Chiral Biarylamido Complexes of Zirconium

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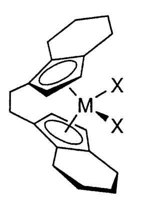
The palladium-catalyzed arylation of 2,2′-diamino-6,6′-dimethylbiphenyl with (variously) bromo-3,5-di-*tert*-butylbenzene, 2-bromopyridine, 2-methylbromopyridine, bromomesitylene, and 2-bromo-4-methylanisole gives three C_2-symmetric and three C_1-symmetric biaryl-bridged diamino proligands H_2L. The subsequent amine elimination (protonolysis) reactions of these with tetrakis(dimethylamido)zirconium yields a range of crystalline complexes $[Zr(L)(NMe_2)_2]$. X-ray crystallography reveals molecular structures of five examples with ligated amido, aminopridinato, and aminoanisolato units.

Introduction

For metal complexes to be successful in enantioselective catalysis, the chirality of the system must be well expressed in the region of the active coordination sites. In early transition metal and lanthanide chemistry, the number of systems which achieve this is rather limited. Perhaps the best examples are provided by the group 4 *ansa*-metallocenes such as **I**.[1,2] In such complexes, cis-coligands in the symmetry-equivalent active sites experience a high degree of diastereofacial discrimination. This manifests itself in the excellent levels of tacticity control achieved by the racemic catalysts in α-alkene polymerization,[3] and the success of nonracemic catalysts in enantioselective processes.[4]



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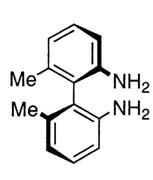

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Amido (R_2N^-) ligands are widespread in early metal chemistry, but reports of chiral nonracemic diamido ligands, which might provide an alternative to the *ansa*-Cp_2 unit, are rare. There are a number of examples of 1,2-daminocyclohexane-based systems, most notably the sulfonamides[5] which have been found to catalyze the addition of dialkylzinc reagents to aldehydes with high enantioselectivity. Cloke et al. have reported a zirconium complex in which two amido groups are linked by the atropisomeric 2,2′-diamino-6,6′-dimethylbiphenyl backbone in **1**.[6] Tilley and co-workers have reported an yttrium complex containing a similar ligand system that gave high enantioselectivity in the hydrosilation of norbornene.[7]

We have been interested in the design of inherently chiral ligands, and particularly a group of quadridentate N_2O_2 Schiff bases based on **1**, which give metallocene-like complex structures.[8] Our most successful catalyses using these Schiff-base ligands have used middle and later transition metals,[9] the early metal catalysts suf-

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(1) (a) Ewen, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 6355. (b) Ewen, J. A.; Atwood, J. L.; Zhang, H. *J. Am. Chem. Soc.* **1987**, *10*9, 6544. (c) Kaminsky, W.; Kulper, K.; Brintzinger, H. H.; Wild, F. R. W. P. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 507. (d) Kaminsky, W.; Ahlers, A.; Moller-Lindenhof *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1216. (e) Roll, W.; Brintzinger, H. H.; Rieger, B.; Zolk, R. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 279. (f) Spaleck, W.; Antberg, M.; Rohrmann, J.; Winter, A.; Bachmann, B.; Kiprof., P.; Behm, J.; Hermann W. A. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1347. (g) Kondakov, D. Y.; Negishi, E. *J. Am. Chem. Soc.* **1995**, *117*, 10771. (h) Schaverien, C. J.; Ernst, R.; Schut, P.; Skiff, W. M.; Resconi, L.; Barbassa, E.; Balboni, D.; Dubitsky, Y. A.; Orpen, A. G.; Mercandelli, P.; Moret, M.; Sironi, A. *J. Am. Chem. Soc.* **1998**, *120*, 9945. (i) Negishi, E. *Chem. Eur. J.* **1999**, *5*, 411. (j) Schaverien, C. J.; Ernst, R.; Schut, P.; DallOcco, T. *Organometallics* **2001**, *20*, 3436.

(2) (a) Haltermann, R. L. *Chem. Rev.* **1992**, *92*, 965. (b) Chen, Z.; Haltermann, R. L. *J. Am. Chem. Soc.* **1992**, *114*, 2276. (c) Haltermann, R. L.; Ramsey, T. M.; Chen, Z. *J. Org. Chem.* **1994**, *59*, 2642. (d) Giardello, M. A.; Yamamoto, Y.; Brard, L.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, 117, 3276. (e) Urabe, H.; Yoshikawa, K.; Sato, F. *Tetrahedron Lett.* **1995**, *36*, 5595. (f) Mitchell, J. P.; Hajela, S.; Brookhart, S. K.; Hardcastle, K. L.; Henling, L. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 1045. (g) Taber, D. F.; Balijepalli, B.; Liu, K. K.; Kong, S.; Rheingold A. L.; Askham, F. R. *J. Org. Chem.* **1999**, *64*, 4525. (h) Ewen, J. A.; Elder, M. J.; Jones, R. L.; Rheingold, A. L.; Liable-Sands, L. M.; Sommer, R. D. *J. Am. Chem. Soc.* **2001**, *123*, 4763.

(3) (a) Brintzinger, H. H.; Fischer, D.; Mulhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143. (b) Resconi, L.; Cavallo, L.; Fait, A.; Piemontes, F. *Chem. Rev.* **2000**, *100*, 1253.

(4) (a) Hong, Y.; Kuntz, B. A.; Collins, S. *Organometallics* **1993**, *12*, 964. (b) Jaquith, J. B.; Guan, J. Y.; Wang, S. T.; Collins, S. *Organometallics* **1995**, *14*, 1079. (c) Jaquith, J. B.; Levy, C. J.; Bondar, G. V.; Wang, S.; Collins, S. *Organometallics* **1998**, *17*, 914. (d) Willoughby, C. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 8952. (e) Carter, M. B.; Schiott, B.; Gutierrez, A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 11667. (f) Didiuk, M. T.; Johannes, C. W.; Morken, J. P.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1995**, *117*, 7097. (g) Verdauguer, X.; Lange, U. E. W.; Reding, M. T.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 6784. (h) Hicks, F. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 11688. (i) Yamaura, Y.; Hyakutake, M.; Mori, M. *J. Am. Chem. Soc.* **1997**, *119*, 7615.

(5) (a) Ackermann, L.; Bergman, R. G. *Org. Lett.* **2002**, 4, 1475. (b) Pritchett, S.; Woodmansee, D. H.; Gantzel, P.; Walsh, P. J. *J. Am. Chem. Soc.* **1998**, *120*, 6423 and references therein.

(6) Cloke, F. G. N.; Geldbach, T. J.; Hitchcock, P. B.; Love, J. B. *J. Organomet. Chem.* **1996**, *506*, 343.

(7) Gountchev, T. I.; Tilley, T. D. *Organometallics* **1999**, *18*, 5661.

(8) Woodman, P. R.; Munslow, I. J.; Hitchcock, P. B.; Scott, P. *J. Chem. Soc., Dalton Trans.* **1999**, 4069.

(9) (a) Sanders, C. J.; Gillespie, K. M.; Bell, D.; Scott, P. *J. Am. Chem. Soc.* **2000**, *122*, 7132. (b) Gillespie, K. M.; Crust, E. J.; Deeth, R. J.; Scott, P. *Chem. Commun.* **2001**, 785. (c) Munslow, I. J.; Gillespie, K. M.; Deeth, R. J.; Scott, P. *Chem. Commun.* **2001**, 1638.

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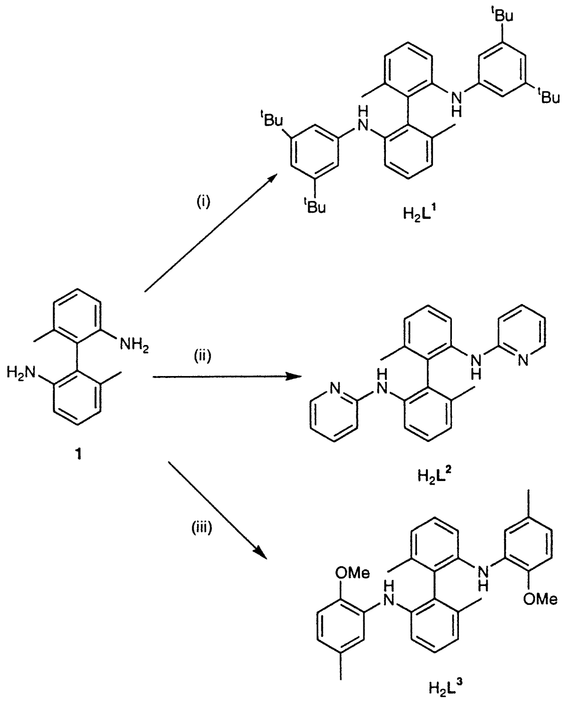
Scheme 1. Synthesis of the C_2-Symmetric Diamine Ligands H_2L^1, H_2L^2, and H_2L^3 [a]



[a] Reagents and conditions: all reactions used Na(OBu^t) in toluene at 90 °C. (i) bromo-3,5-di-*tert*-butylbenzene, $[Pd_2(DBA)_3]$, BINAP; (ii) 2-bromopyridine, $[Pd_2(DBA)_3]$, DPPP; (iii) 2-bromo-4-methylanisole, $[Pd_2(DBA)_3]$, BINAP.

fering from decomposition via 1,2-migratory insertion reactions[10] and radical processes.[11] While these troublesome reactions can be eliminated almost completely in some instances,[12] we recognize that it will be difficult to produce complexes as durable and robust as the metallocenes using Schiff-base ligands. In response to this we set out to synthesize a range of new diamido ligands based on the diamine **1** with bulky and heteroatom donor aryl groups.

Results and Discussion

Ligand Design and Synthesis. 2,2′-Diamino-6,6′-dimethylbiphenyl (**1**) reacts readily with 2 equiv of bromo-3,5-di-*tert*-butylbenzene, 2-bromopyridine, and 2-bromo-4-methylanisole under palladium catalysis[13] to give the corresponding C_2-symmetric diamines $H_2\mathbf{L^1}$, $H_2\mathbf{L^2}$, and $H_2\mathbf{L^3}$ in good yield (Scheme 1). The analogous reactions with bromomesitylene and 2-bromo-6-methylpyridine gave mixtures of products.

