Inorg. Chem. **1995**, *34*, 2921−2930 **2921**

Oxazoline Early Transition Metal Complexes: Functionalizable Achiral Titanium(IV), Titanium(III), Zirconium(IV), Vanadium(III), and Chiral Zirconium(IV) Bis(oxazoline) Complexes

Pier Giorgio Cozzi[†] **and Carlo Floriani***

Institut de Chimie Minérale et Analytique, BCH, Université de Lausanne,
CH-1015 Lausanne, Switzerland

Angiola Chiesi-Villa and Corrado Rizzoli

Dipartimento di Chimica, Università di Parma, I-43100 Parma, Italy

Received December 27, 1994[⊗]

Large-scale syntheses of the (hydroxyphenyl)oxazoline ligands $L^1 = \mathbf{6}$, $L^2 = \mathbf{7}$, $L^3 = \mathbf{8}$, $L^4 = \mathbf{9}$, and $L^5 = \mathbf{10}$ are reported. The conversion of **6**−**10** into the corresponding sodium salts has been employed for metal complexation. The reaction of **6** with $TiCl_4{\cdot}2THF$, $TiCl_3{\cdot}3THF$, $ZrCl_4{\cdot}2THF$, and $VCl_3{\cdot}3THF$ in a 1:2 metal:ligand ratio afforded the corresponding hexacoordinate functionalizable metal complexes: *cis*-$[(Cl)_2Ti(L^1)_2]$, **11**; *cis*-$[(THF)(Cl)Ti(L^1)_2]$, **12**; *cis*-$[(Cl)_2Zr(L^1)_2]$, **13**; *trans*-$[(THF)(Cl)V(L^1)_2]$, **14**. The structures of **11**, **12**, and **14** have been clarified by X-ray analysis. The reaction of the **8** and **9** sodium salts with $ZrCl_4{\cdot}2THF$ in a 1:2 metal:ligand ratio led to the corresponding chiral functionalizable metal complexes, whose structures were clarified by X-ray analysis: *cis*-$[(Cl)_2Zr(L^3)_2]$, **15**; *cis*-$[(Cl)_2Zr(L^4)_2]$, **16**. A common significant feature discovered from these studies is the existence of intramolecular hydrogen bonding, which is probably responsible for the high conformational rigidity of the oxazoline ligand. Crystallographic details are as follows: **11** is monoclinic, space group $I2/a$, with $a = 16.443(2)$ Å, $b = 8.365(1)$ Å, $c = 17.945(2)$ Å, $\beta = 106.93(1)°$, $Z = 4$, and $R = 0.034$; **12** is orthorhombic, space group $Pca2_1$, with $a = 15.669(2)$ Å, $b = 17.750(3)$ Å, $c = 18.971(3)$ Å, $Z = 8$, and $R = 0.050$; **14** is monoclinic, space group $P2_1/n$, with $a = 9.391(4)$ Å, $b = 28.618(6)$ Å, $c = 12.077(4)$ Å, $\beta = 105.79(2)°$, $Z = 4$, and $R = 0.052$; **16** is monoclinic, space group $P2_1$, with $a = 10.161(2)$ Å, $b = 14.151(3)$ Å, $c = 12.361(2)$ Å, $\beta = 93.76(2)°$, $Z = 2$, and $R = 0.033$.

Introduction

The chemistry of early transition metallocene complexes continues to be one of the most actively pursued areas of modern organometallic research. Numerous classes of reaction are supported by the bis(cyclopentadienyl)metal fragment including the insertion of small molecules into metal−alkyl or −hydride bonds, metallocycle formation, and σ-bond metathesis.[1] Attempts to mimic the stereoelectronic properties of the $(cp)_2M$ moiety have led several groups to investigate a range of ancillary ligands such as bulky alkoxides[2] and amides[3] and polydentate ligands such as Schiff bases,[4] tetraaza[14]annulenes,[5] porphy-

---

[*] To whom correspondence should be addressed.

[†] Present address: Dipartimento di Chimica G. Ciamician, Università di Bologna, Via Selmi 2, I-40216 Bologna, Italy.

[⊗] Abstract published in *Advance ACS Abstracts*, May 1, 1995.

(1) (a) Reetz, M. T. *Organotitanium Reagents in Organic Synthesis*; Springer: Berlin, 1986. (b) Wailes, P. C.; Courts, R. P.; Weigold, H. *Organometallic Chemistry of Titanium, Zirconium and Hafnium*; Academic: New York, 1974. (c) Cardin, D. J.; Lappert, M. F.; Raston, C. L. *Chemistry of Organozirconium and Hafnium Compounds*; Wiley: New York, 1986. (d) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047. (e) Reetz, M. T. In *Organometallics in Synthesis*; Schlosser, M., Ed.; Wiley: New York, 1994; Chapter 3. (f) Duthaler, R. O.; Hafner, A.; Riediker, M. In *Organic Synthesis via Organometallics*; Dötz, K. H., Hoffmann, R. W., Eds.; Vieweg: Braunschweig, Germany, 1991; p 285. (g) Negishi, E.-I. In *Comprehensive Organic Synthesis*; Paquette, L. A., Ed.; Pergamon: Oxford, U.K., 1991; Vol. 5; p 1163. (h) Grossman, R. B.; Buchwald, S. L. *J. Org. Chem.* **1992**, *57*, 5803 and references therein. (i) Negishi, E.-I.; Takahashi, T. *Acc. Chem. Res.* **1994**, *27*, 124 and references therein. (j) Schore, N. E. In *Comprehensive Organic Synthesis*; Paquette, L. A., Ed.; Pergamon: Oxford, U.K., 1991; Vol. 5, p 1037. (k) Erker, G.; Krüger, C.; Müller, G. *Adv. Organomet. Chem.* **1985**, *24*, 1 and references therein. (l) Swanson, D. R.; Negishi, E. *Organometallics* **1991**, *10*, 825. (m) G. Erker, G.; Pfaff, R.; Krüger, C.: Werner, S. *Organometallics* **1993**, *12*, 3559. (n) Erker, G.; Noe, R.; Krüger, C.; Werner, S. *Organometallics* **1992**, *11*, 4174. (o) Erker, G.; Pfaff, R. *Organometallics* **1993**, *12*, 1921. (p) Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325.

(2) (a) Chisholm, M. H.; Rothwell, I. P. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, U.K., 1988, Vol. 2, Chapter 15.3. (b) Chamberlain, L. R.; Durfee, L. D.; Fau, P. E.; Fanwick, P. E.; Kobriger, L.; Latesky, S. L.; McMullen, A. K.; Rothwell, I. P.; Folting, K.; Huffman, J. C.; Streib, W. E.; Wang, R. *J. Am. Chem. Soc.* **1987**, *109*, 390, 6068 and references therein. Durfee, L. D.; Fanwick, P. E.; Rothwell, I. P.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 4720. (c) Zambrano, C. H.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1994**, *13*, 1174. (d) Hill, J. E.; Bailich, G.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1993**, *12*, 2911. (e) Bailich, G.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc.* **1993**, *115*, 1581. (f) Hill, J. E.; Bailich, G.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1991**, *10*, 3428. (g) Lubben, T. V.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1987**, *109*, 424 and references therein. (h) Floriani, C.; Corazza, F.; Lesueur, W.; Chiesi-Villa, A.; Guastini, C. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 66.

(3) Lubben, T. V.; Wolczanski, P. T.; Van Duyne, G. D. *Organometallics* **1984**, *3*, 977. Lubben, T. V.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1987**, *109*, 424. Andersen, R. A. *Inorg. Chem.* **1979**, *18*, 2928. Andersen, R. A. *Inorg. Chem.* **1979**, *8*, 2929. Cummins, C. C.; Schaller, C. P.; Van Duyne, G. D.; Wolczanski, P. T.; Chan, A. W. E.; Hoffman, R. *J. Am.Chem. Soc.* **1991**, *113*, 2985.

(4) (a) Gambarotta, S.; Mazzanti, M.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1985**, 829. (b) Floriani, C.; Solari, E.; Corazza, F.; Chiesi-Villa, A.; Guastini, C. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 64. (c) Corazza, F.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1990**, 1335. (d) Rosset, J.-M.; Floriani, C.; Mazzanti, M.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1990**, *29*, 3991. (e) Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Chem. Soc., Dalton Trans.* **1992**, 367.

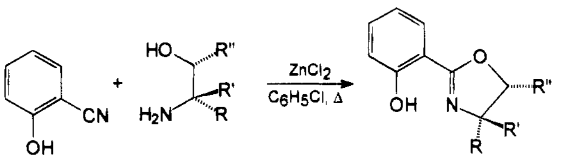
0020-1669/95/1334-2921$09.00/0

rinogens,[6] and porphyrins.[7] The synthesis of enantiomerically-resolved ansa-metallocenes has also allowed such complexes to find increasing application in enantioselective synthesis[8] and especially as initiators for stereoselective Ziegler–Natta polymerization.[9] However, the preparation of these homochiral metal complexes is a difficult, nontrivial task.[10]

Despite a rich and successful history in asymmetric catalysis, the use of oxazoline ligands as ancillary groups in transition metal complexes has only recently started to develop.

