentifiable peaks were also noted; however, no **2a** remained. When this solution was subjected to heating for 2 h at 75 °C, ^{1}H NMR revealed complete conversion to the previously observed complex. Lowering of the relative amount of AlMe$_3$ below 2 equiv consistently provided only partial conversion.

The combination of Me-IAN and trimethylaluminum (1:1 ratio) in toluene resulted in clean conversion to a complex whose spectral characteristics matched those of the complex formed in the above experiments, consistent with (Me-IAN)AlMe$_2$ (**6a**). Additionally, crystals suitable for X-ray crystallography were obtained from a concentrated benzene/hexanes solution (1:1). Selected bond distances and angles are given in Figure 1.

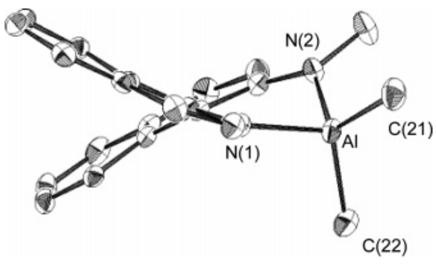


Figure 1. Thermal ellipsoid (50%) plot of **6a**. H atoms are removed for clarity. Selected bond distances (Å) and angles (deg): Al−N(1) = 1.9633(17), Al−N(2) = 1.8582(18), Al−C(21) = 1.961(2); N(1)−Al−N(2) = 92.95(7), N(1)−Al−C(21) = 107.96(8), N(1)−Al−C(22) = 108.17(9), N(2)−Al−C(21) = 113.94(9), N(2)−Al−C(22) = 112.25(9), C(21)−Al−C(22) = 118.26(10).

This four-coordinate complex is necessarily distorted from an ideal tetrahedral geometry due to the demands of the IAN amine bite angle. The binaphthyl dihedral angle of the bound Me-IAN ligand at 46° is substantially decreased from those of both free Me-IAN amine (68°) and (R-IAN)$_2$Zr(NMe$_2$)$_2$ complexes (low of 58°).[13] The nonplanarity of the β-diketimine framework also renders the coordinating nitrogens electronically inequivalent as expected—a significant difference (0.1 Å) is present in the bond distances between aluminum and the pyridyl (1.963 Å) and naphthylamino (1.858 Å) nitrogens. The Al−N(2) distance is 0.03 Å shorter than the range of reported distances, and Al−N(1) is 0.03 Å longer than any previously reported.[19] The aminonaphthalene nitrogen is essentially planar, with a sum of its bond angles equal to 356°. In standard planar β-diketimine systems, the two nitrogens always exhibit equivalent bonding interactions with aluminum, or at most a 0.01 Å difference.

When the reaction of (Me-IAN)$_2$Zr(NMe$_2$)$_2$ (**2a**) and 2 equiv of AlMe$_3$ was performed in a J-Young tube and monitored by ^{1}H NMR, peaks at 2.1 and −0.3 ppm were observed concomitant with those ascribed to **6a**, consistent with the formation of Me$_2$Zr(NMe$_2$)$_2$ (**7**). The formation of **7** is also supported by the empirically determined limiting stoichiometry. On the basis of these observations, we propose that amide/alkyl metathesis (Scheme 1, eq 1) from the initially formed Lewis base−Lewis acid complex **3a**[20] is slow relative to the transmetalation pathway leading to **6** (Scheme 1, eq 2).

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(15) (a) Kim, I.; Jordan, R. F. *Macromolecules* **1996**, *29*, 489. (b) Diamond, G. M.; Jordan, R. F.; Petersen, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 8024. (c) Thiyagarajan, B.; Jordan, R. F.; Young, V. G., Jr. *Organometallics* **1999**, *18*, 5347.

(16) Due to the low solubility of the dihalo derivatives (R-IAN)$_2$ZrX$_2$, the analogous halide/alkyl exchange could not be evaluated.

(17) For an example of a group VI (Cr(III)) β-diketiminate complex in which chloro is converted to methyl in good yield by treatment with AlMe$_3$, see: Gibson, V. C.; Maddox, P. J.; Newton, C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1998**, 1651.

(18) Gibson, V. C.; Kimberley, B. S.; White, A. J. P.; Williams, D. J.; Howard, P. *Chem. Commun.* **1998**, 313.

(19) (a) Coslédan, F.; Hitchcock, P. B.; Lappert, M. F. *Chem. Commun.* **1999**, *8*, 705. (b) Kopp, M. R.; Neumüller, B. *Z. Anorg. Allg. Chem.* **1999**, *625*, 739. (c) Qian, B.; Ward, D. L.; Smith, M. R., III. *Organometallics* **1998**, *17*, 3070. (d) Huang, Y.-L.; Huang, B.-H.; Ko, B.-T.; Lin, C.-C. *J. Chem. Soc., Dalton Trans.* **2001**, 1359. (e) Gornitzka, H.; Stalke, D. *Organometallics* **1994**, *13*, 4398.