Previous examples of arylated diamido ligand systems include McConville's bis(arylaminomethyl)pyridines,[14] Schrock's tridentate diamido ligands $(ArNHCH_2CH_2)_2E$ (E = N, or O; Ar = 2,6-$Me_2C_6H_3$, 2,6-$Et_2C_6H_3$, and 2,6-*i*-$Pr_2C_6H_3$),[15] Gibson's bis(arylsilylaminoethane) and 2,6-bis(dimethylphenylamino)diphenylsilane systems,[16] and Bochmann's dimethylethylene bridged bis-phenylamine ligand.[17] In each of the above cases the aryl groups are introduced by treating the *N*-lithiated anilines with an appropriate precursor. Schrock and co-workers have previously used Pd-catalyzed amine arylation in the synthesis of amido ligands.[15e]

We have noted in the above reactions i and iii (Scheme 1) that the rate of the first arylation of diamine **1** is generally much faster than that of the second, making it possible to monoarylate with high selectivity. This has some precedent in the work of Beletskaya et al.,[18] and opens up the possibility of synthesis of unsymmetrically substituted analogues of $H_2\mathbf{L^{1-3}}$ via sequential arylations. Schrock and co-workers have prepared an unsymmetrically substituted chiral diamine complex system based on *cis*-2,5-bis(amidomethyl)tetrahydrofuran using a protecting group strategy.[15(f)]

Hence the reactions of **1** with 0.5 equiv of 3,5-di-*tert*-butylbromobenzene, bromomesitylene, and 2-bromo-4-methylanisole yield the respective monoarylated products **2**, **3**, and **4** in good yields (>70%). In the crude materials, the disubstituted species were observed as minor products (<10%) necessitating the use of flash chromatography to yield analytically pure compounds. Increasing the stoichiometric ratio of diamine to bromoarene leads to still higher chemoselectivity for monosubstited product. In the case of **4**, lowering the catalyst loading effects a similar result, but there is a concomitant increase in reaction time. To exemplify the method, a chiral nonracemic version of **4** was prepared in essentially the same manner.

The unsymmetrically substituted diamine $H_2\mathbf{L^4}$ can be synthesized by arylation of **2** with 2-bromo-4-methylanisole or **4** with 2,5-di-*tert*-butylbromobenzene (Scheme 2). The latter is the preferred route since the precursor **4** is obtained in higher yield (vide supra) and is easier to purify than is **2**. The diamine $H_2\mathbf{L^4}$ is obtained in good yield as a pale yellow crystalline solid. The reactions of **3** and **4** with 2-bromo-6-methylpyridine under Pd/phosphine catalysis gave the expected diamines $H_2\mathbf{L^5}$ and $H_2\mathbf{L^6}$ in good yield. While these reactions require the presence of a slight excess of the bromoarene, the final products are readily isolated as a yellow crystalline solid and a viscous oil, repectively.

Zirconium Complexes of the C_2-Symmetric Diamine Ligands. The C_2-symmetric proligand $H_2\mathbf{L^1}$

(10) Woodman, P. R.; Alcock, N. W.; Munslow, I. J.; Sanders, C. J.; Scott, P. *J. Chem. Soc., Dalton Trans.* **2000**, 3340.

(11) Woodman, P. R.; Sanders, C. J.; Alcock, N. W.; Munslow, I. J.; Hitchcock P. B.; Scott, P. *New J. Chem.* **1999**, *23*, 815.

(12) Knight, P. D.; Clarke, A. J.; Kimberley, B. S.; Jackson R. A.; Scott, P. *Chem. Commun.* **2002**, 352.

(13) Yang, B. H.; Buchwald, S. L. *J. Organomet. Chem.* **1999**, *576*, 125.

(14) (a) Scollard, J. D.; McConville, D. H.; Vittal, J. J. *Macromolecules* **1996**, *29*, 5241. (b) Guerin, F.; McConville, D. H.; Vittal, J. J. *Organometallics* **1995**, *14*, 3154. (c) Guerin, F.; McConville, D. H.; Payne, N. C. *Organometallics* **1996**, *15*, 5085. (d) Guerin, F.; McConville, D. H.; Vittal, J. J. *Organometallics* **1996**, *15*, 5586. (e) Guerin, F.; McConville, D. H.; Vittal, J. J.; Yap, G. A. P. *Organometallics* **1998**, *17*, 5172.

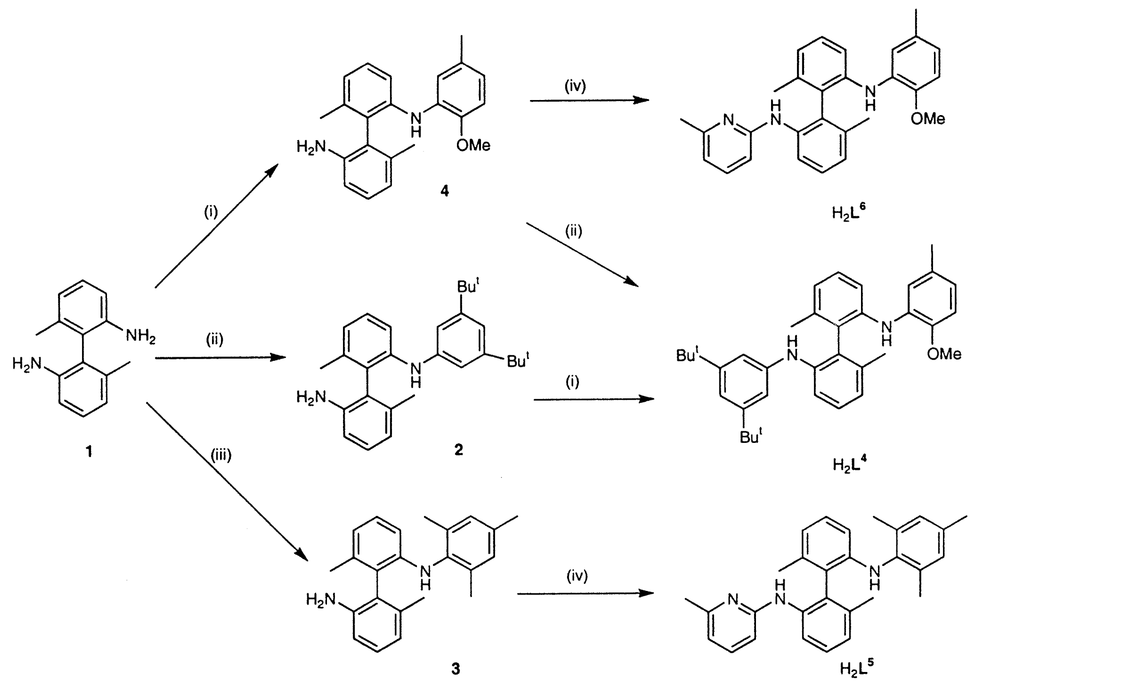
(15) (a) Schrock, R. R.; Schattenmann, F.; Aizenberg, M.; Davis, W. M. *Chem. Commun.* **1998**, 199. (b) Aizenberg, M.; Turculet, L.; Davis, W. M.; Schattenmann, F.; Schrock, R. R. *Organometallics* **1998**, *17*, 4795. (c) Schrock, R. R.; Seidel, S. W.; Schrodi Y.; Davis, W. M. *Organometallics* **1999**, *18*, 428. (d) Graf, D. D.; Schrock, R. R.; Davis, W. M.; Stumpf, R. *Organometallics* **1999**, *18*, 843. (e) Lan-Chang, L.; Schrock, R. R.; Davis, W. M.; McConville, D. H. *J. Am. Chem. Soc.* **1999**, *121*, 5797. (f) Flores, M. A.; Manzoni, M. R.; Baumann, R.; Davis, W. M.; Schrock, R. R. *Organometallics* **1999**, *18*, 3220. (g) Baumann, R.; Stumpf, R.; Davis, W. M.; Liang, L.-C.; Schrock, R. R. *J. Am. Chem. Soc.* **1999**, *121*, 7822. (h) Schrock, R. R.; Baumann, R.; Reid, S. M.; Goodman, J. T.; Stumpf, R.; Davis, W. M. *Organometallics* **1999**, *18*, 3649.

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

(17) Male, N. A. H.; Thornton-Pett, M.; Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1997**, 2487.

(18) Beletskaya, I. P.; Bessmertnyk, A. G.; Guilard, R. *Tetrahedron Lett.* **1997**, *38*, 6462

Scheme 2. Synthesis of the Unsymmetrically Substituted Diamines H_2L^1, H_2L^2, and H_2L^3 Proligands via Sequential Monoarylations[a]



[a] Reagents and conditions: all reactions used Na(OBu^t) in toluene at 90 °C. (i) 2-bromo-4-methylanisole, [Pd_2(DBA)$_3$], BINAP; (ii) bromo-3,5-di-*tert*-butylbenzene, [Pd_2(DBA)$_3$], BINAP; (iii) bromomesitylene, [Pd_2(DBA)$_3$], BINAP; (iv) 2-bromo-6-methylpyridine, [Pd_2(DBA)$_3$], DPPP.

reacts with Zr(NMe$_2$)$_4$ in toluene at room temperature to give the crystalline zirconium amido complex [**L^1**Zr(NMe$_2$)$_2$] (eq 1). Most 4-coordinate (tetrahedral) zirconium amido complexes contain silylamido units,[16,17,19] but examples with aryl and other substiuents are known.[20]

$$H_2\mathbf{L^1} + Zr(NMe_2)_4 \rightarrow [\mathbf{L^1}Zr(NMe_2)_2] + 2NMe_2H \quad (1)$$

The ^{1}H and ^{13}C NMR NMR spectra of [**L^1**Zr(NMe$_2$)$_2$] are consistent with a C_2-symmetric complex in solution. The molecular structure determined by X-ray crystallography (Figure 1) shows the monomeric structure with a distorted tetrahedral geometry about zirconium. As can be seen in Figure 1a, C(29) lies further away from the N(2)−Zr(1)−N(1) plane (+0.63 Å) than does C(14) (−0.10 Å), although of course this difference is not likely to persist in solution. The two di-*tert*-butylphenyl rings also adopt slightly different orientations: that containing C(29) is twisted 44.5° with respect to the N(2)−Zr(1)−N(1) plane while the phenyl ring containing C(14) is twisted by only 24.0°. One effect of the combined orientations of these rings is that the dimethylamido substituents experience very different steric environments, as can be seen in Figure 1b. The zirconium-to-diamido nitrogen bond lengths in **L^1**Zr(NMe$_2$)$_2$ [ca. 2.11 Å] are in the middle-to-high end of the range for such distances in similar tetrahedral zirconium environments [1.999−2.214 Å].[16,17,19] While the sum of the angles around N(1) and N(2) [355.93° and 359.93°] indicates sp^2 hybridization, in both cases the individual Zr−N−C$_{ipso}$ angles are significantly distorted away from ideal at 133.63° and 141.83° away from Zr. This is ascribed to the steric influence of the *tert*-butyl groups.