Two major attractive characteristics of the oxazoline skeleton are (i) its presence in naturally occurring siderophore chelating agents, like micobactine, parabactine, and vibriobactine,[11] and (ii) its ability to form kinetically inert chiral metal complexes of potential for asymmetric synthesis.[12] In particular, oxazoline has been used as a chiral auxiliary[13] in catalytic alkene cyclopropanation,[14] in palladium-catalyzed allylic coupling,[15] and in Diels–Alder reactions.[16] The special properties of oxazoline complexes derive from the high conformational rigidity of the ligand and from the closeness of stereogenic centers to available Lewis acidic metal coordination sites.[17] Within this context, significant examples of coordination complexes behaving as Lewis acids were recently reported.[18] The purpose of the present work is to take advantage of the oxazoline ligand in metal-assisted organometallic chemistry. To this purpose we focused our attention on the replacement of the cyclopentadienyl anion by 2-(2-hydroxyphenyl)-2-oxazoline anions, which are relatively easy to synthesize, even in a chiral form. We report specifically in this paper the synthesis of functionalizable and reducible achiral titanium–, zirconium–, and vanadium–oxazoline complexes. In addition we describe the straightforward preparation of homochiral bis((hydroxyphenyl)oxazoline)zirconium complexes.

Scheme 1



R = Me, R' = Me, R'' = H, **1** R = Me, R' = Me, R'' = H, **6**
R = CH$_2$Ph, R' = H, R'' = H, **2** R = CH$_2$Ph, R' = H, R'' = H, **7**
R = Pr^i, R' = H, R'' = H, **3** R = Pr^i, R' = H, R'' = H, **8**
R = Me, R' = H, R'' = Ph, **4** R = Me, R' = H, R'' = Ph, **9**
R = Ph, R' = H, R'' = H, **5** R = Ph, R' = H, R'' = H, **10**

Results and Discussion

The synthesis of the achiral and homochiral (hydroxyphenyl)-oxazoline ligands **1–5** proceeded without difficulty from commercially available starting materials[19] (Scheme 1). The literature methodology[20] was scaled up considerably, and this allowed us to purify the products by distillation rather than engaging in time-consuming and tedious chromatography. The ligands are stable at the elevated temperatures required, and after two distillations NMR analysis confirmed purities in excess of 95%. The simpler purification procedure adopted allowed the two ligands to be obtained in yields comparable to those of the small-scale chromatographic separation. Full details of the synthesis of **6–10** are given in the Experimental Section.

The deprotonation of **6** with NaH gave a THF-soluble sodium salt, which was reacted *in situ* with the corresponding metal

---

(5) (a) Ciurli, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1986**, 1401. (b) Floriani, C.; Ciurli, S.; Chiesi-Villa, A.; Guastini, C. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 70. (c) Floriani, C.; Mazzanti, M.; Ciurli, S.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1988**, 1361. (d) Solari, E.; De Angelis, S.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chem.* **1992**, *31*, 96. (e) De Angelis, S.; Solari, E.; Gallo, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chem.* **1992**, *31*, 2520. (f) Giannini, L.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2204. (g) Uhrhammer, R.; Black, D. G.; Gardner, T. G.; Olsen, J. D.; Jordan, R. F. *J. Am. Chem. Soc.* **1993**, *115*, 8493. (h) Goedken, V. L.; Ladd, J. A. *J. Chem. Soc., Chem. Commun.* **1981**, 910; **1982**, 142. Housmekerides, C. E.; Pilato, R. S.; Geoffroy, G. L.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1991**, 563. Yang, C. H.; Ladd, J. A.; Goedken, V. L. *J. Coord. Chem.* **1988**, *18*, 317. (i) Floriani, C. *Polyhedron* **1989**, *8*, 1717.

(6) (a) Jacoby, D.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Chem. Soc., Chem. Commun.* **1991**, 790. (b) Jacoby, D.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1993**, *115*, 3595. (c) Jacoby, D.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1993**, *115*, 7025. (d) Rosa, A.; Ricciardi, G.; Rosi, M.; Sgamellotti, A.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1993**, 3759. (e) Solari, E.; Musso, F.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Chem. Soc., Dalton Trans.* **1994**, 2015.

(7) (a) Dawson, D. Y.; Brand, H.; Arnold, J. *J. Am. Chem. Soc.* **1994**, *116*, 9797. (b) Brand, H.; Arnold, J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 95. (c) Arnold, J.; Hoffman, C. G.; Dawson, D. Y.; Hollander, F. J. *Organometallics* **1993**, *12*, 3645. (d) Brand, H.; Arnold, J. *Organometallics* **1993**, *12*, 3655. (e) Martin, P. C.; Arnold, J.; Bocian, D. F. *J. Phys. Chem.* **1993**, *97*, 1332. (f) Kim, H.-J.; Whang, D.; Kim, K.; Do, Y. *Inorg. Chem.* **1993**, *32*, 360. (g) Arnold, J.; Johnson, S. E.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1992**, *114*, 3996. (h) Brand, H.; Arnold, J. *J. Am. Chem. Soc.* **1992**, *114*, 2266. (i) Shibata, K.; Aida, T.; Inoue, S. *Chem. Lett.* **1992**, 1173. (j) Schaverien, C. J.; Orpen, A. G. *Inorg. Chem.* **1991**, *30*, 4968. (k) Arnold, J.; Hoffman, C. G. *J. Am. Chem. Soc.* **1990**, *112*, 8620.

(8) Waymouth, R.; Pino, P. *J. Am. Chem. Soc.* **1990**, *112*, 4911. Grossmann, R. B.; Doyle, R. A.; Buchwald, S. L. *Organometallics* **1991**, *10*, 1501. Grossmann, R. B.; Davis, W. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1991**, *113*, 2321. Willoughby, C. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1992**, *114*, 7562. Hong, Y.; Kuntz, B. A.; Collins, S. C. *Organometallics* **1993**, *12*, 964.

(9) Coates, G. W.; Waymouth, R. M. *J. Am. Chem. Soc.* **1993**, *115*, 91 and references therein.

(10) Ellis, W. W.; Hollis, K. T.; Odenkirk, W.; Whelan, J.; Ostrander, R.; Rheingold, A. R.; Bosnich, B. *Organometallics* **1993**, *12*, 4391 and references therein.

(11) Black, D. St. C.; Wade, M. J. *Aust. J. Chem.* **1972**, *25*, 1792. Maurer, P. J.; Miller, M. J. *J. Am. Chem. Soc.* **1983**, *105*, 240. Nagao, Y.; Miyasaka, T.; Hagiwara, Y.; Fujita, E. *J. Chem. Soc., Perkin Trans.* **1984**, *1*, 183. Bergeron, R. J.; Garlich, J. R.; McManis, J. S. *Tetrahedron* **1985**, *41*, 507.

(12) Pfaltz, A. In *Modern Synthetic Methods*; Sheffold, R., Ed.; Springer Verlag: Berlin, 1989; Vol. 5, p 198. Brunner, H.; Obermann, U. *Chem. Ber.* **1989**, *122*, 499. Brunner, H.; Obermann, U.; Winner, P. *Organometallics* **1989**, *8*, 8.

(13) Meyers, A. I.; Mihelich, E. D. *Angew. Chem.* **1976**, *88*, 321. Meyers, A. I.; Flisak, J. R.; Aitken, R. A. *J. Am. Chem. Soc.* **1987**, *109*, 5446. Andrews, R. C.; Teague, S. J.; Meyers, A. I. *J. Am. Chem. Soc.* **1988**, *110*, 7854. Gant, T. G.; Meyers, A. I. The Chemistry of 2-Oxazoline (1985–present). *Tetrahedron* **1994**, *50*, 2297.

(14) Lowenthal, R. E.; Masamune, S. *Tetrahedron. Lett.* **1991**, *32*, 7373. Evans, D. A.; Woerpel, K. A.; Hinman, M. M.; Faul, M. M. *J. Am. Chem. Soc.* **1991**, *113*, 726. Woerpel, K. A.; Scott, M. J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 430 and references therein. Evans, D. A.; Fault, M. M.; Bilodeau, M. T.; Anderson, B. A.; Barnes, D. M. *J. Am. Chem. Soc.* **1993**, *115*, 5328.

(15) Müller, D.; Umbricht, G.; Weber, B.; Pfaltz, A. *Helv. Chim. Acta* **1991**, *74*, 232.

(16) Corey, E. J.; Imai, N.; Zhang, H. J. *J. Am. Chem. Soc.* **1991**, *113*, 728. Evans, D. A.; Miller, S. J.; Lectka, T. *J. Am. Chem. Soc.* **1993**, *115*, 6460.

(17) Nesper, R.; Pregosin, P. S.; Puntener, K.; Worle, M. *Helv. Chim. Acta* **1993**, *76*, 2239 and references therein.

(18) Merril, R. E. *CHEMTECH* **1981**, *11*, 1120. Mikami, K. M.; Shimizu, M. *Chem. Rev.* **1992**, *92*, 1021. Brown, J. M. *Chem. Br.* **1989**, 276.

