Chiral Titanium Bis(aminopyridinates) Based on a Biaryl Backbone

Ian Westmoreland, Ian J. Munslow, Paul N. O'Shaughnessy, and Peter Scott*

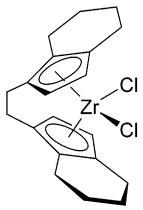
Department of Chemistry, University of Warwick, Coventry CV4 7AL, U.K.

Received January 22, 2003

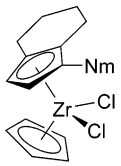
The new chiral biaryl-bridged aminopyridine proligand H_2**L** is synthesized readily via palladium-catalyzed amination. This ligand system provides a very robust environment for reaction chemistry in comparison to known nonchelate aminopyridinate ligands. Reaction with $Ti(NMe_2)_4$ gives the C_2-symmetric amide [**L**$Ti(NMe_2)_2$] (91% isolated), which on reaction with $SiMe_3Cl$ gives the chloride [**L**$TiCl_2$] (95%). Metalation of H_2**L** with KH followed by reaction with $TiCl_3$ and oxidation also gives [**L**$TiCl_2$] (87%). This latter complex has been crystallographically characterized and has the expected cis structure, in which the chirality arising in the biaryl backbone is very well expressed in the reactive coordination sphere of the metal. Reaction of [**L**$TiCl_2$] with MeMgBr gives the dimethyl compound [**L**$TiMe_2$] (72%). The dibenzyl complex [**L**$Ti(CH_2Ph)_2$] is prepared directly from the reaction of H_2**L** with [$Ti(CH_2Ph)_4$] (90%).

Introduction

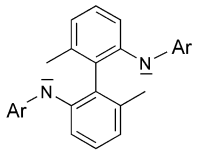
The search for new enantioselective catalysts based on complexes of the early transition metals has been an area of intense interest. Since Brintzinger's landmark publication of 1979,[1] research into the most successful of such systems, the *ansa*-metallocenes, e.g. [(ebthi)$ZrCl_2$] (**I**), has been extensive.[2] Detailed investigations have shown that these remarkable compounds can efficiently mediate both stereoselective polymerization[3] and the enantioselective transformation of small molecules.[4] The success of these catalysts can be traced to the fact that the dissymmetry of the system is very well expressed in the region of the active coordination sites.[5] Some significant drawbacks associated with the synthesis of these compounds have been pointed out,[6] including the coproduction of achiral meso diastereomers, and the necessity for resolution of the complex.[7]



I



II



III

Also, while the tetrahydroindenyl ligand system seems to provide a highly enantioselective catalyst in many cases, it is prohibitively difficult to vary the stereoelectronic properties in a systematic way, since a resolution protocol would have to be developed for each new catalyst envisaged. These issues may preclude the use of nonracemic metallocenes in industrial organic synthesis.

Accordingly, a large number of studies involving, for example, the use of chiral cyclopentadienyl ligands have been carried out. Some systems, including Whitby's catalyst for alkene carbomagnesiation **II**,[8] show promise in this respect, but most others tend to be less attractive than the existing technology, either because they involve relatively exotic ligands or because the expression of the chirality in the resulting active site is less favorable than it is in **I**. Hoveyda has suggested[6] that chiral [(ebthi)MX_2] equivalents may provide more practical alternatives to this powerful class of catalyst.

We have been interested in the design of inherently chiral ligands, particularly a group of quadridentate N_2O_2 Schiff bases based on the biaryl backbone **1**

* To whom correspondence should be addressed. Fax: 024 7657 2710. E-mail: peter.scott@warwick.ac.uk.

(1) Schnutenhaus, H.; Brintzinger, H. H. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 777.

(2) (a) Wild, F. R. W. P.; Zsolnai, L.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1982**, *232*, 233. (b) Kaminsky, W.; Kulper, K.; Brintzinger, H. H.; Wild, F. R. W. P. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 507. (c) Roll, W.; Brintzinger, H. H.; Rieger, B.; Zolk, R. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 279. (d) Haltermann, R. L. *Chem. Rev.* **1992**, *92*, 965.

(3) (a) Brintzinger, H. H.; Fischer, D.; Mulhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143. (b) McKnight, A. L.; Waymouth, R. M. *Chem. Rev.* **1998**, *98*, 2587. (c) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, 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) Verdauguer, X.; Lange, U. E. W.; Reding, M. T.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 6784. (g) Hicks, F. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 11688. (h) Didiuk, M. T.; Johannes, C. W.; Morken, J. P.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1995**, *117*, 7097. (i) Hoveyda, A. H.; Morken, J. P. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1262. (j) Yamaura, Y.; Hyakutake, M.; Mori, M. *J. Am. Chem. Soc.* **1997**, *119*, 7615.

(5) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F.; *Angew. Chem., Int. Ed.* **1999**, *38*, 428.