The potentially quadridentate H$_2$**L^2** gives a complex mixture of products when treated with Zr(NMe$_2$)$_4$ which we were not able to separate, although the ^{1}H NMR spectrum of the crude reaction mixture does indicate complete deprotonation of the diamine ligand. In contrast, the reaction between H$_2$**L^3** and Zr(NMe$_2$)$_4$ in toluene gives exclusively the desired monomeric C_2-symmetric complex [**L^3**Zr(NMe$_2$)$_2$]. Removal of the toluene under reduced pressure yields a foamy material, but the complex may be recrystallized from pentane in good yield. Zirconium amido complexes that contain additional donor functionalities at the periphery of the ligand are relatively rare.[17,21]

An X-ray crystallographic study on [**L^3**Zr(NMe$_2$)$_2$] revealed two independent but similar molecules in the asymmetric unit; the molecular structure of one is shown in Figure 2 with selected bond lengths and angles in Table 1. Both methoxy groups are bound to the metal center forming five-membered planar chelate rings with bite angles of 68.99(11)° and 67.32(11)° for N(1)−Zr(1)−O(1) and N(2)−Zr(1)−O(2), respectively. Both chelate rings are essentially planar. The 6-coordinate zirconium atom adopts, as a result of the constaints of the ligand, a geometry strongly distorted from octahedral. Interestingly, the coordination mode of the **L^3** ligand is different from that expected on the basis of the ^{1}H and ^{13}C NMR spectra which indicate the presence of C_2-symmetry on these chemical shift time scales. In the solid-state

(19) (a) Joen, Y. M.; Park, S. J.; Heo, J.; Kim, K. *Organometallics* **1998**, *17*, 3161. (b) Grocholl, L.; Huch, V.; Stahl, L.; Staples, R. J.; Steinhart, P.; Johnson, A. *Inorg. Chem.* **1997**, *36*, 4451. (c) Lorber, C.; Donnadieu, B.; Choukroun, R. *Organometallics* **2000**, *19*, 1963.

(20) (a) Warren, T. H.; Schrock, R. R.; Davis, W. M. *Organometallics* **1998**, *17*, 308. (b) Latesky, S. L.; McMullen, A. K.; Niccolai, G. P.; Rothwell, I. P.; Huffman, J. C. *Organometallics* **1985**, *4*, 1896.

(21) Amor, F.; Butt, A.; Du Ploy, K. E.; Spaniol, T. P.; Okuda, J. *Organometallics* **1998**, *17*, 5836.

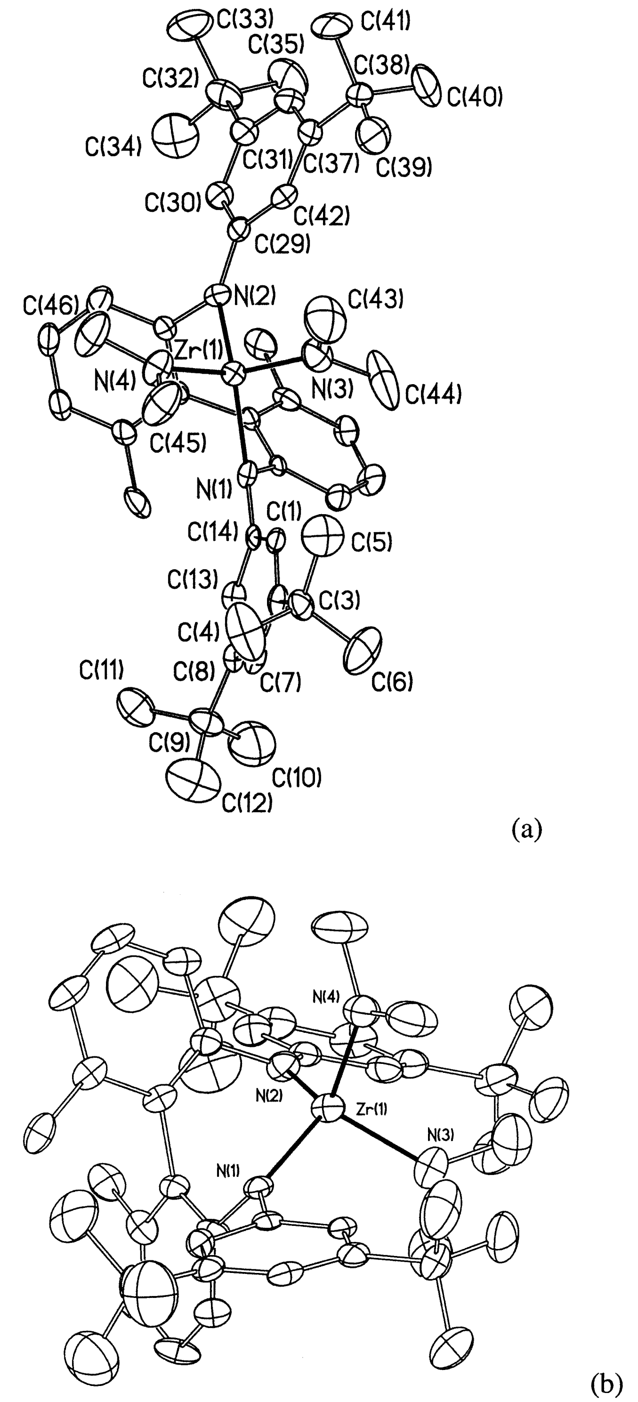


Figure 1. Views of the molecular structure of [$\mathbf{L^1}$Zr(NMe_2)$_2$] (a) along the approximate C_2 axis and (b) showing the different steric environments of the dimethylamido units.

structure, one methoxy donor group is effectively trans to one of the amidos of the ligand groups while the other is cis. Clearly then, in contrast to the case of our titanium Schiff-base complexes based on **1**,[10] the β-cis orientation of [$\mathbf{L^3}$Zr(NMe_2)$_2$] undergoes facile molecular rearrangement, possibly via reversible decoordination of methoxy groups. The Zr−O distances in [$\mathbf{L^3}$Zr(NMe_2)$_2$] (Table 1) fall within the range seen in the few examples for MeO→Zr dative interactions.[21,22] The Zr(1)−O(1) and Zr(1)−O(2) distances are significantly different [2.389(3) and 2.466(3) Å, respectively], perhaps as a result of the differential angle strains resulting from their twist orientations with respect to the biaryl backbone. The Zr−N(biaryl) distances in [$\mathbf{L^3}$Zr(NMe_2)$_2$] (ca. 2.15 Å) are marginally longer than those in [$\mathbf{L^1}$Zr(NMe_2)$_2$] (ca. 2.11 Å).

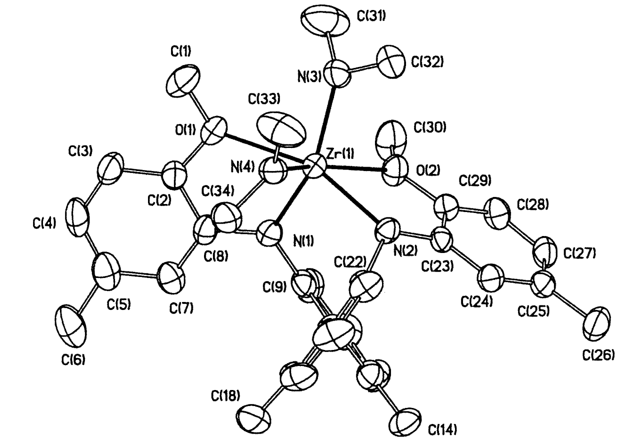


Figure 2. Molecular structure of [$\mathbf{L^3}$Zr(NMe_2)$_2$].

Zirconium Complexes of the C_1-Symmetric Diamine Ligands. The reaction of 1 equiv of $H_2\mathbf{L^4}$ with Zr(NMe_2)$_4$ gave the desired C_1-symmetric complex [$\mathbf{L^4}$Zr(NMe_2)$_2$] (eq 2). X-ray quality crystals of this five-

$$H_2\mathbf{L^4} + Zr(NMe_2)_4 \rightarrow [\mathbf{L^4}Zr(NMe_2)_2] + 2NMe_2H \quad (2)$$

coordinate complex were obtained from a concentrated pentane solution at 0 °C. The geometry around the Zr atom may be described as a distorted trigonal bipyramid (Figure 3), with the methoxy O(1) and the biaryldiamido N(2) occupying the axial positions. In this arrangement the methoxy group sits trans to the biaryl-diamido group on the opposite arm of the ligand in a *mer*-type arrangement similar to the [NON]MMe$_2$ (M = Ti, Zr, and Hf) systems.[15a,b,f,g] The five-membered anisolyl chelate ring has similar distances and angles to those in [$\mathbf{L^3}$Zr(NMe_2)$_2$] [e.g. O(1)−Zr(1)−N(1) = 68.07(17)° cf. 68.99(11)°, and Zr−O(1) = 2.382(4) Å cf. 2.389(3) Å]. The di-*tert*-butylphenyl ring, which is otherwise free to rotate, is oriented such that it is essentially coplanar with the amido Zr(1)−N(2)−C(22) plane, perhaps in order to maximize overlap of the p_z "lone pair" at N(2) with the π system of the phenyl ring. This is in contrast to Schrock's aryl-substituted [NON^{2-}] systems where the planes of the phenyl rings are generally twisted at 90° to the amido planes. The presence of *o*-alkyl substituents on the aryl rings are likely to disfavor such an arrangement in the latter systems. This phenyl ring is also close to coplanarity with the Zr(1)−N(4) bond.

The Zr−N(biaryl) distances in five-coordinate [$\mathbf{L^4}$Zr(NMe_2)$_2$] [ca. 2.129 Å] are intermediate between those of the four- and six-coordinate complexes [$\mathbf{L^1}$Zr(NMe_2)$_2$]-[ca. 2.108 Å] and [$\mathbf{L^3}$Zr(NMe_2)$_2$] [ca. 2.149 Å].

A similar reaction of $H_2\mathbf{L^5}$ with Zr(NMe_2)$_4$ does not yield the desired [$\mathbf{L^5}$Zr(NMe_2)$_2$] species. Instead the ^{1}H

(22) (a) Evans, W. J.; Ansari, M. A.; Ziller, J. W. *Inorg. Chem.* **1999**, *38*, 1160. (b) van der Zeijden, A. A. H.; Mattheis, R.; Frohlich, R *Acta Crystallogr., Sect. C* **1998**, *54*, 458. (c) van der Zeijden, A. A. H.; Mattheis, R.; Frohlich, R.; Zippel, F. *Inorg. Chem.* **1997**, *36*, 4444. (d) van der Zeijden, A. A. H.; Mattheis, R.; Frohlich, R *Organometallics* **1997**, *16*, 2651. (e) Caselli, A.; Giannini, L.; Solari, E.; Floriani, C.; Chiesi-Cilla, A.; Rizzoli, C.; Re, N.; Sgamelloti, A. *Organometallics* **1997**, *16*, 5457. (f) Giannini, L.; Caselli, A.; Solari, E.; Floriani, C.; Re, N.; Chiesi-Cilla, A.; Rizzoli, C. *Organometallics* **1997**, *16*, 5457.