(19) α-Amino alcohols can be prepared in high yield by reduction of the respective α-amino acid: McKennon, M. J.; Meyers, A. I.; Drauz, K.; Schwarm, M. *J. Org. Chem.* **1993**, *58*, 3568. Abiko, A.; Masamune, S. *Tetrahedron Lett.* **1992**, *33*, 5517.

(20) (a) Hoveyda, H. R.; Karunaratne, V.; Rettig, S. J.; Orvig, C. *Inorg. Chem.* **1992**, *31*, 5408. (b) Yang, H.; Khan, M. A.; Nicholas, K. M. *Organometallics* **1993**, *12*, 3485. (c) Bolm, C; Wieghardt, K.; Zehnder, M.; Ranff, T. *Chem. Ber.* **1991**, *124*, 1173. (d) Bolm, C.; Wieghardt, K.; Zehnder, M.; Glasmacher, D. *Helv. Chim. Acta* **1991**, *74*, 717.

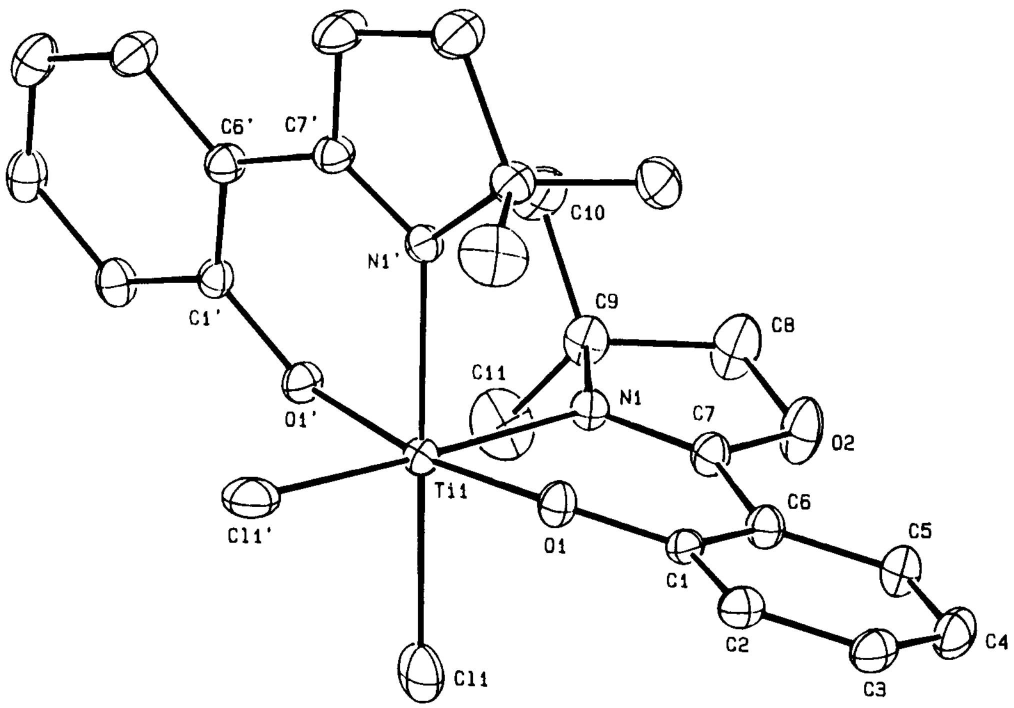


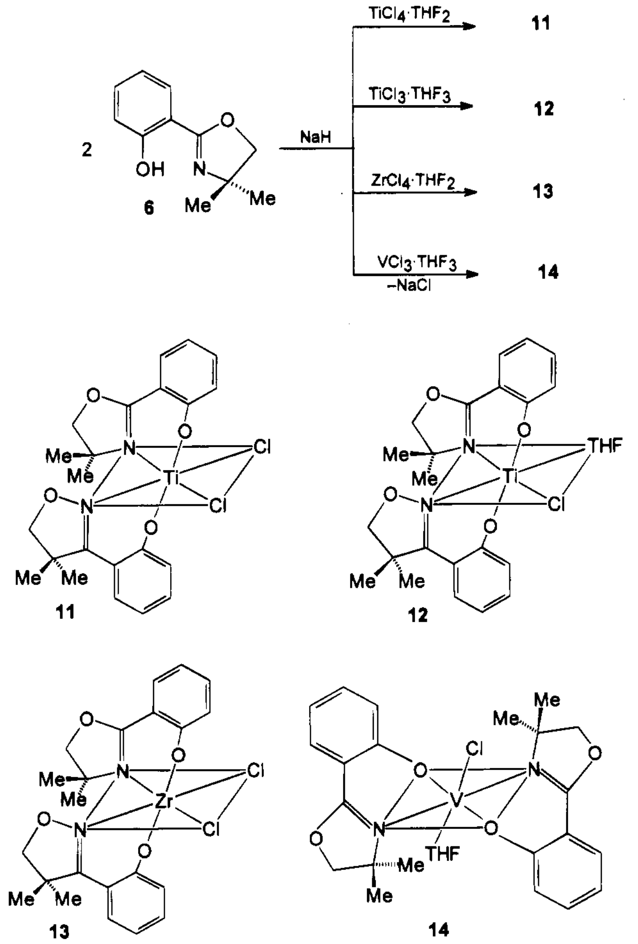
Figure 1. ORTEP drawing for complex **11** (30% probability ellipsoids). Prime denotes a transformation of $-0.5 - x, y, -1 - z$.

chloride.[21] Complexes **11**, **12**, and **14** have been fully characterized, including an X-ray analysis, which demonstrated a *cis* arrangement of the two functionalizable sites in both. This geometrical feature is particularly important for metal-assisted organometallic transformations. These complexes should serve as models for organometallic chemistry of titanium(IV)[22] and the free-radical-like chemistry of titanium(III).[23]

Owing to the relevance of zirconium in metal-assisted transformations,[24] the reaction in Scheme 2 was also carried out with $ZrCl_4{\cdot}THF_2$. Complex **13** was characterized as reported in the Experimental Section. A *trans* coordination geometry was observed in the vanadium(III) derivative **14** (*vide infra*). Our interest in **14** developed from its potential as a precursor to vanadium(II) complexes, which have found a large and interesting use in organic synthesis.[25] The structures of complexes **11** (Figure 1), **12** (Figure 2, molecule A), and **14** (Figure 3) are discussed below.

Complex **11** has crystallographic C_2 symmetry, with the titanium center lying on the crystallographic 2-fold axis (Figure 1). The six-membered chelation rings are somewhat distorted from planarity, as indicated by the folding angle along the N1···O1 line, and are nearly perpendicular to each other (Table 9). The oxazolinato ligand appears to be almost planar, as indicated by the data quoted in Table 9. Bond distances and angles within the chelation ring are in agreement with a double bond mainly localized on the Ni−C7 bond.

Scheme 2



In complex **12** an oxygen atom from a THF molecule replaces a chlorine atom of complex **11**. In the asymmetric unit there

---

(21) Also with lanthanide halide the procedure gives simple access to oxazoline complexes: Cozzi, P. G.; Floriani, C. Unpublished results.

(22) See Reetz, M. T. In *Organometallics in Synthesis*; Schlosser, M., Ed.; Wiley: Chichester, England, 1994.

(23) Nugent, W.; Rajanbabu, T. V. *J. Am. Chem. Soc.* **1994**, *116*, 986.

(24) Hoveyda, A. H.; Xu, Z.; Morken, J. P.; Houri, A. F. *J. Am. Chem. Soc.* **1991**, *113*, 8950. Hoveyda, A. H.; Xu, Z. *J. Am. Chem. Soc.* **1991**, *113*, 5079. Guram, A. S.; Jordan, R. F. *Organometallics* **1991**, *10*, 3470. Grossman, R. B.; Buchwald, S. L. *J. Org. Chem.* **1992**, *57*, 5803. Guram, A. S.; Jordan, R. F. *J. Am. Chem. Soc.* **1992**, *114*, 8991. Coates, G. W.; Waymouth, R. M. *J. Am. Chem. Soc.* **1993**, *115*, 91. Hong, Y.; Kuntz, B. A.; Collins, S. *Organometallics* **1993**, *12*, 964. Guram, A. S.; Guo, Z.; Jordan, R. F. *J. Am. Chem. Soc.* **1993**, *115*, 4902. Guram, A. S.; Jordan, R. F. *J. Org. Chem.* **1993**, *58*, 5595. Houri, A. F.; Didiuk, M. T.; Xu, Z.; Horan, N. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1993**, *115*, 6614. Morken, J. P.; Didiuk, M. T.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1993**, *115*, 6997. Uhrhammer, R.; Black, D. G.; Gardner, T. G.; Olsen, J. D.; Jordan, R. F. *J. Am. Chem. Soc.* **1993**, *115*, 8493.

(25) Freundenberger, J. H.; Konradi, A. W.; Pedersen, S. F. *J. Am. Chem. Soc.* **1989**, *111*, 8014. Park, J.; Pedersen, S. F. *Tetrahedron* **1992**, *48*, 2062.