(20) The transmetalation occurs so rapidly that this complex is not observed here, but its formation as an intermediate is presumed on the basis of Jordan's work.[6]

Table 1. Ethylene Polymerization Activity of IAN Amine Aluminum(III) and Zironium (IV) Precatalysts[a]

entry	precatalyst	amt of cat (μmol)	activator	amt of activator (μmol)	activity	efficiency (g of PE/g of Al)
1	(Bn-IAN)AlMe$_2$ (**6b**)	9.7	PhNMe$_2$HBAr$_f$	5.6	18	662
2	(Bn-IAN)AlMe$_2$ (**6b**)	9.7	Ph$_3$CBAr$_f$	8.7	609	22580
3	(Bn-IAN)AlMe$_2$ (**6b**)	4.0	MMAO	2000	3100	114900
4	(Me-IAN)AlMe2 (**6a**)	4.1	MMAO	4800	780	28928
5	(Bn-IAN)AlMe$_2$ (**6c**)	4.0	MMAO	2000	3250	120460
6	(Ph-IAN)$_2$Zr(NMe$_2$)$_2$ (**2c**)	5.0	MMAO	1000	780	8551[b]

[a] All reactions were performed with 1 L batch reactors using 2000 μmol of ^{i}Bu$_3$Al scavenger at 70 °C (85 °C for entry 6) for 0.5 h. The ethylene pressure was 200 psi. Activity is given in units of g mmol^{-1} h 100 psi^{-1}. [b] Efficiency in g of PE/g of Zr.

However, complex **7** appears volatile, as it is consistently removed under vacuum—not unlike the method for removal of aluminum complex **5**.

That the transmetalation is so rapid is counterintuitive when considering the substantially lower Lewis basicity of the naphthylamino nitrogen relative to the dimethylamino nitrogen.[21] Moreover, the naphthylamino nitrogen is considerably hindered, on the basis of kinetic studies of R-IAN atropisomerization.[11] To test the notion that the transmetalation may be simply a pathway driven by formation of **6** as a thermodynamic sink, a series of attempts to achieve kinetic selectivity for the dimethylamido nitrogens was made. However, addition of AlMe$_3$ to **2a** at temperatures as low as −78 °C led to formation of the same product as that observed at room temperature.

Further evidence that this behavior was not simply due to the hindered nature of the 2:1 complexes in which initially formed adduct **3a** sterically prohibited methyl transfer and release of the first dimethylamido ligand was gathered by combining (Me-IAN)Zr(NMe$_2$)$_3$(HNMe$_2$) and AlMe$_3$ (6 equiv) in an attempt to form the trialkylzirconium complex (Me-IAN)ZrMe$_3$. This reaction also furnished the product of transmetalation. These observations extend to the analogous Bn-IAN (**2b**) and Ph-IAN (**2c**) complexes.

Atypical behavior has been observed in metathesis strategies applied to mixed alkoxide/Schiff base ligands that form an unhindered, relatively strained five-membered chelate.[22−24] Also, tetradentate bis(β-diketimine) complexes of group IV metals typically result in the product of interrupted amido transfer.[6] This behavior is uncharacteristic of bidentate zirconium amido complexes as well. For example, 1,8-bis((trimethylsilyl)amino)naphthalene readily complexes to zirconium(IV) to form a complex that is unreactive toward AlMe$_3$, despite its rapid direct reaction with AlMe$_3$ to form the expected bis(aluminum) complex.[25] The dihalozirconium complexes of chelating silyl bis(amides) also readily exchange chloride with methyl upon exposure to AlMe$_3$.[26]