Table 1. Crystallographic Data, Collection Parameters, and Refinement Parameters for $L^1Zr(NMe_2)_2$, $L^3Zr(NMe_2)_2$, $(HL^5)_2Zr(NMe_2)_2 \cdot C_5H_{12}$, $L^4Zr(NMe_2)_2$, and $L^6Zr(NMe_2)_2$

	$L^1Zr(NMe_2)_2$	$L^3Zr(NMe_2)_2$	$(HL^5)_2Zr(NMe_2)_2 \cdot C_5H_{12}$	$L^4Zr(NMe_2)_2$	$L^6Zr(NMe_2)_2$
empirical formula	$C_{46}H_{66}N_4Zr$	$C_{34}H_{42}N_2O_2Zr$	$C_{67}H_{84}N_8Zr$	$C_{40}H_{54}N_4OZr$	$C_{32}H_{39}N_5OZr$
fw	766.25	629.94	1092.64	698.09	600.90
cryst size (mm^3)	0.22 × 0.20 × 0.06	0.31 × 0.23 × 0.14	0.26 × 0.18 × 0.11	0.35 × 0.27 × 0.15	0.21 × 0.14 × 0.08
cryst system	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_12_12_1$	$P2_1$	$P2_1/c$	Ia	$P2_1/c$
a (Å)	10.4593(10)	11.587(10)	20.250(7)	14.4964(19)	10.6816(16)
b (Å)	13.2155(13)	16.203(14)	20.197(9)	18.818(3)	10.8516(16)
c (Å)	31.978(3)	17.005(15)	16.306(5)	15.159(2)	26.123(4)
α (deg)	90	90	90	90	90
β (deg)	90	92.256(17)	110.313(18)	113.613	99.99(2)
γ (deg)	90	90	90	90	90
V	4420.2 (8)	3190(5)	6254(4)	3788.9(9)	2982.0(8)
D_{calcd} (Mg/m^3)	1.151	1.312	1.160	1.224	1.338
μ (mm^{-1})	0.282	0.380	0.221	0.325	0.401
F_{000}	1640	1320	2328	1480	1256
total reflns	27481	21738	29681	12634	18862
independent reflns	7783	14733	8159	6707	7272
R_{int}	0.1150	0.0275	0.1166	0.065	0.1062
data/restraints/ parameters	7783/18/479	14733/1/759	8159/133/759	6707/20/429	7272/0/362
$R1$,[a] [$I > 2\sigma(I)$]	0.0797	0.0455	0.0895	0.0574	0.0700
$wR2$[b]	0.1388	0.0970	0.2304	0.1282	0.1363
GoF[c] on F^2	1.110	1.034	1.188	0.962	1.008
abs struct parameter[b]	0.03(6)	0.01(3)		0.00(2)	

[a] Conventional $R = \sum||F_o| - |F_c||/\sum|F_o|$ for observed reflections having $F_o^2 > 2\sigma(F_o^2)$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$ for all data. [c] GoF $= [\sum w(F_o^2 - F_c^2)^2/(\text{no. of unique reflections} - \text{no. of parameters})]^{1/2}$. [b] Checked by refinement of the $\Delta f''$ multiplier.

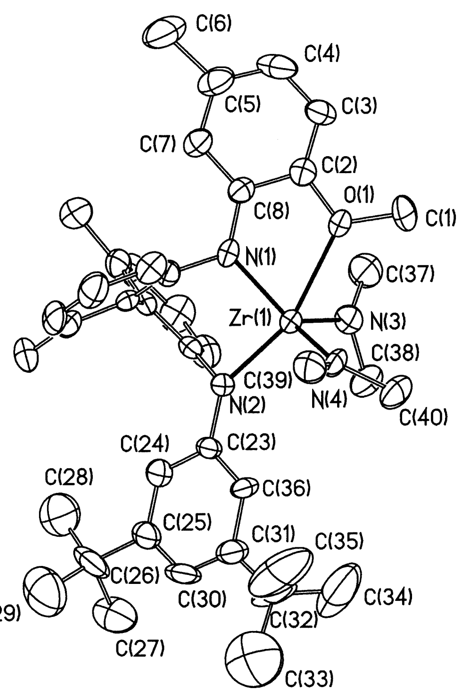


Figure 3. Molecular structure of [$L^4Zr(NMe_2)_2$].

NMR spectrum indicated the presence of a species [$L^5{}_2ZrX_2$] in which only the NH group adjacent to the pyridine had undergone deprotonation. We have previously noted the sluggish deprotonation of mesityl-substituted amines,[23] which may be attributed to the highly sterically demanding nature of the −NHMes unit. Here, intramolecular metalation of these units is evidently unfavorable in comparison to intermolecular reaction with a second aminopryridine proligand. A subsequent reaction between 2 equiv of H_2L^5 and $Zr(NMe_2)_4$ (eq 3) gives exclusively the monomeric zirconium bis-aminopyridinato complex, [$(HL^5)_2Zr(NMe_2)_2$].

(23) Morton, C.; Gillespie, K. M.; Sanders, C. J.; Scott, P. *J. Organomet. Chem.* **2000**, *606*, 141.

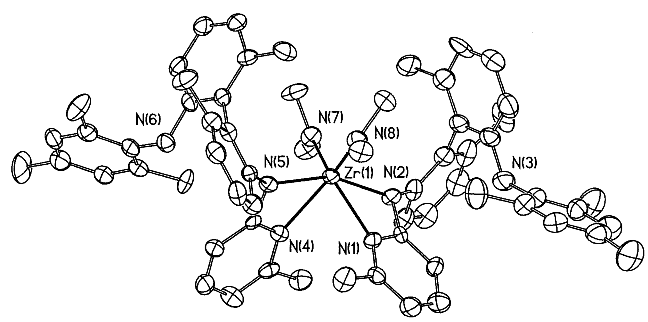


Figure 4. Molecular structure of [$(HL^5)_2Zr(NMe_2)_2$].

$$2H_2L^5 + Zr(NMe_2)_4 \rightarrow [(HL^5)_2Zr(NMe_2)_2] + 2NMe_2H \quad (3)$$

X-ray quality crystals of [$(HL^5)_2Zr(NMe_2)_2$] were obtained from a concentrated pentane solution. The zirconium center is coordinated by two aminopyridinate units (Figure 4). Both biaryl units within the complex have the same absolute configuration, i.e., the complex is homochiral with respect to these units (vide infra). The severe trigonal distortion of the metal geometry away from octahedral is a consequence of the small bite angles [N(2)−Zr(1)−N(1) = 57.7(2)° and N(5)−Zr(1)−N(4) = 57.8(2)°] of the aminopyridinate ligands. The molecule is C_2-symmetric such that the dimethylamido groups are mutually cis, the amido nitrogens from each ligand unit are mutually trans, and the pyridyl donor nitrogens are mutually cis to each other. This arrangement minimizes the steric interaction between the methyl groups on the pyridine rings and the bulky biaryl fragments on each ligand.

Since the proligand H_2L^5 used in the synthesis of this complex was racemic we might expect the formation of two sets of diastereomers, ignoring for the moment the

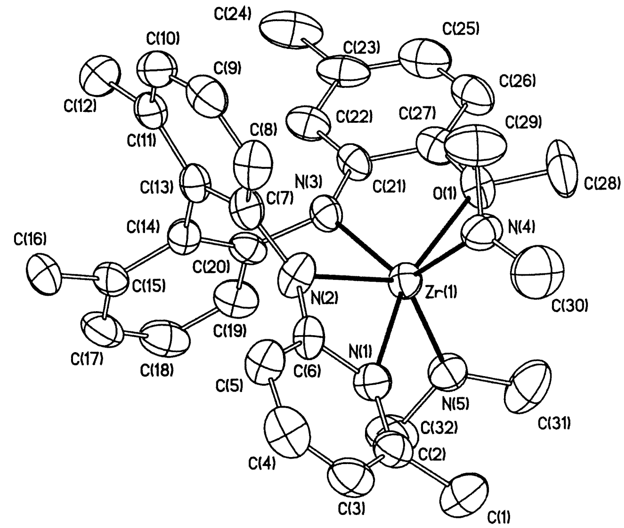


Figure 5. Molecular structure of [($\mathbf{L^6}$)Zr(NMe_2)$_2$].

chirality-at-metal: homochiral (*R*,*R*)/(*S*,*S*) and meso (*R*,*S*)/(*S*,*R*). Examination of crude reaction mixtures indicates that only one such pair is formed, i.e. the homochiral system. Given that intermolecular exchange of aminopyridinate ligands does not occur in related systems[24] this diastereoselection must be kinetically controlled, i.e., the formation of the homochiral complex is much faster than that of the meso diastereomer. In a conceptually similar pyridinealcoholate system, Jordan measured a kinetic diastereomeric ratio of ca. 97:3.[25]

The complex [(H$\mathbf{L^5}$)$_2$Zr(NMe_2)$_2$] is also chiral-at-metal.[26] We are currently investigating a number of rather simpler but related complexes in the hope that we will be able to predetermine[27] the absolute sense of this element of chirality.

The C_1-symmetric proligand $H_2\mathbf{L^6}$ reacts in a manner similar to $H_2\mathbf{L^4}$ with 1 equiv of Zr(NMe_2)$_4$ in toluene to yield the monomeric complex [$\mathbf{L^6}$Zr(NMe_2)$_2$] after crystallization from pentane. The ^{1}H and ^{13}C NMR spectra exhibit two distinct NMe_2 resonances. The molecular structure is shown in Figure 5. The six-coordinate geometry is close to trigonal prismatic. The five-membered chelate ring containing the anisole chelate has similar bite angle (68.24°) and bond lengths to those in [$\mathbf{L^3}$Zr(NMe_2)$_2$] and [$\mathbf{L^4}$Zr(NMe_2)$_2$]. However, while the Zr(1)−N(1)$_{pyridine}$ distance is comparable to those observed in [(H$\mathbf{L^5}$)$_2$Zr(NMe_2)$_2$], the Zr(1)−N(2) distance [2.204(4) Å] is shorter than the analogous distances in this complex. This could be attributed to the absence of a destabilizing trans influence on this bond in [$\mathbf{L^6}$Zr(NMe_2)$_2$], unlike in [($\mathbf{L^5}$)$_2$Zr(NMe_2)$_2$] where the amido N atoms are mutually trans.

Concluding Remarks

The versatile palladium-catalyzed arylation of **1** with simple and donor-atom functionalized arenes provides an efficient route to a range of new chiral amido ligand environments with various denticities and geometries.