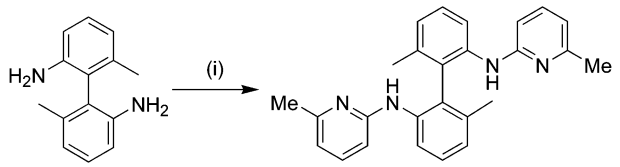
(6) Hoveyda, A. H.; Morken, J. P. Chiral Titanocenes and Zirconocenes in Synthesis. In *Metallocenes*; Togni, A., Halterman, R., Eds.; Wiley-VCH: Weinheim, Germany, 1998; Vol. 2, Chapter 10.

(7) Nevertheless, their synthetic utility has encouraged the discovery of various process improvements.

(8) Bell, L.; Brookings, D. C.; Dawson, G. J.; Whitby, R. J.; Jones, R. V. H.; Standen, M. C. H. *Tetrahedron* **1998**, *54*, 14617. Bell, L.; Whitby, R. J.; Jones, R. V. H.; Standen, M. C. H. *Tetrahedron Lett.* **1996**, *37*, 7139.

10.1021/om030055k CCC: $25.00
Publication on Web 06/12/2003

Scheme 1. Synthesis of the C_2-Symmetric Diamine Ligand H_2L[a]



1 **H_2L**

[a] Reagents and conditions: (i) bromopyridine, Na(OBu^t), [Pd_2(DBA)$_3$], DPPP, toluene (77%).

(Scheme 1). These compounds give nonplanar architectures of the C_2-symmetric cis-α and C_1-symmetric cis-β classes when coordinated to suitable transition metals.[9] The inherent chirality of the biaryl backbone directs the helicity of the complex such that usually only a single diastereomer is formed on complexation. These systems are potentially well suited for application to enantioselective catalysis, since they contain two mutually cis coordination sites at which stereoselective reactions can be mediated under the potent influence of the well-expressed chiral-at-metal architecture. We have recently reported a ruthenium(II) complex which gives extremely high diastereoselectivity (≤99:1) and enantioselectivity (≤98%) in the catalytic cyclopropanation of alkenes.[9g] Unfortunately, early-transition-metal complexes of these ligands have suffered from decomposition via 1,2-migratory insertion reactions[9e] and radical processes.[9b] While these reactions can be eliminated almost completely in some cases,[10] we have recognized that the production of robust complexes will be difficult with Schiff base ligands. Consequently, our more recent research has included the synthesis of a range of new diamido ligands **III** with various functionalized and nonfunctionalized Ar groups.[11] Since aminopyridine[12] and the related amidinate[13] complexes have been shown to display catalytic and other activity, we were particularly interested in the chiral variant of **III** where Ar = pyridines, e.g. **L** (Scheme 1). In light also of the excellent performance of CpZr(amidinate) systems in the polymerization of olefins[14] we have attempted to access the complexes [**L**ZrX_2]. Unfortunately, however, this has been relatively unsuccessful, and for example the reaction of K_2**L** with $ZrCl_4(THF)_2$ gives a poorly defined and probably polymeric mixture.[11] In this report we detail a straightforward entry to the titanium series and subsequent well-defined reaction chemistry.

Results and Discussion

The racemic diamine **1**, for which we have recently detailed a large-scale synthesis and resolution procedure,[9i] reacts readily with slightly less than 2 equiv of 2-bromo-6-methylpyridine under standard palladium-catalyzed arylation conditions[15] to give the corresponding C_2-symmetric diamine H_2**L** in good yield (Scheme 1).[16]

The in situ reaction of C_2-symmetric proligand H_2**L** with potassium hydride in THF cleanly gives the doubly deprotonated species K_2**L**·*n*THF, as evidenced by ^{1}H NMR spectroscopy. Reaction of the potassium salt solution with titanium(III) chloride gives a complex which is assumed to be [**L**TiCl] on the basis that treatment with lead(II) chloride gives the oxidized product [**L**TiCl_2]. While this material has been obtained in good yield (87%), the route is somewhat capricious. We have thus developed a more convenient and reproducible method via the amide (vide infra).

The proligand H_2**L** reacts cleanly with Ti$(NMe_2)_4$ in diethyl ether at room temperature to give the product titanium amido complex [**L**Ti$(NMe_2)_2$] as a bright red solid (91% yield) via amine elimination.[17] The ^{1}H and ^{13}C NMR spectra of [**L**Ti$(NMe_2)_2$] are consistent with a C_2-symmetric complex in solution. Reaction of [**L**Ti$(NMe_2)_2$] with an excess of chlorotrimethylsilane in diethyl ether at room temperature gave the previously mentioned dichloride [**L**TiCl_2] as a purple microcrystalline solid (95% yield). NMR spectra again indicate C_2 symmetry.