Ethylene Polymerization. Table 1 describes initial ethylene polymerization results for a representative group of (R-IAN)AlMe$_2$ complexes (**6a**−**c**). Using (Bn-IAN)AlMe$_2$ as a representative example, activation with anilinium−BAr$_f$ salt provided a catalyst with only low activity. Use of the more potent activator trityl−BAr$_f$ salt provided a substantially more active catalyst (Table 1, entry 2).[27] Gratifyingly, MMAO further increased the activity by 6-fold. Under otherwise identical conditions, (Me-IAN)AlMe$_2$, (Bn-IAN)AlMe$_2$, and (Ph-IAN)AlMe$_2$ produced catalysts with increasing activity, corresponding to efficiencies of 28 928, 114 900, and 120 460 g of PE/g of Al, respectively (Table 1, entries 4, 3, and 5). Direct activation of (Ph-IAN)$_2$Zr(NMe$_2$)$_2$, a complex that readily transmetalates in the presence of AlMe$_3$, did give rise to an active catalyst (Table 1, entry 6); however, the comparison in Table 1 clearly shows a difference relative to the corresponding aluminum complex (Table 1, entry 5). This result can be interpreted in two ways: (1) the polymerization activity for (Ph-IAN)$_2$Zr(NMe$_2$)$_2$ is derived from a catalyst of general structure (Ph-IAN)$_2$ZrX$_2$ that is only weakly active or (2) the polyethylene is produced by a small amount of (Ph-IAN)AlX$_2$ that is moderately active, as demonstrated in Table 1, entry 5.[28] Despite this ambiguity, this represents to our knowledge the first case in which the aluminum complex was found to be a more reactive olefin polymerization precatalyst than its zirconium counterpart.[29] This may in part be due to the potential reactivity of the carbon backbone of typical aluminum β-diketiminates for which side reactions with ethylene have been observed.[29] Our current hypothesis is that the electronics of the IAN-amine ligand (β-amido Schiff base) provides an opportunity unique among typical planar, electronically delocalized β-diketimines to slow β-hydride elimination and/or ligand incorporation of ethylene.

We have also considered the possibility that the counterion formed upon activation of a zirconium dimethylamide may render the catalyst less reactive than that formed from the corresponding aluminum alkyl. However, we have previously determined that L$_2$Zr(NMe$_2$)$_2$ and L$_2$ZrCl$_2$ (L = IAN-amine) exhibit comparable reactivity,[13] and in general, the variability of activity in counterion studies is typically limited to less than a factor of 10. Moreover, aluminum complexes are

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(21) For an example of partial transmetalation of a bis(amide), see: Ison, E. A.; Abboud, K. A.; Ghiviriga, I.; Boncella, J. M. *Organometallics* **2004**, *23*, 929.

(22) Bei, X.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1997**, *16*, 3282.

(23) Coles, M. P.; Hitchcock, P. B. *Dalton* **2001**, 1169.

(24) (a) Tsukahara, T.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1997**, *16*, 3303. (b) Kim, I.; Nishihara, Y.; Jordan, R. F. *Organometallics* **1997**, *16*, 3314.

(25) Lee, C. H.; La, Y.-H.; Park, S. J.; Park, J. W. *Organometallics* **1998**, *17*, 3648.

(26) Hill. M. S.; Hitchcock, P. B. *Organometallics* **2002**, *21*, 3258.

(27) Polymerizations are normally done in concert with activator-only runs, as well as standard (highly active) activators that provide the proper controls.

(28) Use of polymer molecular weight or PDI to determine whether the catalyst is aluminum or zirconium is not possible, since zirconium complexes produce such a variety of polymers.

(29) For examples of cationic three-coordinate aluminum complexes that undergo β-hydride elimination and reversible ethylene addition to the anionic ligand, see: (a) Radzewich, C. E.; Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* **1998**, *120*, 9384. (b) Korolev, A. V.; Ihara, E.; Guzei, I. A.; Young, V. G., Jr.; Jordan, R. F. *J. Am. Chem. Soc.* **2001**, *123*, 8291. Calculations: (c) Talarico, G.; Busico, V.; Budzelaar, P. H. M. *Organometallics* **2001**, *20*, 4721.

typically multiple orders of magnitude less reactive than their zirconium counterparts. Although a direct comparison cannot be made for the IAN-amine ligands and other aluminum β-diketimines, these systems compare favorably to the monoanionic nitrogen-based aluminum systems previously reported.[30]

In summary, complexes of the type $(\text{R-IAN})_2\text{ZrNMe}_2$ readily transmetalate to aluminum to give $(\text{R-IAN})\text{AlMe}_2$, and these complexes exhibited substantial activity in the polymerization of ethylene. This behavior is counterintuitive on the basis of an analysis of the Lewis basicity of the three nitrogen types present in **2a** and underscores the care one must apply when interpreting polymerization activity of catalysts bearing amido-type ligands with aluminum activating agents. Although it remains to be determined whether this behavior is more general for planar and/or hindered β-diketimines, we have established it in the context of a β-diketimine that binds at the extreme as a β-amido Schiff base. Future studies are aimed at further clarification of this guideline and a more precise weighting of the roles of both steric and electronic effects on transmetalation.

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Supporting Information Available: Text giving general experimental procedures and spectral data for all new compounds, and a CIF file giving complete X-ray structural data. This material is available free of charge via the Internet at http://pubs.acs.org.

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[30] (a) Ihara, E.; Young, V. G., Jr.; Jordan, R. F. *J. Am. Chem. Soc.* **1998**, *120*, 8277. (b) Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* **1997**, *119*, 8125.