Table 2. Selected Bond Lengths and Angles for the C_2-Symmetric Zirconium Diamides $\mathbf{L^1}$Zr(NMe_2)$_2$ and $\mathbf{L^3}$Zr(NMe_2)$_2$

$\mathbf{L^1}$Zr(NMe_2)$_2$	$\mathbf{L^3}$Zr(NMe_2)$_2$ (1 of 2 molecule in asymmetric unit)
Zr(1)−N(1) = 2.114(5)	Zr(1)−N(1) = 2.149(3) ; Zr(2)−N(5) = 2.144(3)
Zr(1)−N(2) = 2.102(5)	Zr(1)−N(2) = 2.148(3); Zr(2)−N(6) = 2.155(3)
Zr(1)−N(3) = 2.021(5)	Zr(1)−N(3) = 2.050(3); Zr(2)−N(7) = 2.045(3)
Zr(1)−N(4) = 2.015(5)	Zr(1)−N(4) = 2.023(3); Zr(2)−N(8) = 2.042(3)
	Zr(1)−O(1) = 2.389(3); Zr(2)−O(3) = 2.485(3)
	Zr(1)−O(2) = 2.466(3) ; Zr(2)−O(4) = 2.386(3)
N(2)−Zr(1)−N(1) = 119.22(17)	O(1)−Zr(1)−O(2) = 115.86(11)
N(3)−Zr(1)−N(1) = 103.2(2)	N(1)−Zr(1)−O(1) = 68.99(11)
N(4)−Zr(1)−N(1) = 111.8(2)	N(2)−Zr(1)−O(1) = 158.09(10)
N(3)−Zr(1)−N(2) = 111.0(2)	N(3)−Zr(1)−O(1) = 82.97(12)
N(4)−Zr(1)−N(2) = 107.0(2)	N(4)−Zr(1)−O(1) = 82.98(11)
N(4)−Zr(1)−N(3) = 103.5(2)	N(1)−Zr(1)−O(2) = 82.40(12)
	N(2)−Zr(1)−O(2) = 67.32(11)
	N(3)−Zr(1)−O(2) = 79.10(13)
	N(4)−Zr(1)−O(2) = 161.11(12)
	N(2)−Zr(1)−N(1) = 90.73(13)
	N(3)−Zr(1)−N(1) = 135.00(14)
	N(4)−Zr(1)−N(1) = 107.32(13)
	N(3)−Zr(1)−N(2) = 118.37(13)
	N(4)−Zr(1)−N(2) = 95.86(13)
	N(4)−Zr(1)−N(3) = 103.13(15)

We are currently engaged in the application of these and related complexes in enantioselective catalysis, and hope to be able to relate the relative efficiencies of the systems to the structural motifs we have recorded here.

Experimental Section

General Comments. All manipulations were carried out with standard Schlenk/glovebox techniques under an atmosphere of dry argon, except for the workup procedures for the ligands which were performed under aerobic conditions. Solvents were distilled from Na/K alloy (pentane, diethyl ether), potassium (THF), or sodium (toluene) under an atmosphere of dinitrogen. Deuterated benzene and toluene were heated to reflux in vacuo over potassium for 3 days, distilled under vacuum, degassed by 3 freeze−pump−thaw cycles, and stored in a glovebox. The reagent tris(dibenzylideneacetone)dipalladium [Pd_2(DBA)$_3$] was obatined from Strem. The reagents 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl [BINAP], 1,3-bis(diphenylphosphino)propane [DPPP], 2-bromopyridine, 2-bromo-6-methylanisole, 2-bromomesitylene, and Na(OBu^t) were obtained from Aldrich and used as purchased. Zr(NMe_2)$_4$,[28] 2,2′-diamino-6,6′-dimethylbiphenyl **1**,[29] and 1-bromo-3,5-di-*tert*-butylbenzene[30] were synthesized by literature procedures.

H_2L^1. **1** (0.43 g, 2.10 mmol), 1-bromo-3,5-di-*tert*-butylbenzene (1.10 g, 4.20 mmol), [Pd_2(DBA)$_3$] (50.0 mg, 1.3 mol %), BINAP (58.0 mg, 2.2 mol %), and Na(OBu^t) (0.64 g, 6.65 mmol) were loaded into a Schlenk flask containing a magnetic stirrer bar. Toluene (50 mL) was added and the mixture was stirred at 90 °C for 24 h. A small aliquot was removed from the solution under argon and analyzed by TLC and ^{1}H NMR spectroscopy. Conversion was >90%. The toluene was removed in vacuo and diethyl ether was added (50 mL). The mixture

(24) Morton, C.; O'Shaughnessy, P. N.; Scott, P. *Chem. Commun.* **2000**, 2099.
(25) Kim, I.; Nishihara, Y.; Jordan, R. F.; Rodgers, R. D.; Rheingold, A. L.; Yap, G. P. A. *Organometallics* **1997**, *16* (15), 3314−3323.
(26) Brunner, H. *Angew. Chem., Int. Ed.* **1999**, *38*, 1194.
(27) Knof, U.; von Zelewsky, A. *Angew. Chem., Int. Ed.* **1999**, *38*, 302.
(28) Bradley, D. C.; Thomas, I. M. *J. Chem. Soc.* **1960**, 3857.
(29) (a) Carlin, R. B.; Foltz, G. E. *J. Am. Chem. Soc.* **1956**, *78*, 1997. (b) Meisenheimer, J.; Horing, M. *Chem. Ber.* **1927**, *60*, 1425.
(30) Bartlett, P. D.; Roha, M.; Stiles, R. M. *J. Am. Chem. Soc.* **1954**, *76*, 2349.

Table 3. Selected Bond Lengths and Angles for the C_1-Symmetric Zirconium Diamides $L^4Zr(NMe_2)_2$, $(HL^5)_2Zr(NMe_2)_2$, and $L^6Zr(NMe_2)_2$

$\mathbf{L^4}Zr(NMe_2)_2$	$(H\mathbf{L^5})_2Zr(NMe_2)_2$•$C_5H_{12}$	$\mathbf{L^6}Zr(NMe_2)_2$
Zr(1)−O(1) = 2.383(4)	Zr(1)−N(1) = 2.369(6)	Zr(1)−O(1) = 2.372(3)
Zr(1)−N(1) = 2.134(5)	Zr(1)−N(2) = 2.271(6)	Zr(1)−N(1) = 2.394(4)
Zr(1)−N(2) = 2.123(5)	Zr(1)−N(4) = 2.354(6)	Zr(1)−N(2) = 2.204(4)
Zr(1)−N(3) = 2.047(6)	Zr(1)−N(5) = 2.283(6)	Zr(1)−N(3) = 2.191(4)
Zr(1)−N(4) = 2.012(5)	Zr(1)−N(7) = 2.037(6)	Zr(1)−N(4) = 2.033(5)
	Zr(1)−N(8) = 2.043(6)	Zr(1)−N(5) = 2.047(4)
N(1)−Zr(1)−O(1) = 68.07(17)	N(2)−Zr(1)−N(1) = 57.7(2)	O(1)−Zr(1)−N(1) = 162.27(13)
N(2)−Zr(1)−O(1) = 157.65(15)	N(4)−Zr(1)−N(1) = 78.8(2)	O(1)−Zr(1)−N(2) = 134.84(14)
N(3)−Zr(1)−O(1) = 79.7(2)	N(5)−Zr(1)−N(1) = 104.0(2)	O(1)−Zr(1)−N(3) = 68.24(13)
N(4)−Zr(1)−O(1) = 94.2(2)	N(7)−Zr(1)−N(1) = 144.1(2)	O(1)−Zr(1)−N(4) = 78.46 (15)
N(2)−Zr(1)−N(1) = 96.3(2)	N(8)−Zr(1)−N(1) = 92.3(2)	O(1)−Zr(1)−N(5) = 89.27 (14)
N(3)−Zr(1)−N(1) = 130.4(15)	N(2)−Zr(1)−N(4) = 104.0(2)	N(2)−Zr(1)−N(1) = 57.30 (14)
N(4)−Zr(1)−N(1) = 111.2(2)	N(2)−Zr(1)−N(5) = 158.0(2)	N(3)−Zr(1)−N(1) = 129.45(13)
N(3)−Zr(1)−N(2) = 100.9(2)	N(7)−Zr(1)−N(2) = 90.5(2)	N(4)−Zr(1)−N(1) = 87.76(15)
N(4)−Zr(1)−N(2) = 106.6(2)	N(8)−Zr(1)−N(2) = 102.3(3)	N(5)−Zr(1)−N(1) = 87.28 (15)
N(4)−Zr(1)−N(3) = 107.82(16)	N(5)−Zr(1)−N(4) = 57.8(2)	N(3)−Zr(1)−N(2) = 80.15(14)
	N(7)−Zr(1)−N(4) = 95.4(2)	N(4)−Zr(1)−N(2) = 96.58(16)
	N(8)−Zr(1)−N(4) = 141.5(2)	N(5)−Zr(1)−N(2) = 130.19(16)
	N(7)−Zr(1)−N(5) = 102.4(2)	N(4)−Zr(1)−N(3) = 126.06(15)
	N(8)−Zr(1)−N(5) = 89.2(3)	N(5)−Zr(1)−N(3) = 103.52(15)
	N(7)−Zr(1)−N(8) = 112.0(3)	N(5)−Zr(1)−N(4) = 117.57(16)

was passed through a short pad of silica gel on a sinter funnel, and the ether was removed in vacuo. The product was further purified by flash chromatography (6:1 hexane/ether) to give $H_2\mathbf{L^1}$ as a yellow powder. Anal. Calcd for $C_{42}H_{56}N_2$: C, 85.66; H, 9.58; N, 4.76. Found: C, 85.45; H, 9.61; N, 4.71. ^1H NMR (C_6D_6, 297 K): δ 1.19 (s, 36H, *t*-Bu), 2.10 (s, 6H, biaryl-Me), 5.73 (s, 2H, NH), 6.80 (d, 2H, biaryl-ArH), 7.05 (s, 6H, Ar−H), 7.11 (m, 2H, biaryl-ArH), 7.44 (d, 2H, biaryl-ArH). $^{13}C\{^1H\}$ NMR (C_6D_6, 297 K): δ 20.45 (biaryl-Me), 31.9 [C(CH$_3$)$_3$], 35.24 [C(CH$_3$)$_3$], 113.8, 116.2, 117.1, 122.6, 125.0, 129.4, 139.0, 143.2, 143.9, 152.5 (Ar).