Crystals of [**L**TiCl_2] suitable for X-ray crystallography were obtained from a concentrated solution in benzene, and the molecular structure is shown in Figure 1. Crystallgraphic data, collection parameters, and refinement parameters and selected bond distances and angles are given in Tables 1 and 2, respectively. The inner coordination sphere of this six-coordinate complex is necessarily distorted from octahedral because of the small aminopyridine unit bite angle. Nevertheless, the complex is essentially C_2 symmetric, with the auxiliary chlorine atoms occupying mutually cis positions (Figure 1), although the Cl−Ti−Cl angle is rather obtuse at 121.92(6)° (vide infra). The amido N(1)−Ti and

(9) (a) Woodman, P.; Hitchcock, P. B.; Scott, P. *Chem. Commun.* **1996**, 2735. (b) Woodman, P. R.; Sanders, C. J.; Alcock, N. W.; Hitchcock, P. B.; Scott, P. *New J. Chem.* **1999**, *23*, 815. (c) Woodman, P. R.; Munslow, I. J.; Hitchcock, P. B.; Scott, P. *J. Chem. Soc., Dalton Trans.* **1999**, 4069. (d) Sanders, C. J.; Gillespie, K. M.; Bell, D.; Scott, P. *J. Am. Chem. Soc.* **2000**, *122*, 7132. (e) Woodman, P. R.; Alcock, N. W.; Munslow, I. J.; Sanders, C. J.; Scott, P. *J. Chem. Soc., Dalton Trans.* **2000**, 3340. (f) Gillespie, K. M.; Crust, E. J.; Deeth, R. J.; Scott, P. *Chem. Commun.* **2001**, 785. (g) Munslow, I. J.; Gillespie, K. M.; Deeth, R. J.; Scott, P. *Chem. Commun.* **2001**, 1638. (h) Sanders, C. J.; Gillespie, K. M.; Scott, P. *Tetrahedron: Asymmetry* **2001**, *12*, 1055. (i) Gillespie, K. M.; Sanders, C. J.; O'Shaughnessy, P. N.; Westmoreland, I.; Thickitt, C. P.; Scott, P. *J. Org. Chem.* **2002**, *67*, 3450.

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

(11) O'Shaughnessy, P. N.; Gillespie, K. M.; Morton, C.; Westmoreland, I.; Scott, P. *Organometallics* **2002**, *21*, 4496.

(12) (a) Fuhrmann, H.; Brenner, S.; Arndt, P.; Kempe, R. *Inorg. Chem.* **1996**, *35*, 6742. (b) Kempe, R. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 468. (c) Schareina, T.; Hillebrand, G.; Fuhrmann, H.; Kempe, R. *Eur. J. Inorg. Chem.* **2001**, 2421. (d) Schareina, T.; Kempe, R. *Angew. Chem., Int. Ed. Engl.* **2002**, *41*, 1520.

(13) (a) Hagadorn, J. R.; Arnold, J. *J. Chem. Soc., Dalton Trans.* **1997**, 3087. (b) Hagadorn, J. R.; Arnold, J. *Organometallics* **1998**, *17*, 1355. (c) Hagadorn, J. R.; Arnold, J. *J. Organomet. Chem.* **2001**, *637*, 521. (d) Schmidt, J. A. R.; Arnold, J. *J. Chem. Soc., Dalton Trans.* **2002**, 2890. (e) Schmidt, J. A. R.; Arnold, J. *J. Chem. Soc., Dalton Trans.* **2002**, 3454. (f) Herskovics-Korine, D.; Eisen, M. S. *J. Organomet. Chem.* **1995**, *503*, 307. (g) Volkis, V.; Shmulinson, M.; Averbuj, C.; Lisovskii, A.; Edelmann, F. T.; Eisen, M. S. *Organometallics* **1998**, *17*, 3155. (h) Averbuj, C.; Tish, E.; Eisen, M. S. *J. Am. Chem. Soc.* **1998**, *120*, 8640.

(14) (a) Jayaratne, K. C.; Sita, L. R. *J. Am. Chem. Soc.* **2000**, *122*, 958. (b) Jayaratne, K. C.; Keaton, R. J.; Henningsen, D. A.; Sita, L. R. *J. Am. Chem. Soc.* **2000**, *122*, 10490. (c) Keaton, R. J.; Jayaratne, K. C.; Fettinger, J. C.; Sita, L. R. *J. Am. Chem. Soc.* **2000**, *122*, 12909. (d) Keaton, R. J.; Jayaratne, K. C.; Henningsen, D. A.; Koterwas, L. A.; Sita, L. R. *J. Am. Chem. Soc.* **2001**, *123*, 6197. (e) Jayaratne, K. C.; Sita, L. R. *J. Am. Chem. Soc.* **2001**, *123*, 10754.

(15) (a) Yang, B. H.; Buchwald, S. L. *J. Organomet. Chem.* **1999**, *576*, 125. (b) Wolfe, J. P.; Tomori, H.; Sadighi, J. P.; Yin, J.; Buchwald, S. L. *J. Org. Chem.* **2000**, *65*, 1158.

(16) Control of the stoichiometry is very important for this reaction. Using 2 equiv of the bromoarene gives, in addition to H_2L, the triple-arylation product; removal of this material is extremely difficult.