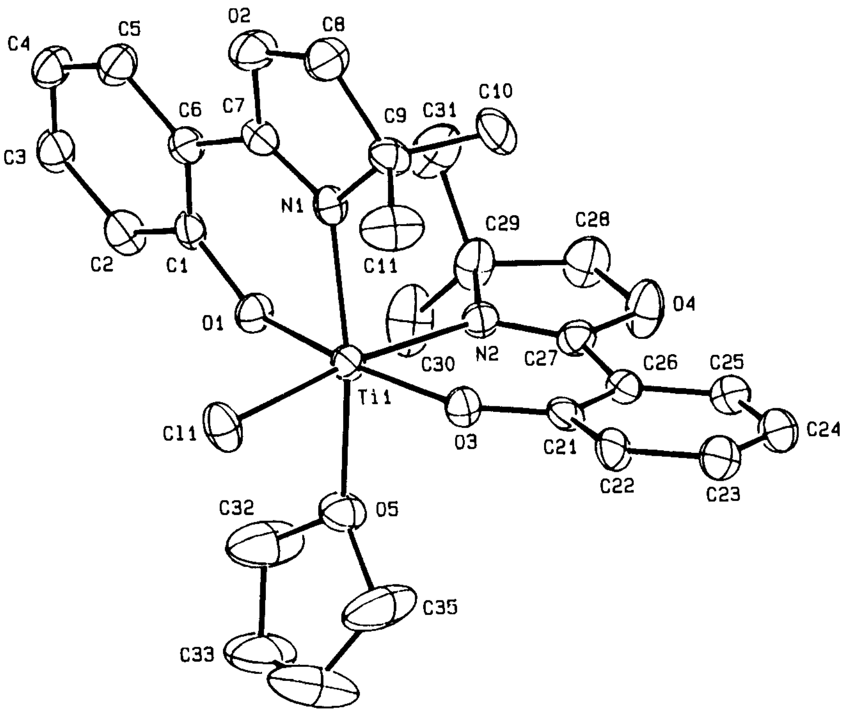


Figure 2. ORTEP drawing for complex **12** (molecule A, 30% probability ellipsoids).

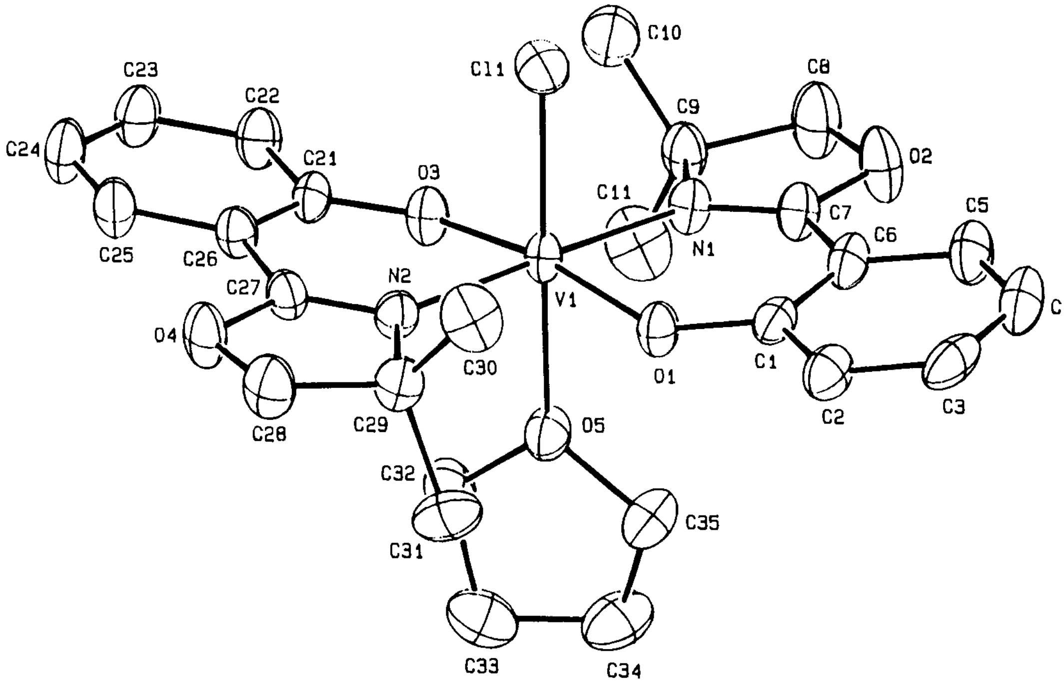


Figure 3. ORTEP drawing for complex **14** (30% probability ellipsoids).

are two crystallographically independent molecules (A and B, Figure 2). Hereafter the values for molecule B will be given in square brackets. The most significant difference with respect to complex **11** concerns the lengthening of the Ti–Cl bond (Ti–Cl, 2.424(2) Å [2.433(3) Å] in complex **12** *vs* 2.319(1) Å in complex **11**) (Tables 6, 7) which could be ascribed to the decreased oxidation state of the metal as well as to inter- and intraligand steric interactions, which are also responsible for the asymmetry within the Ti–O (Ti–O1, 1.860(4) Å [1.876(4) Å]; Ti–O3, 1.951(4) Å [1.951(5) Å]) and Ti–N bond distances (Ti–N1, 2.185(6) Å [2.153(6) Å]; Ti–N2, 2.281(6) Å [2.233(3) Å]). The conformation of the ligand is very similar to that found in complex **11** with an intramolecular CH···O interaction which could be regarded as a hydrogen bond stabilizing the near coplanarity of the six- and five-membered rings [C5···O2, 2.713(7) Å [2.683(6) Å]; H5···O2, 2.46 Å [2.41 Å]; C5–H5···O2, 93° [91°]; C25···O4, 2.676(7) Å [2.722(8) Å]; H25···O4, 2.39 Å [2.19 Å]; C5–H25···O4, 101° [104°].

In complex **14** the two oxazolinato ligands arrange their donor atoms in a *trans*-planar configuration (Figure 3). Coordination is completed by a chlorine and a THF molecule *trans* to each other. The most relevant conformational parameters are quoted in Table 9, from which it can be inferred that the best equatorial plane is not provided by the set of N_2O_2 donor atoms, but by the N2,Cl1,N1,O5 atoms with O1 and O3 at the apices. As in complexes **11** and **12**, the two oxazoline ligands are almost planar. The methyl groups of the oxazolinato ligands are almost symmetrically arranged with respect to the coordination plane

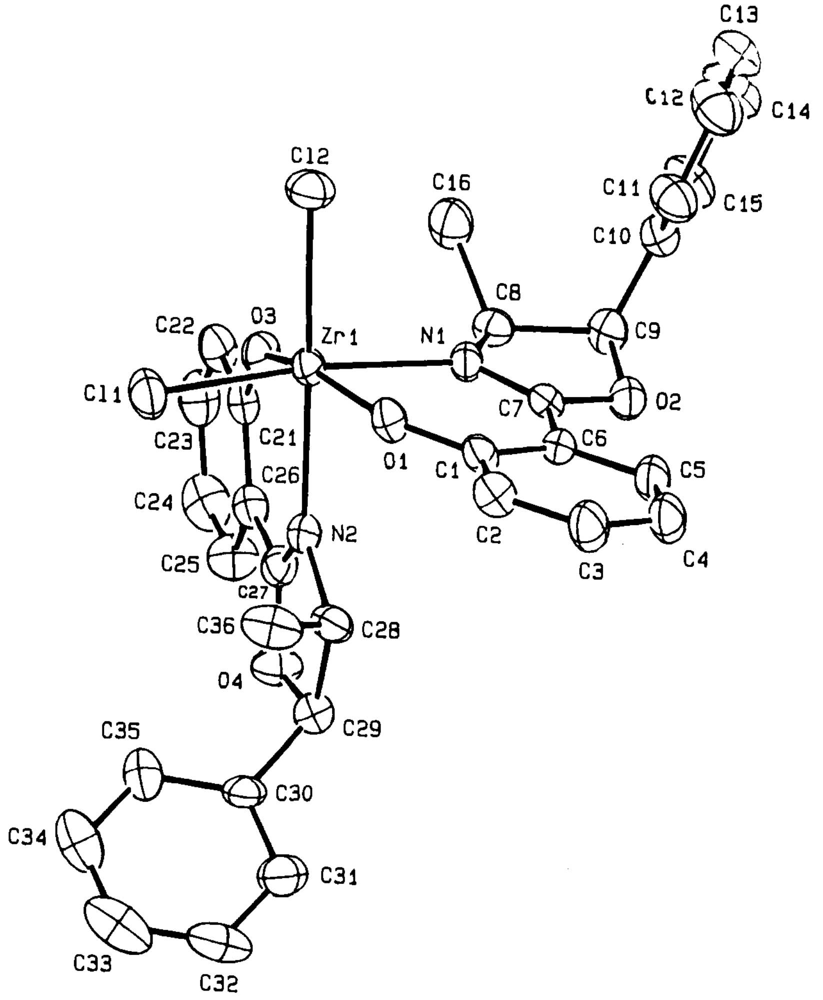


Figure 4. ORTEP drawing for complex **16**.