H_2L^2. **1** (0.98 g, 4.71 mmol,), [$Pd_2(DBA)_3$] (86.2 mg, 1.1 mol %), DPPP (78.4 mg, 2 mol %), and Na(OBu^t) (0.63 g, 6.55 mmol) were loaded into a Schlenk flask containing a magnetic stirrer bar. Toluene (50 mL) was added followed by 2-bromopyridine (0.89 mL, 9.42 mmol) via syringe. The solution was stirred for 48 h at room temperature until all **1** was consumed as judged by TLC. The toluene was removed in vacuo and diethyl ether (50 mL) was added. The mixture was passed through a pad of silica gel on a sinter funnel, and the ether was removed in vacuo to give a yellow solid. This was washed with a 1:1 mixture of diethyl ether and petroleum ether until colorless. The remaining solid $H_2\mathbf{L^2}$ was dried in vacuo for 2 h. Yield 1.18 g, 68%. Anal. Calcd for $C_{24}H_{22}N_4$: C, 78.66; H, 6.05; N, 15.29. Found: C, 78.55; H, 6.00; N, 15.34. ^1H NMR (C_6D_6, 297 K): δ 1.89 (s, 6H, biaryl-Me), 5.95 (d, 2H, Ar−H), 6.24 (t, 2H, Ar−H), 6.33 (s, 2H, NH), 6.74 (t, 2H, Ar−H), 6.86 (d, 2H, Ar−H), 7.23 (t, 2H, Ar−H) 8.09 (d, 2H, Ar−H), 8.43 (d, 2H, Ar−H). $^{13}C\{^1H\}$ NMR (C_6D_6, 297 K): δ 20.3 (biaryl-CH$_3$), 110.4, 115.5, 118.3, 124.6, 126.7, 129.4, 137.5, 138.2, 140.1, 148.6, 156.5 (Ar).

H_2L^3. **1** (1.00 g, 4.71 mmol), [$Pd_2(DBA)_3$] (91.3 mg, 1 mol %), BINAP (125 mg, 2 mol %), and Na(OBu^t) (1.34 g, 13.9 mmol) were loaded into a Schlenk flask containing a magnetic stirrer bar. 2-Bromo-6-methylanisole (1.45 mL, 10.0 mmol) was added to the Schlenk flask via syringe under argon flow. Toluene (50 mL) was added and the resulting purple solution was stirred at 90 °C until all **1** was fully converted, as judged by TLC (ca. 12 h). The toluene was removed in vacuo and diethyl ether (50 mL) was added. The mixture was passed through a pad of silica gel on a sinter funnel, and the ether was removed in vacuo. The product was further purified by flash chromatography (4:1 hexane/ether) to give $H_2\mathbf{L^3}$ as pale yellow crystals. Yield 1.61 g, 71.2%. Anal. Calcd for $C_{30}H_{32}N_2O_2$: C, 79.57; H, 7.17; N, 6.19. Found: C, 79.41; H, 7.23; N, 6.16. ^1H NMR (C_6D_6, 297 K): δ 2.21 (s, 6H, biaryl-Me), 2.23 (s, 6H, anisole-Me), 3.15 (s, 6H, OMe), 6.30 (s, 2H, NH), 6.46 (d, 2H, Ar−H), 6.68 (d, 2H, Ar−H), 6.71 (d, 2H, Ar−H), 6.98 (d, 2H, Ar−H), 7.20 (t, 2H, Ar−H), 7.52 (s, 2H, Ar−H). $^{13}C\{^1H\}$ NMR (C_6D_6, 297 K): δ 20.4 (biaryl-CH$_3$), 21.5 (anisole-CH$_3$), 55.6 (OCH$_3$), 111.5, 114.0, 118.5, 121.6, 122.8, 126.5, 129.1, 130.0, 133.2, 138.9. 142.6, 148.4 (Ar). MS (EI) *m/z* 452 [M$^+$], 437 [M$^+$ − CH$_3$], 315, 226.

(*R*)-H_2L^3. As for (*R*,*S*)-$H_2\mathbf{L^3}$, but with *R*-**1**. Yield 1.70 g, 75%. Anal. Calcd for $C_{30}H_{32}N_2O_2$: C, 79.57; H, 7.17; N, 6.19. Found: C, 79.22; H, 7.25; N, 5.90. Spectroscopic data were indistinguishable from the racemic compound.

***N*-Mesityl-2,2′-diamino-6,6′-dimethylbiphenyl (3).** **1** (2.00 g, 9.44 mmol), [$Pd_2(DBA)_3$] (64 mg, 1.5 mol %), BINAP (120 mg, 4 mol %), and Na(OBu^t) (0.67 g, 6.97 mmol) were loaded into a Schlenk flask containing a magnetic stirrer bar. Toluene (50 mL) was added followed by 2-bromomesitylene (0.95 g, 4.77 mmol). The resulting purple solution was stirred at 90 °C until all **1** was consumed, as judged by TLC (ca. 12 h). The toluene was removed in vacuo and diethyl ether was added. The mixture was passed through a pad of silica gel on a sinter funnel, and the ether was removed in vacuo to give a brown oil that was further purified by flash chromatography (6:1 hexane/ether) to yield **3** as a yellow powder. Yield 1.04 g, 66%. Anal. Calcd for $C_{23}H_{26}N_2$: C, 83.59; H, 7.93; N, 8.48. Found: C, 83.51; H, 8.01; N, 8.43. ^1H NMR (C_6D_6, 297 K): δ 2.07 (s, 9H, 3-mesityl-Me), 2.16 (s, 3H, biaryl-Me), 2.22 (s, 3H, biaryl-Me), 3.05 (s, 2H, NH$_2$), 4.79 (s, 1H, NH), 6.31 (d, 1H, Ar−H), 6.44 (s, 1H, Ar−H), 6.76 (s, 1H, Ar−H), 6.79 (s, 1H, Ar−H), 6.70 (s, 2H, Mes), 7.13 (t, 1H, Ar−H), 7.17 (t, 1H, Ar−H). $^{13}C\{^1H\}$ NMR (C_6D_6, 297 K): δ 18.6 (Mes), 20.1 (biaryl-Me), 20.3 (biaryl-Me), 21.4 (Mes), 109.3, 113.3, 115.2, 120.2, 120.7, 129.3, 129.4, 129.8 (Ar).

***N*-(4-Methyl-2-anisolyl)-2,2′-diamino-6,6′-dimethylbiphenyl (4).** **1** (2.00 g, 9.44 mmol), [$Pd_2(DBA)_3$] (21 mg, 0.5 mol %), BINAP (47 mg, 1.5 mol %), and Na(OBu^t) (0.67 g, 6.97 mmol) were loaded into a Schlenk flask containing a magnetic stirrer bar in a glovebox. 2-Bromo-4-methylanisole (0.71 mL, 4.97 mmol) was added to the flask via syringe. Toluene (50 mL) was added, and the resulting purple solution was stirred at 90 °C until all **1** was consumed, as judged by TLC (ca. 12 h). The toluene was removed in vacuo and diethyl ether (50 mL) was added. The mixture was passed through a silica pad on a sinter funnel, and the ether was removed in vacuo to give a yellow oil. Flash chromatography (5:1 hexane/ether) gave the major product **4** as a bright yellow crystalline solid. Yield 1.45 g, 87% ($H_2\mathbf{L^3}$ is also isolated as a minor product, yield 0.23 g, 10%). Anal. Calcd (for **4**) for $C_{22}H_{24}N_2O$: C, 79.48; H, 7.28; N, 8.43. Found: C, 79.53; H, 7.40; N, 8.34. ^1H NMR (C_6D_6, 297 K): δ 2.15 (s, 6H, biaryl-Me), 2.27 (s, 3H, anisole-Me), 3.09 (s, 2H, NH_2), 3.21 (s, 3H, OMe), 6.24 (s, 1H, NH), 6.50 (t, 2H, Ar−H), 6.71 (d, 1H, Ar−H), 6.83 (d, 1H, Ar−H), 6.94 (d, 1H, Ar−H), 7.17 (t, 1H, Ar−H), 7.20 (t, 1H, Ar−H), 7.50 (s, 1H, Ar−H), 7.62 (d, 1H, Ar−H). $^{13}C\{^1H\}$ NMR (C_6D_6, 297 K): δ 20.3 (biaryl-CH_3), 20.3 (biaryl-CH_3), 21.5 (anisolyl-CH_3), 55.7 (OCH_3), 111.6, 113.4, 114.1, 117.8, 120.6, 121.5, 122.4, 122.8, 126.7, 128.9, 129.2, 130.5, 133.4, 138.4, 139.0, 142.3, 145.5, 148.2 (Ar). MS (EI) *m/z* 332 [M^+], 317 [$M^+ - CH_3$], 302 [$M^+ - OCH_3$], 210 [$M^+ - C_6H_3OMe$], 195, 180.

(*R*)-*N*-(4-Methyl-2-anisolyl)-2,2′-diamino-6,6′-dimethylbiphenyl (4). As for (*R*,*S*)-**4**, with (*R*)-(+)-**1**. Yield 1.19 g, 72%. Anal. Calcd for $C_{22}H_{24}N_2O$: C, 79.48; H, 7.28; N, 8.43. Found: C, 79.37; H, 7.36; N, 8.39. Spectroscopic data were indistinguishable from the racemic compound.

***N*-(3,5-Di-*tert*-butyl-1-phenyl)-2,2′-diamino-6,6′-dimethylbiphenyl (2).** **1** (0.86 g, 2.10 mmol), bromo-3,5-di-*tert*-butylbenzene (0.50 g 1.86 mmol), [$Pd_2(DBA)_3$] (20 mg 1.2 mol %), BINAP (30 mg, 2.5 mol %), and Na(OBu^t) (0.32 g, 3.33 mmol) were loaded into a Schlenk flask containing a magnetic stirrer bar. Toluene (50 mL) was added and the solution was stirred at 90 °C overnight. The toluene was removed in vacuo and diethyl ether (50 mL) was added. The mixture was passed through silica pad on a sinter funnel and the solvent was removed. TLC and ^{1}H NMR indicated the presence of some disubstituted diamine H_2**L**^{1} as a minor product. Flash chromatography (6:1 hexane/ether) gave **2** as a pale yellow powder. Yield 0.52 g, 70%. Anal. Calcd for $C_{28}H_{36}N_2$: C, 83.95; H, 9.06; N, 6.99. Found: C, 83.89; H, 9.12; N, 6.93. ^{1}H NMR ($CDCl_3$, 297 K): δ 1.28 (s, 18H, *t*-Bu), 2.00 (s, 3H, biaryl-Me), 2.01 (s, 3H, biaryl-Me), 3.51 (s, 2H, NH_2), 5.30 (s, 1H, NH), 6.67 (d, 1H, Ar−H), 6.74 (d, 1H, Ar−H), 6.81 (d, 1H, Ar−H), 6.89 (s, 2H, Ar−H), 7.01 (t, 1H, Ar−H), 7.08−7.25 (m, 3H, Ar−H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 297 K): δ 15.9 (biaryl-Me), 31.5 [$C(CH_3)_3$], 35.2 [$C(CH_3)_3$], 111.2, 111.6, 111.7, 113.8, 116.4, 120.2, 120.7, 128.3, 128.5 (Ar).