(17) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. *Metal and Metalloid Amides*; Ellis Horwood: Chichester, U.K., 1980.

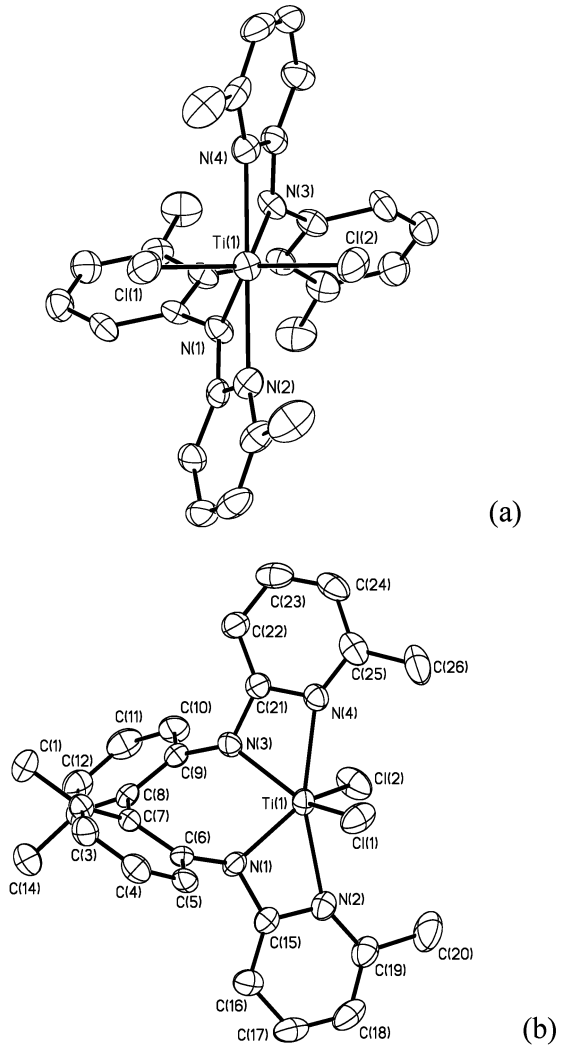


Figure 1. Views of the molecular structure of $[LTiCl_2]$ (a) along the approximate C_2 axis and (b) showing the coordination sphere.

N(3)−Ti distances of 1.975(4) and 1.985(4) Å are only slightly smaller than the distances observed in simple aminopyridinato complexes of titanium (2.00−2.10 Å).[18] The similar distances observed in a siloxane-bridged bis(aminopyridinato) complex are rather larger at 2.13−2.15 Å, presumably as a result of ring strain effects in this latter complex.[19]

Treatment of the dichloro complex $[\mathbf{L}TiCl_2]$ with 2 equiv of the Grignard reagent methylmagnesium bromide gave the dimethyl complex $[\mathbf{L}TiMe_2]$ as a brown microcrystalline solid (72% yield). The ^1H and ^{13}C NMR spectra of $[\mathbf{L}TiMe_2]$ are similar to those of the amide and chloride complexes above, with ^1H and ^{13}C resonances for the $TiMe_2$ unit at 0.95 and 71.8 ppm, respectively.

The dibenzyl compound $[\mathbf{L}Ti(CH_2Ph)_2]$ was obtained as dark red microcrystals by direct reaction[20] of $H_2\mathbf{L}$ with tetrabenzyltitanium(IV) in toluene (90% yield). The ^1H NMR spectrum of this complex contains a pair of AB doublets centered at ca. 3.0 ppm for the benzyl CH_2 protons as a result of the nonfluxional C_2-symmetric environment in solution.

Several polymerization experiments were carried out with the titanium complexes described above. In combination with methylaluminum oxide (MAO), the titanium dichloride $[\mathbf{L}TiCl_2]$ exhibited a low activity for the polymerization of ethylene at 1.1 bar, calculated at 18 kg mol^{-1} bar^{-1} h^{-1}. This may be attributed to the relatively large Cl−Ti−Cl angle in the precatalyst (vide supra), but similar activity was observed with Sita's CpTi(amidinate) system.[21] When the titanium alkyl compounds were used in combination with the stoichiometric activators $[(C_6F_5)_3B]$ and $[Me_2NHPh][(C_6F_5)_4B]$, no polymer was produced. NMR tube scale reactions of $[\mathbf{L}Ti(CH_2Ph)_2]$ and $[\mathbf{L}TiMe_2]$ with these activators gave unpromising mixtures, suggesting that well-defined species $[\mathbf{L}TiR]^+$ will be inaccessible.