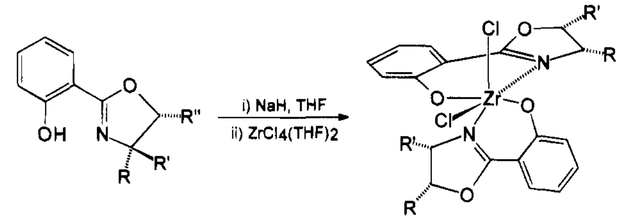
to give short intramolecular contacts with the coordinated oxygen atoms [C10···O3, 3.158(8) Å; H102···O3, 2.36 Å; C10–H102···O3, 130°; C11···O3, 3.275(10) Å; H112···O3, 2.57 Å; C11–H112···O3, 130°; C30···O1, 3.168(8) Å; H301···O1, 2.35 Å; C30–H301···O1, 135°; C31···O1, 3.306(8) Å; H313···O1, 2.58 Å; C31–H313···O1, 136°].

We used ligands **8** and **9** for preparing homochiral complexes. Although previously described as being unstable,[20c,d] both **8** and **9** have shown no appreciable decomposition after prolonged periods under nitrogen at room temperature. The synthetic procedure described gave both ligands as oils, although **9** occasionally crystallized over a period of several days following the distillation.

The ligands **8** and **9** were deprotonated in anhydrous THF using sodium hydride;[26] this reaction appears to be complete after just a few minutes at room temperature. However, in order to ensure complete deprotonation, the solution was typically stirred for 2 h or more. The resultant pale yellow solution was filtered in order to remove a small quantity of an unidentified insoluble brown purity which formed during the ligand distillation step. Addition of a THF suspension of $ZrCl_4\cdot 2THF$ afforded the dichloride complexes **15** and **16** (Scheme 3).

Complexes **15** and **16** have been fully characterized, and an X-ray structure determination has been performed on a crystal of **16** (Figure 4). Zirconium exhibits an octahedral coordination mode involving the oxygen (O1, O3) and nitrogen(N1, N2) atoms from two (hydroxyphenyl)oxazoline ligands derived from norephedrine. The two chlorine atoms are in a *cis* arrangement, and in this respect, **16** is reminiscent of $(cp)_2ZrCl_2$. The N1 and N2 nitrogen atoms of the oxazolidine ligands are *cis*-arranged in the equatorial plane, while the O1 and O3 oxygen atoms are *trans*-arranged, providing the apices of the octahedron. The six-membered chelating rings are significantly distorted from planarity, as indicated by the folding angle along the N1···O1 and N2···O3 lines, and the corresponding planes are almost perpendicular to each other. The oxazolinato ligands are nearly planar. The bond angles and distances of the oxazolinato ring are as expected and are in agreement with a double bond mainly localized on the N1–C7 and N2–C27 bonds. Pertinent bond parameters are given in Table 8.

Scheme 3



R = Pri, R' = H, R'' = H, **8**
R = Me, R' = H, R'' = Ph, **9**

R = Pri, R' = H, **15**
R = Me, R' = Ph, **16**

The present report deals with the synthesis of interesting materials of possible use in metal-mediated organic synthesis *via* organometallic functionalities[27] or low-valent metals.[28]

---

(26) We have also prepared other zirconium and titanium complexes with ligands **7** and **10**, but due to the difficulties in eliminating sodium chloride, we do not obtain a good elemental analysis.

Table 1. Experimental Data for the X-ray Diffraction Studies on Crystalline Compounds **11**, **12**, **14**, and **16**[a]

	11	**12**	**14**	**16**
chem formula	$C_{22}H_{24}Cl_2N_2O_4Ti$	$C_{26}H_{32}ClN_2O_5Ti$	$C_{26}H_{32}ClN_2O_5V\cdot C_4H_8O$	$C_{32}H_{28}Cl_2N_2O_4Zr\cdot C_6H_6$
a, Å	16.443(2)	15.669(2)	9.391(4)	10.161(2)
b, Å	8.365(1)	17.750(3)	28.618(6)	14.151(3)
c, Å	17.945(2)	18.971(3)	12.077(4)	12.361(2)
α, deg	90	90	90	90
β, deg	106.93(1)	90	105.79(2)	93.76(2)
γ, deg	90	90	90	90
V, Å^3	2361.3(5)	5276.3(14)	3123.2(18)	1773.5(6)
Z	4	8	4	2
fw	499.2	535.9	611.1	744.8
space group	$I2/a$ (No. 15)	$Pca2_1$ (No. 29)	$P2_1/n$ (No. 14)	$P2_1$ (No. 4)
T, °C	22	22	22	22
λ, Å	0.710 69	1.541 78	1.541 78	0.710 69
ϱ_{calc}, g cm^{-3}	1.404	1.349	1.300	1.395
μ, cm^{-1}	6.15	40.23	38.29	5.02
transm coeff	0.953−1.000	0.730−1.000	0.864−1.000	0.974−1.000
R	0.034	0.050	0.052	0.033[b]
R_w	0.029	0.048	0.064	
w$R2$				0.078[c]

[a] $R = \Sigma|\Delta F|/\Sigma|F_o|$. $R_w = \Sigma w^{1/2}|\Delta F|/\Sigma w^{1/2}|F_o|$. $wR2 = [\Sigma(w\Delta F^2)^2/\Sigma(wF_o^2)^2]^{1/2}$. $GOF = [\Sigma(w\Delta F^2)^2/(NO - NV)]^{1/2}$. [b] Calculated for the unique observed data. [c] Calculated for the unique total data.

Table 2. Fractional Atomic Coordinates ($\times 10^4$) for Complex **11**

atom	x/a	y/b	z/c
Ti1	−2500(−)	−1250.3(6)	−5000(−)
Cl1	−2515.2(4)	610.1(7)	−4046.0(3)
O1	−1324(1)	−1437(2)	−4651(1)
O2	−1850(1)	−4489(2)	−3036(1)
N1	−2447(1)	−3114(2)	−4131(1)
C1	−716(1)	−1883(2)	−4017(1)
C2	127(1)	−1405(2)	−3917(1)
C3	754(1)	−1870(3)	−3263(1)
C4	571(1)	−2824(3)	−2699(1)
C5	−252(1)	−3322(2)	−2799(1)
C6	−907(1)	−2857(2)	−3457(1)
C7	−1769(1)	−3445(2)	−3577(1)
C8	−2707(1)	−5071(3)	−3274(1)
C9	−3175(1)	−4045(2)	−3982(1)
C10	−3604(1)	−5113(3)	−4663(1)
C11	−3797(2)	−2919(3)	−3776(2)

Comparisons of the chemistry of these complexes and their organometallic derivatives with that of the extremely important but far less accessible ansa-metallocenes will form the basis of subsequent reports.

Experimental Section

All operations were carried out under an atmosphere of purified nitrogen. All solvents were purified by standard methods and freshly distilled prior to use. NMR spectra were recorded on a 200-AC Bruker instrument.

Preparation of 6. In a 1000 mL flask $ZnCl_2$ (1.02 g, 7.48 mmol) was melted under vacuum and cooled under nitrogen; then hydroxybenzonitrile (17.8 g, 149.6 mmol), 2-amino-2-methyl-1-propanol (20 g, 224 mmol), and chlorobenzene (300 mL) were added. The mixture was refluxed under nitrogen for 1 day and then was allowed to cool to room temperature. The chlorobenzene was evaporated under low pressure, and the resulting brown slurry dissolved in CH_2Cl_2 (300 mL) was washed twice with water (2 × 150 mL). The aqueous phases were then extracted with CH_2Cl_2 (2 × 50 mL). The organic phases were combined, dried over sodium sulfate, and evaporated under low pressure. The residue which contains some white solid (zinc complexes of the ligand) was transferred to a flask and distilled twice under vacuum. (100 °C, 0.1 mmHg) to give a clear oil that occasionally crystallized (21.7 g, 76%). ^{1}H NMR (CD_2Cl_2): δ 12.14 (s, 1H, OH phen), 7.64 (dd, 1H, J = 0.9, 3.9 Hz, Ph), 7.36 (d, t, 1H, J = 0.9, 4 Hz), 6.93 (d, 1H, J = 2.9 Hz), 6.87 (t, 1H, J = 3.6 Hz), 4.11 (s, 2H, OCH_2), 1.39 (s, 6H, CH_3). ^{13}C NMR: δ 164.50, 160.23, 133.88, 128.60, 119.28, 117.23, 111.8, 79.10, 68.17, 28.90. IR (Nujol air): 1649 cm^{-1} (C=N).