H_2L^5. **3** (1.09 g, 3.29 mmol), [$Pd_2(DBA)_3$] (60 mg, 2 mol %), DPPP (54 mg, 4 mol %), and Na(OBu^t) (0.44 g, 1.4 equiv) were loaded into a Schlenk flask containing a magnetic stirrer. 2-Bromo-6-methylpyridine (0.36 mL, 3.25 mmol) was added to the flask via syringe. Toluene (50 mL) was added and the resulting purple solution was stirred at 90 °C until all the diamine was consumed, as judged by TLC (ca. 12 h). The toluene was removed in vacuo and diethyl ether (50 mL) added. The mixture was passed through a silica pad on a sinter funnel, and the ether was removed to give a yellow oil. Flash chromatography (6:1 hexane/ether) gave H_2**L**^{5} as a yellow powder. This compound rapidly absorbs moisture from the atmosphere. Yield 1.81 g, 89%. Anal. Calcd for $C_{29}H_{31}N_3$: C, 82.62; H, 7.41; N, 9.97. Found: C, 82.41; H, 7.32; N, 10.14. ^{1}H NMR ($CDCl_3$, 297 K): δ 1.74 (br, 3H, 2,6-mesityl-Me), 1.90 (s, 3H, biaryl-Me), 2.02 (br, 3H, 2,6-mesityl-Me), 2.07 (s, 3H, biaryl-Me), 2.15 (s, 3H, 4-mesityl-Me), 2.30 (s, 3H, pyridyl-Me), 4.63 (s, 1H, NH), 5.94 (d, 1H, Ar−H), 6.18 (s, 1H, NH), 6.45 (d, 1H, Ar−H), 6.51 (d, 1H, Ar−H), 6.60 (d, 1H, Ar−H), 6.71 (br, 2H, Ar−H), 6.90 (m, 2H, Ar−H), 7.19 (m, 2H, Ar−H), 7.92 (d, 1H, Ar−H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 297 K): δ 15.9 (2,6-mesityl-Me), 17.8 (biaryl-Me), 17.9 (biaryl-Me), 18.9 (pyridyl-Me), 22.3 (4-mesityl-Me), 104.1, 106.6, 112.4, 114.3, 117.5, 118.7, 121.6, 124.1, 126.3, 127.0, 127.1, 133.1, 133.5, 134.3, 135.6, 135.8, 136.5, 137.3, 142.0, 153.2, 155.2 (Ar).

H_2L^4. **4** (1.28 g, 3.89 mmol), bromo-3,5-di-*tert*-butylbenzene (1.05 g 3.90 mmol), [$Pd_2(DBA)_3$] (84.0 mg, 2 mol %), BINAP (97 mg, 4 mol %), and Na(OBu^t) (0.52 g, 5.41 mmol) were loaded into a Schlenk flask containing a magnetic stirrer bar. Toluene (50 mL) was added and the reaction was stirred at 90 °C for 4 days. The toluene was removed in vacuo and diethyl ether (50 mL) was added. The mixture was passed through a pad of silica on sintered funnel and the solvent removed on a rotary evaporator. The product was purified by flash chromatography (5:1 hexane/ether) to give a pale yellow oil. Addition of petroleum ether (40−60, 2 mL) and scratching yielded H_2**L**^{4} as a pale yellow crystalline solid. Yield 1.81 g, 89%. Anal. Calcd for $C_{36}H_{44}N_2O$: C, 83.03; H, 8.52; N, 5.38. Found: C, 82.49; H, 8.33; N, 5.20. ^{1}H NMR (C_6D_6, 297 K): δ 1.24 (s, 18H, *t*-Bu), 2.10 (s, 3H, anisyl-Me), 2.15 (s, 6H, biaryl-Me), 3.11 (s, 3H, OMe), 5.76 (s, 1H, NH), 6.21 (s, 1H, NH), 6.43 (d, 1H, Ar−H), 6.62 (d, 1H, Ar−H), 6.87 (d, 2H, Ar−H), 7.06 (d, 2H, Ar−H), 7.20 (m, 3H, Ar−H), 7.32 (d, 1H, Ar−H), 7.51 (d, 2H, Ar−H). $^{13}C\{^1H\}$ NMR (C_6D_6, 297 K): δ 20.4 (biaryl-CH_3), 20.5 (anisolyl-CH_3), 21.5 (biaryl-CH_3), 31.9 (*t*-Bu), 55.8 (OCH_3), 111.7, 113.3, 114.2, 116.4, 117.0, 118.8, 122.1, 122.4, 123.0, 125.1, 126.1, 129.2, 129.3, 130.6, 133.1, 138.9, 139.0, 140.1, 142.7, 143.2, 143.5, 143.9, 148.6, 152.4 (Ar).

(*R*)-H_2L^4. As for (*R*,*S*)-H_2**L**^{4}, with (*R*)-(+)-**1**. Yield 1.73 g, 85%. Anal. Calcd for $C_{36}H_{44}N_2O$: C, 83.03; H, 8.52; N, 5.38. Found: C, 82.61; H, 8.29; N, 5.51. Spectroscopic data were indistinguishable from the racemic compound.

H_2L^6. **4** (1.26 g, 3.82 mmol), [$Pd_2(DBA)_3$] (84 mg, 2 mol %), DPPP (63.0 mg, 4 mol %), and Na(OBu^t) (0.51 g, 5.31 mmol) were loaded into a Schlenk flask containing a magnetic stirrer bar. 2-Bromo-6-methylpyridine (0.45 mL, 4.06 mmol) was added to the flask via syringe. Toluene (50 mL) was added, and the resulting purple solution was stirred at 90 °C until all **1** was converted, as judged by TLC (ca. 24 h). The toluene was removed in vacuo and diethyl ether (50 mL) added. The mixture was passed through a pad of silica on a sinter funnel, and the ether removed in vacuo to give a yellow oil. Excess 2-Bromo-6-methylpyridine was removed by distillation at 100 °C and rotary pump vacuum. Flash chromatography (5:1 hexane/ether) gave H_2**L**^{4} as a yellow viscous oil. Yield 1.44 g, 89%. Anal. Calcd for $C_{28}H_{29}N_3O$: C, 79.40; H, 6.90; N, 9.92. Found: C, 79.29; H, 7.10; N, 9.74. ^{1}H NMR (C_6D_6, 297 K): δ 2.08 (s, 3H, anisole-Me), 2.19 (s, 3H, biaryl-Me), 2.23 (s, 3H, biaryl-Me), 2.36 (s, 3H, pyridyl-Me), 3.17 (s, 3H, OMe), 6.08 (s, 1H, NH), 6.30 (d, 1H, Ar−H), 6.36 (d, 1H, Ar−H), 6.45 (d, 1H, Ar−H), 6.59 (s, 1H, NH), 6.71 (d, 1H, Ar−H), 6.88 (d, 1H, Ar−H), 6.94 (t, 1H, Ar−H), 7.02 (d, 1H, Ar−H), 7.19 (t, 1H, Ar−H), 6.34 (s, 1H, Ar−H), 6.38 (t, 1H, Ar−H), 7.51 (d, 1H, Ar−H), 8.49 (d, 1H, Ar−H). $^{13}C\{^1H\}$ NMR (C_6D_6, 297 K): δ 20.4 (anisole-CH_3), 20.4 (biaryl-CH_3), 21.4 (biaryl-CH_3), 55.6 (OCH_3), 106.7, 11.5, 113.6, 114.6, 117.5, 120.1, 122.5, 122.7, 124.3, 125.4, 127.0, 129.1, 129.4, 130.4, 132.7, 137.8, 138.5, 138.6, 140.3, 143.0, 148.9, 157.7 (Ar).

(*R*)-H_2L^6. As for (*R*,*S*)-H_2**L**^{6}, with (*R*)-(+)-**1**. Yield 1.73 g, 85%. Anal. Calcd for $C_{36}H_{44}N_2O$: C, 83.03; H, 8.52; N, 5.38. Found: C, 82.61; H, 8.29; N, 5.51. Spectroscopic data were indistinguishable from the racemic compound.

[L^{1}Zr(NMe$_2$)$_2$]. H_2**L**^{1} (0.35 g 0.59 mmol) and [$Zr(NMe_2)_4$] (0.16 g 0.59 mmol) were loaded into a Schlenk flask in a glovebox. Toluene (5 mL) was added and the solution was stirred at room temperature for 2 d. The toluene was removed in vacuo to give a yellow powder. Pentane was added until most of the solid dissolved. The solution was filtered via cannula and the pentane was removed in vacuo to give [**L**^{1}Zr(NMe$_2$)$_2$] as a yellow powder. Yield 0.28 g, 61.5%. X-ray quality crystals were obtained from a concentrated pentane solution at 0 °C. Anal. Calcd for $C_{46}H_{66}N_4Zr$: C, 72.10; H, 8.68; N, 7.31. Found: C, 71.92; H, 8.58; N, 7.41. ^{1}H NMR (C_6D_6, 297 K): δ 1.35 (s, 36H, *t*-Bu), 2.04 (s, 6H, biaryl-Me), 2.87 (s, 12H, NMe_2), 6.69 (d, J = 7.28 Hz, 2H, Ar−H), 7.04 (t, J = 7.28 Hz, 2H, Ar−H), 7.13 (m, 12H, Ar−H), 7.35 (d, J = 8.03 Hz, 2H, Ar−H). $^{13}C\{^1H\}$ NMR (C_6D_6, 297 K): δ 32.2 (biaryl-Me), 35.4 (*t*-Bu), 41.1 (NMe_2), 114.4, 114.8, 123.6, 125.4, 125.9, 130.3, 132.4, 137.7, 140.0, 144.8, 146.0, 152.4 (Ar). MS (EI) *m/z* 764 [M^+], 588, 383, 294.