Table 1. Crystallographic Data, Collection Parameters, and Refinement Parameters for the C_2-Symmetric Titanium Complex $[LTiCl_2]$

empirical formula	$C_{32}H_{30}N_4Cl_2Ti$
fw	589.40
cryst size (mm^3)	0.25 × 0.14 × 0.12
cryst syst	orthorhombic
space group	*Pbca*
a (Å)	15.5864(7)
b (Å)	16.2149(7)
c (Å)	23.5128(11)
α (deg)	90
β (deg)	90
γ (deg)	90
V (Å^3)	5942.4(5)
D_{calcd} (Mg/m^3)	1.318
μ (mm^{-1})	0.496
F_{000}	2448
total no. of rflns	23 213
no. of indep rflns	3872
R_{int}	0.0805
no. of data/restraints/ params	3872/0/356
R1[a] ($I > 2\sigma(I)$)	0.0506
wR2[b]	0.1121
GOF[c] on F^2	1.078

[a] Conventional $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ 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] $GOF = [\sum w(F_o^2 - F_c^2)^2/((\text{no. of unique rflns}) - (\text{no. of params}))]^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for the C_2-Symmetric Titanium Complex $[LTiCl_2]$

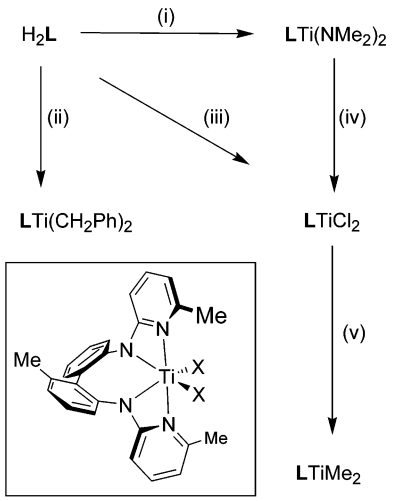
Ti(1)−N(1)	1.975(4)	N(1)−C(6)	1.423(5)
Ti(1)−N(3)	1.985(4)	N(2)−C(19)	1.342(6)
Ti(1)−N(4)	2.254(4)	N(2)−C(15)	1.349(6)
Ti(1)−N(2)	2.267(4)	N(3)−C(21)	1.381(6)
Ti(1)−Cl(1)	2.2803(15)	N(3)−C(9)	1.421(6)
Ti(1)−Cl(2)	2.2835(15)	N(4)−C(21)	1.354(5)
N(1)−C(15)	1.380(5)	N(4)−C(25)	1.349(6)
N(1)−Ti(1)−N(3)	81.57(14)	N(4)−Ti(1)−Cl(1)	86.15(11)
N(1)−Ti(1)−N(4)	134.93(14)	N(2)−Ti(1)−Cl(1)	84.92(10)
N(3)−Ti(1)−N(4)	61.61(14)	N(1)−Ti(1)−Cl(2)	125.92(12)
N(1)−Ti(1)−N(2)	61.65(14)	N(3)−Ti(1)−Cl(2)	97.81(12)
N(3)−Ti(1)−N(2)	135.14(15)	N(4)−Ti(1)−Cl(2)	86.40(10)
N(4)−Ti(1)−N(2)	162.34(13)	N(2)−Ti(1)−Cl(2)	85.44(11)
N(1)−Ti(1)−Cl(1)	98.03(12)	Cl(1)−Ti(1)−Cl(2)	121.92(6)
N(3)−Ti(1)−Cl(1)	127.41(12)		

Concluding Remarks

The new chiral bis(aminopyridinate) ligand **L** forms C_2-symmetric complexes with titanium in which two

(18) (a) Kempe, R.; Arndt, P. *Inorg. Chem.* **1996**, *35*, 2644. (b) Fuhrmann, H.; Brenner, S.; Arndt, P.; Kempe, R. *Inorg. Chem.* **1996**, *35*, 6742.
(19) Oberthür, M.; Arndt, P.; Kempe, R. *Chem. Ber.* **1996**, *129*, 1087.
(20) Tjaden, E.; Swansen, D.; Jordan, R.; Petersen, J. *Organometallics* **1995**, *14*, 371.
(21) Sita, L. R.; Babcock, J. R. *Organometallics* **1998**, *17*, 5228.

Scheme 2. Synthesis and Reactions of [LTiX$_2$] (X = Chloride, Amide, Alkyl)[a]



[a] Reagents and conditions: (i) $Ti(NMe_2)_4$, Et_2O; (ii) $Ti(CH_2Ph)_4$, toluene; (iii) KH, $TiCl_3$, $PbCl_2$, THF; (iv) TMSCl, toluene; (v) MeMgBr, Et_2O.

further ancillary ligands are retained in cis coordination sites (i.e. cis-α structure). Several features of this system make it a good candidate for study as an alternative to the *ansa*-metallocene complexes described earlier. The chirality of these compounds arises in the biaryl ligand but is expressed efficiently in the metal coordination sphere. Thus, for example, the *R* diamine backbone will give rise to Λ helicity at the metal, as depicted in the inset to Scheme 2. This means that a chiral nonracemic C_2-symmetric structure will be assembled directly without the need for resolution of the complex. Also, we have shown that substitution and redox processes at the metal can be supported by the aminopyridinate ligand framework in **L**; such reactivity is previously unknown for the aminopyridinates, in contrast to the related amidinates[12,13] and of course the cyclopentadienyls.