Preparation of 7. $ZnCl_2$ (0.57 g, 4.20 mmol) was melted under vacuum in a flask and cooled under nitrogen to room temperature, and hydroxybenzonitrile (10.2 g, 84.08 mmol), L-phenylalaninol (19.07 g, 126.12 mmol), and chlorobenzene (200 mL) were added. The stirring mixture was refluxed for 1 day to afford a brown solution. The solvent was evaporated under reduced pressure, and the brown oil was dissolved in CH_2Cl_2 (200 mL). The brown solution was then washed with H_2O (2 × 70 mL) and the aqueous phase extracted with CH_2Cl_2 (1 × 60 mL). The organic phases were combined, dried, and evaporated under reduced pressure to afford a brown oil purified by two succesive distillations (187 °C, 0.5 mmHg) (46%). ^{1}H NMR (CD_2Cl_2): δ 12.19 (s, 1H), 7.7 (dd, 1H, J = 1.61, 7.81 Hz), 7.5−7.2 (m, 6H, aromatic H), 7.09 (dd, 1H, J = 0.8, 8.26 Hz), 6.90 (dt, 1H, J = 1, 8.1 Hz), 4.67 (m, 1H), 4.44 (dd, 1H, J = 8.4, 9.20 Hz), 4.18 (dd, 1H, J = 7.34, 8.4 Hz), 3.17 (B part of ABX, 1H, J = 6.31, 13.65 Hz), 2.86 (A part of ABX, 1H, J = 7.5, 13.65 Hz). IR (neat): ν(C=N) 1645 cm^{-1}. $[\alpha]^2 = -9.87$, c = 2 ($CHCl_3$).

Preparation of 8. $ZnCl_2$ (0.57 g, 4.20 mmol) was melted in a flask under vacuum and cooled to room temperature under nitrogen; then hydroxybenzonitrile (9.8 g, 82.14 mmol), L-Valinol (11.23 g, 106.78 mmol), and chlorobenzene (250 mL) were added and the mixture was refluxed with stirring for 1 day. The mixture was worked up as described for ligand **5**, affording a clear pale yellow oil (115 °C, 0.1 mmHg) (62%). ^{1}H NMR (CD_2Cl_2): δ 12.28 (s, 1H), 8.65 (dd, 1H, J = 1.2, 7.8 Hz), 7.35−7.38 (m, 1H), 6.98 (d, 1H, J = 8.3 Hz), 6.85 (dt, 1H, J = 0.8, 7.5 Hz), 4.37−4.44 (m, 1H; NCH), 4.13 (m, 2H, OCH_2), 1.8 (sept, 1H, J = 6.7 Hz, $CH(CH_3)_2$), 1.02 (d, 3H, J = 6.7 Hz, CH_3), 0.95 (d, 3H, J = 6.7Hz, CH_3). IR (neat): ν(C=N) 1645 cm^{-1}. $[\alpha]^{23} = -67$, c = 4.5 ($CHCl_3$).

Preparation of 9. $ZnCl_2$ (1.52 g, 11.13 mmol) was melted under vacuum in a flask and cooled under nitrogen to room temperature; then hydroxybenzonitrile (20 g, 149.6 mmol), (1*R*,2*S*)-norephedrine (29.4 g, 194.48 mmol) and chlorobenzene (500 mL) were added and the mixture was refluxed for 1 day with stirring. The mixture was worked up as described for ligand **7** (175 °C, 0.1 mmHg) (68%). ^{1}H NMR (CD_2Cl_2): δ 12 (br, 1H, OH), 7.78 (dd, 1H, 1.2, J = 7.6 Hz), 7.44−7.3 (m, 5H, aromatic), 7.05 (d, 1H, J = 7.6 Hz), 6.91 (t, 1H, J = 7.6 Hz), 5.76 (d, 1H, J = 9.6 Hz, NCHPh), 4.76−4.66 (m, 1H, $OCHCH_3$), 0.88 (d, 3H, J = 7.0 Hz, CH_3). IR (neat): ν(C=N) 1645 cm^{-1}. $[\alpha]^{32}$ = -400, c = 3 ($CHCl_3$).

Preparation of 10. $ZnCl_2$ (0.5 g, 3.71 mmol) was melted in a flask under vacuum and cooled to room temperature under nitrogen; then

---

(27) We have prepared dialkylbis(oxazoline)zirconium complexes bearing chiral and achiral oxazolines and also related cationic species: Cozzi, P. G.; Floriani, C. submitted for publication.

(28) The reduction of **14** with sodium sand gave an octahedral V(II) species with two molecules of THF coordinated in *trans* positions: Cozzi, P. G.; Floriani, C. Unpublished results.

Table 3. Fractional Atomic Coordinates ($\times 10^4$) for Complex **12**

	mol A			mol B		
atom	*x*/*a*	*y*/*b*	*z*/c	*x*/a	*y*/b	*z*/c
Ti1	2114.5(8)	4110.6(6)	0(−)	1719.5(8)	−1021.9(6)	−1511.3(8)
Cl1	1393.0(13)	5180.4(9)	525.0(11)	253.5(12)	−886.0(10)	−1914.1(12)
O1	1876(3)	3436(2)	724(2)	1528(3)	−389(2)	−735(2)
O2	−420(3)	3185(3)	−390(3)	688(3)	−2432(2)	127(3)
O3	2458(3)	4684(2)	−830(2)	2033(3)	−1634(3)	−2325(2)
O4	3796(3)	2738(3)	−1394(3)	4498(3)	−1464(3)	−1491(3)
O5	3241(3)	4432(3)	572(3)	2044(3)	−3(3)	−2136(3)
N1	895(4)	3721(3)	−424(3)	1318(4)	−1924(3)	−829(3)
N2	2915(4)	3221(3)	−562(3)	3121(4)	−1123(3)	−1320(3)
C1	1228(3)	3009(2)	966(2)	1134(3)	−424(2)	−117(2)
C2	1344(3)	2624(2)	1600(2)	1032(3)	238(2)	270(2)
C3	681(3)	2192(2)	1879(2)	630(3)	218(2)	926(2)
C4	−97(3)	2146(2)	1524(2)	330(3)	−464(2)	1195(2)
C5	−212(3)	2531(2)	891(2)	432(3)	−1126(2)	807(2)
C6	450(3)	2963(2)	611(2)	834(3)	−1106(2)	152(2)
C7	342(4)	3311(4)	−82(4)	971(4)	−1813(4)	−224(4)
C8	−428(5)	3611(4)	−1046(4)	773(5)	−3062(4)	−370(4)
C9	484(5)	3906(4)	−1132(4)	1372(5)	−2769(4)	−939(4)
C10	956(5)	3499(5)	−1711(4)	2280(5)	−3017(4)	−793(5)
C11	467(5)	4750(4)	−1262(5)	1064(5)	−3009(4)	−1662(4)
C21	2919(3)	4644(2)	−1423(2)	2691(3)	−2013(3)	−2602(3)
C22	2915(3)	5253(2)	−1888(2)	2539(3)	−2478(3)	−3182(3)
C23	3393(3)	5223(2)	−2507(2)	3208(3)	−2883(3)	−3484(3)
C24	3875(3)	4584(2)	−2663(2)	4030(3)	−2823(3)	−3207(3)
C25	3879(3)	3974(2)	−2199(2)	4183(3)	−2357(3)	−2628(3)
C26	3401(3)	4004(2)	−1579(2)	3513(3)	−1952(3)	−2326(3)
C27	3338(4)	3328(4)	−1143(4)	3664(5)	−1486(4)	−1710(4)
C28	3667(5)	2121(4)	−915(5)	4523(5)	−1002(5)	−873(5)
C29	3045(5)	2413(4)	−351(4)	3616(5)	−779(4)	−709(4)
C30	3407(6)	2344(5)	362(5)	3529(6)	68(4)	−720(5)
C31	2187(6)	1994(4)	−416(6)	3312(6)	−1112(5)	−17(4)
C32	3378(8)	4309(7)	1284(6)	1519(6)	685(4)	−2081(4)
C33	3981(8)	4813(8)	1566(6)	1878(8)	1182(6)	−2635(7)
C34	3979(9)	5422(6)	1064(8)	2325(8)	724(6)	−3127(7)
C35	3721(8)	5108(8)	433(7)	2504(10)	32(7)	−2759(7)