[L^{3}Zr(NMe$_2$)$_2$]. H_2**L**^{3} (0.20 g, 0.49 mmol) and [$Zr(NMe)_2$] (0.13 g, 0.49 mmol) were loaded into a Schlenk flask. Toluene (10 mL) was added and the pale yellow solution was stirred overnight at ambient temperature. The toluene was removed in vacuo to give a foamy material. On addition of pentane (ca. 1 mL) followed by vigorous stirring, a colorless crystalline solid

L[3]Zr(NMe_2)$_2$ began to precipitate from solution. After standing at 0 °C overnight the mother liquor was filtered off and the remaining solid was washed with pentane (ca. 1 mL). The combined filtrate and washings were concentrated and kept at 0 °C for 2 days to give X-ray quality crystals of [**L**[3]Zr(NMe_2)$_2$]. Combined yield 0.21 g, 69%. Anal. Calcd for $C_{34}H_{42}N_4O_2Zr$: C, 64.83; H, 6.72; N, 8.89. Found: C, 64.51; H, 6.85; N, 9.01. ^{1}H NMR (d_8-toluene, 297 K): δ 2.05 (s, 6H, biaryl-Me), 2.10 (s, 6H, anisole-Me), 2.71 (s, 12H, NMe_2), 3.52 (s, 6H, OMe), 2.29 (m, 4H, Ar−H), 6.40 (m, 2H, Ar−H), 6.76 (m, 2H, Ar−H), 7.00−7.12 (m, 4H, Ar−H).^{13}C{^{1}H} NMR (C_6D_6, 297 K): δ 20.8 (biaryl-Me), 21.0 (anisole-Me), 42.3 (NMe_2), 58.6 (OMe), 109, 115.8, 116.1, 125.2, 125.5, 125.8, 125.9, 126.4, 127.6, 132.8, 136.5, 137.8 (Ar).

[(HL[5])$_2$Zr(NMe$_2$)$_2$]. H$_2$**L**[5] (0.52 g, 1.23 mmol) and [Zr(NMe_2)$_4$] (0.16 g, 0.62 mmol) were loaded into a Schlenk flask. Toluene (10 mL) was added and the yellow solution was stirred overnight at ambient temperature. The toluene was removed in vacuo to yield a foamy material. Pentane (ca. 1 mL) was added and the solution stirred vigorously for 5−10 min after which time a yellow precipitate had formed. The mother liquor was filtered off and the solid [(H**L**[6])$_2$Zr(NMe_2)$_2$] was washed once with a minimal amount of pentane (1 mL) and dried under vacuum for 2 h. Yield 0.31 g, 52%. Pentane was carefully added to the solid [(H**L**[6])$_2$Zr(NMe_2)$_2$] until most had dissolved; a few drops of diethyl ether was subsequently added to dissolve the remaining solid. The resulting solution was kept at 0 °C for 2 d yielding X-ray quality crystals of [(H**L**[5])$_2$Zr(NMe_2)$_2$·C_5H_{12}]. The solvent of crystallization, pentane, is lost after prolonged exposure to Schlenk line vacuum (>5 h). Anal. Calcd for $C_{67}H_{84}N_8Zr$: C, 72.97; H, 7.11; N, 10.98. Found: C, 72.59; H, 6.94; N, 11.06. ^{1}H NMR (C_6D_6, 297 K): δ 1.66 (br, 6H, biaryl-Me), 2.06 (br, 6H, biaryl-Me), 2.09 (s, 12H, 2,6-mesityl-Me), 2.10 (s, 6H, 4-mesityl-Me), 2.11 (s, 6H, pyridyl-Me), 4.83 (s, 2H, NH), 5.57 (d, 2H, Ar−H), 5.88 (d, 2H, Ar−H), 6.16 (d, 2H, Ar−H), 6.41 (t, 2H, Ar−H), 6.68 (d, 2H, Ar−H), 6.75 (br, 4H, Ar−H), 6.92 (t, 2H, Ar−H), 7.17 (d, 2H, Ar−H), 7.28 (t, 2H, Ar−H), 7.42 (d, 2H, Ar−H). ^{13}C{^{1}H} NMR (C_6D_6, 297 K): δ 19.5 (biaryl-Me), 20.8 (biaryl-Me), 21.2 (4-mesityl-Me), 21.3 (2,6-mesityl-Me), 23.3 (pyridyl-Me), 41.8 (NMe_2), 103.3, 108.3, 108.9, 109.7, 118.2, 119.5, 120.8, 125.9, 126.6, 127.3, 128.2, 128.6, 129.9, 133.5, 135.3, 136.0, 136.5, 140.0, 145.6, 147.4, 148.3, 150.5, 155.7 (Ar). MS (EI) *m/z* 1018 [M$^+$], 928, 597, 556, 552, 507, 421.

[L[4]Zr(NMe$_2$)$_2$]. H$_2$**L**[4] (0.44 g, 0.84 mmol) and [Zr(NMe_2)$_4$] (0.25 g, 9.34 mmol) were loaded into a Schlenk flask. Toluene (10 mL) was added and the resulting yellow solution was stirred overnight at ambient temperature. The solvent was removed in vacuo to yield a foamy material. Pentane (ca. 1 mL) was added and the solution was stirred vigorously for 1−2 min resulting in the formation of an off-white precipitate. The solution was left at 0 °C. The mother liquor was decanted and the remaining solid was washed with a minimal amount of pentane and dried under vacuum for 30 min. The combined filtrate and washings were concentrated and kept at 0 °C for 2 days to give X-ray quality crystals of **L**[5]Zr(NMe_2)$_2$. Combined yield 0.48 g, 82%. Anal. Calcd for $C_{40}H_{54}N_4OZr$: C, 68.82; H, 7.80; N, 8.03. Found: C, 69.19; H, 7.93; N, 8.21. ^{1}H NMR (C_6D_6, 297 K): δ 1.37 (s, 18H, *t*-Bu), 2.09 (s, 6H, biaryl-Me), 2.14 (s, 3H, anisole-Me), 2.62 (s, 6H, NMe_2), 3.16 (s, 6H, NMe_2), 3.47 (s, 3H, OMe), 6.37 (t, J = 8.1 Hz, 2H, NMe_2), 6.65 (d, J = 7.53 Hz, 1H, Ar−H), 6.85 (m, 4H, Ar−H), 6.94 (s, 1H, Ar−H), 7.05 (t, J = 7.53 Hz, 1H, Ar−H), 7.20 (m, 2H, Ar−H), 7.35 (d, J = 8.1 Hz, 1H, Ar−H). ^{13}C{^{1}H} NMR (C_6D_6, 297): δ 21.1 (biaryl-Me), 21.3 (biaryl-Me), 21.6 (anisole-Me), 32.4 (*t*-Bu), 41.3 (NMe_2), 42.3 (NMe_2), 57.9 (OMe), 109.8, 111.9, 113.0, 114.4, 116.6, 122.4, 126.4, 127.8, 130.5, 133.7, 134.3, 134.5, 138.1, 142.2, 143.0, 145.0, 146.3, 147.1, 149.1, 147.3, 148.0, 151.2, 154.8 (Ar).

[L[6]Zr(NMe$_2$)$_2$]. H$_2$**L**[6] (0.40 g, 0.95 mmol) and Zr(NMe_2)$_4$ (0.25 g 9.5 mmol) were loaded into a Schlenk flask. Toluene (10 mL) was added and the resulting yellow solution was stirred overnight at ambient temperature. The solvent was removed in vacuo to yield a foamy material. Pentane (ca. 1 mL) was added and the solution was stirred vigorously for 1−2 min resulting in the formation of an off-white precipitate. The solution was then placed in a fridge overnight at 0 °C. The mother liquor was decanted and the solid was washed with a minimal amount of pentane and dried under vacuum for 30 min. Combined yield 0.41 g, 72.2%. Anal. Calcd for $C_{32}H_{39}N_5OZr$: C, 63.96; H, 6.54; N, 11.62. Found: C, 63.82; H, 6.45; N, 11.74. ^{1}H NMR (C_6D_6, 297 K): δ 2.09 (s, 3H, pyridyl-*Me*), 2.11 (s, 3H, biaryl-Me), 2.12 (s, 3H, biaryl-*Me*), 2.21 (s, 3H, anisole-Me), 2.76 (s, 6H, NMe_2), 2.77 (s, 6H, 6H, NMe_2), 3.51 (s, 3H, O*Me*), 5.81 (d, J = 7.28 Hz 1H, Ar−H), 6.20 (d, J = 8.53 Hz, 1H, Ar−H), 6.28 (m, 2H, Ar−H), 6.41 (s, 1H, Ar−H), 6.77 (m, 2H, Ar−H), 6.94 (d, J = 7.28 Hz, 1H, Ar−H), 7.06 (m, 3H, Ar−H), 7.19 (d, J = 1.76 Hz, 1H, Ar−H).^{13}C{^{1}H} NMR (C_6D_6, 297): δ 20.6 (Me), 20.8 (Me), 21.6 (Me), 22.2 (Me), 41.8 (NMe_2), 41.9 (NMe_2), 57.9 (OMe), 102.82, 108.9, 109.4, 114.4, 115.42, 118.8, 125.4, 126.6, 126.8, 133.4, 135.0, 138.1, 138.4, 140.67, 146.1, 147.5, 149.4, 154.9, 167.2 (Ar).

Crystallography. Crystals were coated in an inert oil prior to transfer to a cold nitrogen gas stream on a Bruker-AXS SMART three-circle CCD area detector diffractometer system equipped with Mo Kα radiation (λ = 0.71073 Å). Data were collected with narrow (0.3° in ω) frame exposures. Intensities were corrected semiempirically for absorption, based on symmetry-equivalent and repeated reflections (SADABS). Reflection data for [(H**L**[5])$_2$Zr(NMe_2)$_2$·C_5H_{12}] were weak and no significant data were collected for $2\theta > 45°$. The structures [**L**[3]Zr(NMe_2)$_2$], [**L**[4]Zr(NMe_2)$_2$], [(H**L**[5])$_2$Zr(NMe_2)$_2$·C_5H_{12}], and [**L**[6]Zr(NMe_2)$_2$] were solved by direct methods (SHELXS) with additional light atoms found by Fourier methods The zirconium atoms in **L**[1]Zr(NMe_2)$_2$ were located by Patterson methods (SHELXS); subsequent least-squares refinements revealed the atomic positions of the remaining non-hydrogen atoms. The crystal structure of [(H**L**[5])$_2$Zr(NMe_2)$_2$·C_5H_{12}] contains one disorded molecule of the crystallization solvent, pentane, within the asymmetric unit of the unit cell. This disorder was modeled across two alternative positions and geometrical and displacement parameter restraints were applied to aid refinement. All structures were refined on F^2 values for all unique data. Table 1 gives further details. All non-hydrogen atoms were refined anisotropically, and the carbon atoms C10, C12, and C14 in [**L**[1]Zr(NMe_2)$_2$] and C28, C29, and C33 in [**L**[4]Zr(NMe_2)$_2$] were subject to displacement parameter restraints. All H atoms were constrained with a riding model; U(H) was set at 1.2 (1.5 for methyl groups) times U_{eq} for the parent atom. Programs used were Bruker AXS SMART (control) and SAINT (integration) and SHELXTL for structure solution, refinement, and molecular graphics.

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Supporting Information Available: Tables of crystal data, atomic coordinates, distances and angles, anisotropic displacement parameters, and hydrogen coordinates, as well as molecular structure drawings. This material is available free of charge via the Internet at http://pubs.acs.org.

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