Experimental Details

General Comments. Where necessary, procedures were carried out under an inert atmosphere of argon by using a dual-manifold vacuum/argon line and standard Schlenk techniques, or in an MBraun drybox. Solvents were dried by refluxing for 3 days under dinitrogen over the appropriate drying agents (sodium for toluene; potassium for THF and benzene; sodium−potassium alloy for diethyl ether, petroleum ether, and pentane; calcium hydride for dichloromethane) and degassed before use. Solvents were stored in glass ampules under argon. All glassware and cannulas were stored in an oven (>373 K) and flame-dried immediately prior to use. Most chemicals and reagents were purchased from either Aldrich Chemical Co. or Acros Chemical Co. and used without further purification. Deuterated solvents were freeze−thaw degassed and dried by refluxing over potassium (or calcium hydride for d_2-dichloromethane) for 3 days before being vacuum-distilled (trap-to-trap) to a clean, dry Young's tap ampule and being stored in the drybox. Deuterated chloroform was dried in the bottle over molecular sieves (4Å).

NMR spectra were recorded on Bruker ACF-250, DPX-300, DPX-400, and AV-400 spectrometers, and the spectra were referenced internally using residual protio solvent resonances relative to tetramethylsilane (δ 0 ppm). EI/CI mass spectra were obtained on a VG Autospec mass spectrometer. Infrared spectra were obtained either as Nujol mulls using a Perkin-Elmer Paragon 1000 FTIR spectrometer or directly using an Avatar 320 FTIR instrument. Elemental analyses were performed by Warwick Analytical Services. Flash chromatography was performed either in standard glassware or with a Flash-Master Personal chromatography system and a selection of prepacked disposable columns. Thin-layer chromatography was performed using Merck 0.25 mm silica layer foil-backed plates. The low carbon values obtained in the elemental analysis of the two titanium alkyls are attributed to the partial formation of metal carbides in the combustion process, which is occasionally observed with organometallic complexes of this type.

H_2L. Toluene (40 mL) was added to a Schlenk vessel charged with **1** (3.0 g, 0.014 mol), 2-bromo-6-methylpyridine (4.4 g, 0.026 mol), [Pd_2(DBA)$_3$] (260 mg, 1 mol %), DPPP (240 mg, 2 mol %), and NaO^{t}Bu (3.0 g, 0.03 mol). The purple solution obtained was stirred and heated to 90 °C. The progress of the reaction was monitored by TLC. After 20 h, the mixture was diluted with diethyl ether (50 mL) and was filtered twice through silica gel. Following filtration, the silica gel and residual solid material was washed with ether (2 × 20 mL). The filtrate and washings were combined and decolorized with charcoal powder. The solution was then filtered and concentrated in vacuo to give a yellow residue. The solid material was washed with cold petroleum ether and dried under suction to afford H_2**L** as a fine white powder. Yield: 2.30 g, 77%. Anal. Calcd for $C_{26}H_{26}N_4$: C, 79.16; H, 6.64; N, 14.20. Found: C, 79.13; H, 6.66; N, 14.18. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 7.73 (2H, d, $^3J_{HH}$ = 8 Hz, Ar *H*), 7.27 (2H, dd, $^3J_{HH}$ = 8 Hz, Ar *H*), 7.17 (2H, t, $^3J_{HH}$ = 8 Hz, Ar *H*), 6.99 (2H, d, $^3J_{HH}$ = 7 Hz, Ar *H*), 6.52 (2H, d, $^3J_{HH}$ = 8 Hz, Ar *H*), 6.46 (2H, d, $^3J_{HH}$ = 8 Hz, Ar *H*), 5.93 (2H, s, N*H*), 2.34 (6H, s, *Me*), 1.98 (6H, s, *Me*). ^{13}C{^{1}H} NMR (100.6 MHz, 298 K, $CDCl_3$): δ 157.6, 155.8, 140.2, 138.2, 137.9, 129.4, 126.3, 124.3, 117.7, 114.8, 107.0 (*Ar*), 24.7 (*Me*), 20.3 (*Me*). MS (EI): *m*/*z* 394 [M^+], 379 [$M^+ - CH_3$], 286 [M^+ − Ar]. IR (Golden Gate; ν, cm^{-1}): 3390 (N−H), 1569, 1506, 1446, 1325, 1152, 770.