Table 4. Fractional Atomic Coordinates ($\times 10^4$) for Complex **14**

atom	*x*/*a*	*y*/*b*	*z*/*c*
V1	1351.2(9)	1465.6(3)	577.9(7)
Cl1	3785.5(16)	1727.6(5)	1180.2(12)
O1	480(4)	1998(1)	1058(3)
O2	1659(6)	1206(2)	4134(3)
O3	1826(4)	877(1)	−11(3)
O4	1245(5)	1739(1)	−2939(3)
O5	−902(4)	1209(1)	67(3)
N1	1534(5)	1183(1)	2244(4)
N2	1082(5)	1731(1)	−1116(3)
C1	416(5)	2160(2)	2069(4)
C2	−117(7)	2618(2)	2108(5)
C3	−151(7)	2813(2)	3165(7)
C4	336(8)	2568(2)	4164(6)
C5	816(7)	2112(2)	4137(5)
C6	875(6)	1910(2)	3095(5)
C7	1359(6)	1428(2)	3085(4)
C8	2122(9)	736(3)	3966(6)
C9	1990(7)	698(2)	2663(5)
C10	3500(8)	574(3)	2523(6)
C11	815(10)	353(2)	2064(7)
C21	2239(6)	754(2)	−926(4)
C22	2867(7)	311(2)	−943(5)
C23	3333(7)	168(2)	−1880(5)
C24	3186(8)	454(2)	−2819(5)
C25	2591(7)	885(2)	−2819(5)
C26	2106(6)	1045(2)	−1890(4)
C27	1459(6)	1512(2)	−1922(4)
C28	691(8)	2196(2)	−2792(5)
C29	451(6)	2196(2)	−1603(5)
C30	1276(9)	2598(2)	−896(6)
C31	−1229(7)	2199(3)	−1677(7)
C32	−1504(8)	889(3)	−871(6)
C33	−3127(9)	922(3)	−1101(7)
C34	−3382(8)	1040(3)	52(8)
C35	−2072(7)	1347(2)	586(6)
C41A	6242(34)	749(12)	5535(27)
C42A	6595(34)	1197(11)	5268(24)
C43A	7833(29)	1197(10)	4617(25)
C44A	7790(45)	852(17)	4106(35)
C45A	7062(23)	435(7)	4998(18)
C41B	6960(51)	673(15)	5752(34)
C42B	7610(37)	1215(12)	5587(26)
C43B	8709(57)	892(20)	5471(46)
C44B	8381(29)	565(10)	4873(24)
C45B	7739(28)	409(9)	5537(23)

hydroxybenzonitrile (8.86 g, 74.33 mmol), L-phenylglycinol (15.3 g, 111.5 mmol), and chlorobenzene (150 mL) were added and the mixture was refluxed 1 day with stirring. The brown solution containing some insoluble impurity was worked up as described for ligand **7**, affording a brown oil purified by two successive distillations (170 °C, 0.5 mmHg) (42%). ^{1}H NMR (CD_2Cl_2): δ 13 (br, 1H, OH), 7.73 (dd, 1H, *J* = 1.54, 7.85 Hz), 7.5-7.28 (m, 6H), 6.97 (dd, 1H, *J* = 0.8, 8.35 Hz), 6.92 (dt, 1H, *J* = 1, 7.39 Hz), 5.47 (dd, 1H, *J* = 8.3, 10 Hz), 4.82 (dd, 1H, *J* = 8.6, 10 Hz), 4.25 (t, 1H, *J* = 8.3 Hz). IR (neat): ν(C=N) 1645 cm^{-1}. $[\alpha]^{23} = +40.4$, *c* = 2.3 ($CHCl_3$).

Preparation of 11. To a solution of **6** (3.6 g, 18.56 mmol) in THF (100 mL) was added NaH (0.49 g, 20.42 mmol), and the mixture was stirred under nitrogen for 4 h at room temperature. The mixture was filtered into a pressure-equalized dropping funnel. The resulting clear yellow solution was then slowly added to a suspension of $TiCl_4 \cdot 2THF$ (3.1 g, 9.28 mmol) in THF (100 mL), and the mixture was stirred and refluxed overnight. The resulting suspension was extracted with the mother liquor, and after the extraction the solvent was pumped off and Et_2O (80mL) was added. The resulting red crystalline product was collected and recrystallized in 1:2 Et_2O/THF (56% yield). ^{1}H NMR:

Table 5. Fractional Atomic Coordinates ($\times 10^4$) for Complex **16**

atom	*x/a*	*y/b*	*z/c*	atom	*x/a*	*y/b*	*z/c*
Zr1	−656.0(5)	0(−)	−4218.3(4)	C16	−245(7)	−667(6)	−7116(5)
Cl1	−2054(2)	773(2)	−2938(2)	C21	−2778(4)	−1458(3)	−5242(3)
Cl2	−511(2)	1407(2)	−5346(2)	C22	−3646(4)	−1568(3)	−6150(3)
O1	1034(3)	137(4)	−3321(3)	C23	−4372(4)	−2396(4)	−6292(3)
O2	2636(4)	−1614(3)	−5609(3)	C24	−4228(4)	−3115(3)	−5528(4)
O3	−2082(4)	−653(3)	−5104(3)	C25	−3359(5)	−3005(3)	−4620(4)
O4	−1749(5)	−2808(3)	−2811(4)	C26	−2634(4)	−2177(3)	−4477(3)
N1	815(4)	−815(4)	−5229(4)	C27	−1715(6)	−2084(5)	−3513(5)
N2	−912(4)	−1400(4)	−3265(4)	C28	−129(6)	−1663(5)	−2230(5)
C1	2289(3)	−185(3)	−3192(3)	C29	−715(7)	−2644(5)	−1952(5)
C2	3074(4)	109(3)	−2292(3)	C30	−1261(4)	−2725(4)	−854(3)
C3	4384(3)	−176(4)	−2163(3)	C31	−456(4)	−3087(3)	0(4)
C4	4908(3)	−756(4)	−2934(4)	C32	−874(6)	−3066(4)	1048(4)
C5	4122(4)	−1051(3)	−3834(3)	C33	−2097(7)	−2684(4)	1242(3)
C6	2813(3)	−765(3)	−3963(3)	C34	−2901(5)	−2322(4)	388(5)
C7	2014(6)	−1062(4)	−4943(5)	C35	−2483(4)	−2343(4)	−661(4)
C8	463(6)	−1325(5)	−6293(5)	C36	−236(8)	−900(5)	−1346(5)
C9	1837(6)	−1652(5)	−6630(5)	C41	−7354(6)	−4556(4)	−1161(8)
C10	2483(4)	−1082(3)	−7464(3)	C42	−7230(6)	−3989(7)	−2067(5)
C11	3200(5)	−277(3)	−7164(3)	C43	−6709(7)	−3084(7)	−1946(8)
C12	3720(4)	286(3)	−7952(5)	C44	−6312(6)	−2746(5)	−921(11)
C13	3521(5)	45(4)	−9041(4)	C45	−6435(6)	−3313(8)	−15(7)
C14	2803(5)	−760(5)	−9341(3)	C46	−6956(6)	−4218(7)	−135(6)
C15	2284(5)	−1324(4)	−8552(4)				

Table 6. Selected Bond Distances (Å) and Angles (deg) for Complex **11**

Ti1−Cl1	2.319(1)	N1−C7	1.289(2)
Ti1−O1	1.857(2)	N1−C9	1.516(3)
Ti1−N1	2.189(2)	C1−C2	1.403(2)
O1−C1	1.331(2)	C6−C7	1.456(2)
O2−C7	1.341(3)	C8−C9	1.541(3)
O2−C8	1.433(2)		
N1−Ti1−N1′	89.2(1)	Ti1−N1−C9	128.5(1)
O1−Ti1−N1′	90.1(1)	Ti1−N1−C7	123.3(1)
O1−Ti1−N1	83.0(1)	C7−N1−C9	107.7(1)
O1−Ti1−O1′	170.3(1)	O1−C1−C6	120.5(2)
Cl1−Ti1−N1′	175.7(1)	O1−C1−C2	119.8(2)
Cl1−Ti1−N1	87.6(1)	C2−C1−C6	119.6(2)
Cl1−Ti1−O1′	94.1(1)	N1−C7−C6	128.9(2)
Cl1−Ti1−O1	92.4(1)	O2−C7−C6	114.2(2)
Cl1−Ti1−Cl1′	95.7(1)	O2−C7−N1	116.9(2)
Ti1−O1−C1	139.5(1)	O2−C8−C9	105.5(1)
C7−O2−C8	107.6(1)		

[a] Prime = $-0.5 - x, y, -1 - z$.

δ 7.87 (dt, 2H, J = 1.3, 7.3 Hz), 7.58 (dq, 2H, J = 1.3, 7.3 Hz), 7.06 (dq, 2H, J = 1.3, 7.3 Hz), 6.9 (br, 1H), 6.82 (d, 1H, J = 1.3, 7.3 Hz), 4.31 (s, 2H), 4.25 (d, 1H, J = 8.5 Hz), 4.10 (d, 1H, J = 8.5 Hz), 1.83 (s, 6H), 1.78 (s, 3H), 1.05 (br, 3H). Anal. Calcd for $C_{22}H_{24}Cl_2O_4Ti$: C, 52.92; H, 4.82; N, 5.60. Found: C, 52.93; H, 4.85; N, 5.69. IR (Nujol): 1606, 1585, 1552 cm^{-1}.

Preparation of 12. To a solution of **6** (9.6 g, 49.95 mmol) in THF (200 mL) was added NaH (1.49 g, 54.95 mmol). The mixture was stirred at room temperature for 5 h and then filtered into a pressure-equalized dropping funnel. The resulting solution was slowly added to a suspension of $TiCl_3{\cdot}3THF$ (9.2 g, 24.98 mmol) in THF (200 mL). The resulting violet mixture was refluxed overnight and then extracted with the mother liquor. A deep violet solution was obtained. The solvent was pumped off, and pentane was added (100 mL). The resulting violet solid was transferred into a flask, and a minimum quantity of THF was added. To the resulting solution was added pentane just to start the precipitation.The flask was put at −20 °C for a few days, and the crystalline violet product was collected. The recrystallization was repeated another time, and 9.6 g of crystalline product (73%) was obtained. Anal. Calcd for $C_{26}H_{32}ClN_2O_5Ti$: C, 58.27; H, 6.02; N, 5.23. Found: C, 58.76; H, 6.29; N, 5.11. IR (Nujol) 1608, 1586, 1555 cm^{-1}.