[LTi(CH$_2$Ph)$_2$]. A Schlenk vessel was charged with $Ti(CH_2Ph)_4$[22] (233 mg, 0.57 mmol) and H_2**L** (223 mg, 0.57 mmol). Toluene (25 mL) was added, and the dark red solution obtained was stirred for 15 h in the absence of light. Concentration under reduced pressure gave a dark red residue which was washed with pentane. Drying in vacuo gave the product as a dark red microcrystalline solid. Yield: 320 mg, 90%. Anal. Calcd for $C_{40}H_{38}N_4Ti$: C, 77.16; H, 6.15; N, 9.00. Found: C, 76.57; H, 6.43; N, 8.76. ^{1}H NMR (400 MHz, 298 K, C_6D_6): δ 7.11 (8H, m, Ar *H*), 6.88 (4H, m, Ar *H*), 6.61 (2H, dd, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz, Ar *H*), 6.56 (4H, d, *J* = 8 Hz, Ar *H*), 6.32 (2H, d, $^3J_{HH}$ = 8 Hz, Ar *H*), 6.13 (2H, d, $^3J_{HH}$ = 8 Hz, Ar *H*), 3.07 (2H, d, *J* = 10 Hz, C*H*$_2$), 2.92 (2H, d, *J* = 10 Hz, C*H*$_2$), 2.47 (6H, s, *Me*), 2.27 (6H, s, *Me*). ^{13}C{^{1}H} NMR (100.6 MHz, 298 K, C_6D_6): δ 164.5, 151.8, 149.5, 147.3, 139.6, 137.1, 131.0, 127.9, 125.6, 125.5, 124.3, 120.5, 113.0, 112.5, 102.6 (*Ar*), 97.2 (*C*H$_2$), 20.9, 19.4 (*Me*). MS (EI): *m*/*z* 531 [M^+], 379 [M^+ − CH_2Ph]. IR (Nujol; ν, cm^{-1}): 1594, 1565, 1459, 1377, 1262, 1242, 1208, 1155, 1028, 913, 830, 775, 729, 695.

[LTi(NMe$_2$)$_2$]. A solution of H_2**L** (615 mg, 1.56 mmol) in diethyl ether (20 mL) was added dropwise over 10 min to a Schlenk vessel charged with $Ti(NMe_2)_4$ (350 mg, 1.56 mmol). A color change from orange-yellow to deep red was observed over the course of the addition. The resulting mixture was stirred for 90 min. After this time the solvent was removed under reduced pressure to give a bright red microcrystalline solid. This material was washed with pentane and dried in vacuo. Yield: 750 mg, 91%. Anal. Calcd for $C_{30}H_{36}N_6Ti$: C, 68.05; H, 6.87; N, 15.78. Found: C, 68.05; H, 6.86; N, 15.78. ^{1}H NMR (400 MHz, 298 K, CD_2Cl_2): δ 6.98 (4H, t, $^3J_{HH}$ = 8 Hz, Ar *H*), 6.84 (2H, d, $^3J_{HH}$ = 8 Hz, Ar *H*) 6.79 (2H, d, $^3J_{HH}$ =

(22) Zucchini, U.; Albizatti, E.; Gianni, U. *J. Organomet. Chem.* **1971**, *26*, 357.

8 Hz, Ar *H*), 6.02 (2H, d, $^3J_{HH}$ = 7 Hz, Ar *H*), 5.89 (2H, d, $^3J_{HH}$ = 8 Hz, Ar *H*), 3.17 (12H, s, *Me*), 2.15 (6H, s, *Me*) 1.97 (6H, s, *Me*). $^{13}C\{^1H\}$ NMR (100.6 MHz, 298 K, CD_2Cl_2): δ 165.7, 156.0, 147.1, 138.9, 138.6, 127.7, 125.5, 125.1, 121.2, 110.2, 105.3 (*Ar*), 45.7 (N*Me*) 23.2, 20.7 (*Me*). MS (EI): *m*/*z* 528 [M^+], 484 [$M^+ - NMe_2$]. IR (Nujol; ν, cm^{-1}): 2360, 1596, 1463, 1377, 1238, 1153, 945, 917, 807, 771, 743, 729.

[LTiCl$_2$]. Method A. A Schlenk vessel was charged with H_2**L** (500 mg, 1.27 mmol) and potassium hydride (205 mg, 5.12 mmol). THF (30 mL) was added, and the yellow solution was stirred for 12 h, with regular venting of evolved gas. The mixture was filtered, and the filtrate was cooled to −60 °C. It was then transferred at −60 °C to a separate Schlenk vessel charged with a purple suspension of titanium(III) chloride (200 mg, 1.27 mmol) in toluene (40 mL) at −60 °C. The resulting dark brown mixture was warmed to ambient temperature and stirred for 12 h. After this time the solution was filtered and added to a Schlenk vessel charged with lead(II) chloride (450 mg, 1.60 mmol). The mixture was stirred for 15 h, and a color change to deep purple was observed after this time. The solution was concentrated and extracted with toluene (30 mL) and filtered. The filtrate was concentrated, and the dark purple residue was washed with pentane (2 × 10 mL). Drying under reduced pressure gave a dark purple microcrystalline solid. Yield: 690 mg, 87%.

Method B. Toluene (20 mL) was added to a Schlenk vessel charged with **L**Ti(NMe$_2$)$_2$ (190 mg, 0.36 mmol), to give a dark red solution. Chlorotrimethylsilane (0.11 mL, 0.9 mmol) was added via cannula to the reaction solution, and the mixture was stirred for 15 h in the absence of light. After this time, a color change to dark purple was observed. The volatiles were removed under reduced pressure to give a dark purple microcrystalline solid. This material was washed with pentane and dried in vacuo. Yield: 175 mg, 95%. Anal. Calcd for $C_{26}H_{24}N_4Cl_2Ti$: C, 61.08; H, 4.73; N, 10.96. Found: 60.76; H, 4.69; N, 10.75. ^1H NMR (400 MHz, 298 K, CD_2Cl_2): δ 7.45 (2H, t, $^3J_{HH}$ = 8 Hz, Ar *H*), 7.06 (2H, t, $^3J_{HH}$ = 8 Hz, Ar *H*) 6.99 (2H, d, $^3J_{HH}$ = 8 Hz, Ar *H*), 6.78 (2H, d, $^3J_{HH}$ = 8 Hz, Ar *H*), 6.65 (2H, d, $^3J_{HH}$ = 8 Hz, Ar *H*), 6.27 (2H, d, $^3J_{HH}$ = 8 Hz, Ar *H*), 2.51 (6H, s, *Me*), 2.05 (6H, s, *Me*) $^{13}C\{^1H\}$ NMR (100.6 MHz, 298 K, CD_2Cl_2): δ 164.2, 154.0, 151.0, 142.2, 139.5, 132.4, 128.2, 128.8, 118.8, 113.1, 102.1 (*Ar*), 22.1, 20.7 (*Me*). MS (EI): *m*/*z* 510 [M^+], 475 [$M^+ - Cl$]. IR (Nujol; ν, cm^{-1}): 1595, 1566, 1463, 1377, 1260, 1238, 1154, 833, 772, 728.

[LTiMe$_2$]. A Schlenk vessel was charged with [**L**TiCl$_2$] (225 mg, 0.44 mmol), and diethyl ether (20 mL) was added. The resultant purple solution was cooled to 0 °C, and methylmagnesium bromide (0.29 mL, 0.88 mmol) was added dropwise over 10 min via cannula. The dark brown mixture was warmed to ambient temperature and was stirred for 15 h in the absence of light. After this time a fine brown precipitate had formed, which was isolated by filtration. The solid material was extracted with toluene (2 × 10 mL), and the combined extracts were concentrated under reduced pressure. A brown microcrystalline solid was obtained, which was washed with pentane and dried in vacuo. Yield: 149 mg, 72%. Anal. Calcd for $C_{28}H_{30}N_4Ti$: C, 71.49; H, 6.43; N, 11.91. Found: C, 70.34; H, 6.12; N, 11.59. ^1H NMR (400 MHz, 298 K, CD_2Cl_2): δ 7.33 (2H, t, $^3J_{HH}$ = 8 Hz, Ar *H*), 6.95 (4H, m, Ar *H*), 6.85 (2H, dd, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 2 Hz Ar *H*), 6.38 (4H, m, Ar *H*), 2.49 (6H, s, *Me*), 2.00 (6H, s, *Me*) 0.95 (6H, s, *Me*). $^{13}C\{^1H\}$ NMR (100.6 MHz, 298 K, CD_2Cl_2): δ 166.1, 154.4, 148.5, 141.8, 139.1, 133.3, 127.6, 125.6, 114.3, 114.1, 103.7, (*Ar*), 71.8, 22.4, 20.8 (*Me*) ppm. MS (EI): *m*/*z* 455 [$M^+ - CH_3$]. IR (Nujol; ν, cm^{-1}): 2282, 1591, 1563, 1460, 1377, 1260, 1152, 1091, 1020, 799, 728.

Crystallography. Crystals of [**L**TiCl$_2$] were obtained as fine purple prisms from a concentrated solution in benzene at 0 °C. The 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 = 0.710 73 Å). Data were collected using narrow (0.3° in ω) frame exposures. Intensities were corrected semiempirically for absorption, based on symmetry-equivalent and repeated reflections (SADABS). Statistical analysis (via XPREP) revealed data for $\theta \geq 45°$ to be weak. Omitting data from this point significantly improved the refinement and convergence characteristics. The structure was solved by direct methods (SHELXS), with additional light atoms found by Fourier methods. The crystal structure contains one molecule of the crystallization solvent, benzene, within the asymmetric unit of the unit cell. All non-hydrogen atoms were refined anisotropically. All H atoms were constrained with a riding model; *U*(H) was set at 1.2 (1.5 for methyl groups) times the U_{eq} value for the parent atom. Programs used were Bruker AXS SMART (control), SAINT (integration), and SHELXTL for structure solution, refinement, and molecular graphics.

Acknowledgment. P.S. thanks the EPSRC for postdoctoral fellowhships (to I.J.M. and P.N.O.). I.W. is a University of Warwick Postgraduate Research Fellow and a Society of the Chemical Industry Messel Scholar.

Supporting Information Available: Tables of crystal data, atomic coordinates, distances and angles, and hydrogen coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

OM030055K