Preparation of 13. To a solution of **6** (7.70 g, 40.22 mmol) in THF (150 mL) was added NaH (1.061 g, 44.21 mmol). The mixture was stirred at room temperature for 4 h and then filtered into a pressure-equalized dropping funnel. The resulting solution was added over 30 min to a stirred suspension of $ZrCl_4{\cdot}2THF$ (7.6 g, 20.11 mmol) in THF (150 mL), and then the mixture was refluxed overnight. The white resulting suspension was filtered, and the resulting solid was extracted with the mother liquor following the procedure reported in detail in ref 29. The extracted solution yielded crystalline complex **13** (64%). ^1H NMR: δ 7.88 (dd, 2H, J = 1.3, 7.9 Hz), 7.58 (dt, 2H, J = 1.3, 7.9 Hz), 7.00 (t, 4H, J = 7.9 Hz), 4.19 (s, 4H), 1,77 (s, 6H), 0.96 (s, 6H). Anal. Calcd for $C_{22}H_{24}Cl_2N_2O_4Zr$: C, 48.70; H, 4.46; N, 5.16. Found: C, 48.65; H, 4.67; N, 4.84. IR (Nujol): 1611, 1590, 1557 cm^{-1}.

Preparation of 14. To a solution of **6** (8.02 g, 41.92 mmol) in THF (150 mL) was added NaH (1.51 g, 43.90 mmol). The mixture was stirred at room temperature for 4 h and then filtered into a pressure-equalized dropping funnel. The resulting pale yellow solution was slowly added to a solution of $VCl_3{\cdot}3THF$ (7.83 g, 20.95 mmol) in THF (100 mL), and the mixture was refluxed overnight. The resulting red suspension was filtered, and the resulting solid was extracted with the mother liquor by following the procedure given in ref 29. The extracted solution was concentrated to 70 mL. Heptane (100 mL) was added and a green-yellow solid was collected, which was further purified by extraction[29] with Et_2O (80 mL). A yellow powder product was obtained (54%). Anal. Calcd for $C_{22}H_{24}Cl_2N_2O_4V$: C, 56.60; H, 5.18; N, 6.00. Found: C, 56.93; H, 5.39; N, 5.90. IR (Nujol): 1611, 1590, 1557 cm^{-1}.

Preparation of 15. To a solution of ligand **8** (6.34 g, 30.92 mmol) in THF (100 mL) was added NaH (0.9 g, 37.5 mmol). H_2 evolved immediately, and the suspension became pale yellow. The solution containing some unreacted NaH in small excess was stirred 4 h at room temperature and then filtered. The pale yellow solution was added dropwise to a stirred suspension of $ZrCl_4{\cdot}2THF$ (5.83 g, 15.46 mmol) in THF (70 mL), and the mixture was refluxed overnight. NaCl was filtered off, and the solution was concentred to about 40 mL. The zirconium complex that precipitated was collected by filtration and dried under vacuum (40%). Another crop was obtained after several days, leaving the mother liquor at −20 °C (53%). ^1H NMR (CD_2Cl_2): δ 7.83 (dd, 2H, J = 0.7, 8 Hz), 7.56 (dt, 2H, J = 1.2, 7.5 Hz), 7.2−7.0 (m, 2H), 6.97 (dt, 2H, J = 0.7, 6.9 Hz), 4.4-3.8 (m, 6H), 2.8−2.6 (m, 2H), 0.79 (d, 12H, J = 6.25 Hz). IR: 1609, 1582, 1543 cm^{-1}. $[\alpha]^{23}$ = −20.4, c = 1.71 (CH_2Cl_2). Anal. Calcd for $C_{24}H_{28}Cl_2N_2O_4Zr$: C, 50.52; H, 4.95; N, 4.91. Found: C, 49.69; H, 5.16; N, 4.82.

Preparation of 16. To a solution of ligand **9** (3.13 g, 12.39 mmol) in THF (80mL) was slowly added NaH (0.38 g, 15.8 mmol), and the solution containing unreacted hydride was stirred 2 h at room

---

(29) Floriani, C.; Mange, V. *Inorg. Synth.* **1990**, *28*, 263.

Table 7. Selected Bond Distances (Å) and Angles (deg) for Complexes **12** and **14** (M = Ti for **12**, M = V for **14**)

	12		
	mol A	mol B	**14**
M−Cl1	2.424(2)	2.433(2)	2.326(2)
M−O1	1.860(4)	1.876(4)	1.893(4)
M−O3	1.951(4)	1.951(5)	1.927(3)
M−O5	2.149(5)	2.221(6)	2.165(4)
M−N1	2.185(6)	2.153(6)	2.132(5)
M−N2	2.281(6)	2.233(6)	2.132(4)
O1−C1	1.348(6)	1.326(6)	1.323(6)
O2−C7	1.348(8)	1.359(8)	1.376(6)
O2−C8	1.456(9)	1.469(9)	1.445(10)
O3−C21	1.339(6)	1.338(7)	1.315(7)
O4−C27	1.356(9)	1.372(9)	1.355(6)
O4−C28	1.437(10)	1.431(11)	1.436(7)
O5−C32	1.385(13)	1.476(9)	1.447(8)
O5−C35	1.440(15)	1.386(15)	1.460(8)
N1−C7	1.304(9)	1.285(9)	1.281(7)
N1−C9	1.525(10)	1.517(9)	1.499(6)
N2−C27	1.300(9)	1.299(10)	1.286(7)
N2−C29	1.503(9)	1.522(10)	1.509(6)
C6−C7	1.462(8)	1.459(8)	1.453(8)
C8−C9	1.531(11)	1.522(11)	1.548(10)
C26−C27	1.461(8)	1.451(9)	1.464(8)
C28−C29	1.537(12)	1.508(11)	1.513(9)
N1−M−N2	95.1(2)	97.5(2)	177.5(2)
O5−M−N1	171.1(2)	173.3(2)	87.8(2)
O3−M−N2	80.3(2)	80.6(2)	86.3(2)
O1−M−N2	90.6(2)	94.5(2)	93.4(1)
O1−M−N1	83.8(2)	85.8(2)	86.9(2)
O1−M−O3	170.9(2)	174.2(2)	168.2(2)
Cl1−M−N2	172.2(1)	171.0(2)	92.0(1)
Cl1−M−O3	93.0(1)	92.5(1)	95.2(1)
Cl1−M−O1	96.1(1)	92.1(1)	96.6(1)
M−O1−C1	139.9(3)	137.7(3)	134.2(3)
C7−O2−C8	107.0(5)	105.7(5)	107.1(4)
M−O3−C21	143.1(3)	141.7(4)	134.0(3)
C27−O4−C28	107.0(6)	106.9(5)	107.1(4)
M−N1−C9	128.7(4)	129.5(4)	127.7(4)
M−N1−C7	125.0(5)	123.1(5)	123.1(3)
C7−N1−C9	106.1(6)	107.3(6)	109.0(4)
M−N2−C29	127.6(4)	126.3(4)	128.3(3)
M−N2−C27	125.1(5)	126.3(5)	124.6(3)
C27−N2−C29	107.2(6)	107.4(6)	107.1(4)
O1−C1−C6	121.8(4)	121.4(3)	124.1(5)
O1−C1−C2	118.1(4)	118.6(4)	117.6(4)
N1−C7−C6	127.3(6)	129.1(6)	129.3(5)
O2−C7−C6	115.0(5)	114.1(5)	114.6(4)
O2−C7−N1	117.7(6)	116.8(6)	116.0(5)
O2−C8−C9	105.1(6)	104.5(5)	105.3(6)
C25−C26−C27	118.8(4)	120.1(5)	120.1(5)
C21−C26−C27	120.8(4)	119.8(5)	120.3(4)
N2−C27−C26	129.4(6)	129.4(7)	128.5(4)
O4−C27−C26	113.6(5)	114.5(6)	114.8(4)
O4−C27−N2	117.0(6)	115.9(6)	116.7(4)
O4−C28−C29	105.8(6)	107.1(7)	105.7(4)

temperature. The mixture was filtered, and the filtrate was added dropwise to a suspension of $ZrCl_4 \cdot THF_2$ (2.34 g, 6.19 mmol) in THF (50 mL). The mixture was refluxed overnight; then NaCl was filtered off. The solvent was pumped off, and Et_2O (50 mL) was added to the resulting yellow oil. The oil was stirred at room temperature for 2 h, during which a white solid precipitated. The solid was collected and dried under vacuum. Another crop of the white zirconium complex was obtained from the mother liquor after 2 days at −20 °C (48%). ^1H NMR (C_6D_6): δ 7.83 (dd, 2H, J = 0.8, 8.5 Hz), 7.2-6.5 (m, 16H), 4.96 (d, 2H, J = 7.4 Hz, CHPh), 1.14 (br s, 6H). IR: 1608, 1582, 1543 cm^{-1}. $[\alpha]^{23} = -59.6$, c = 0.89 (CH_2Cl_2). Anal. Calcd for $C_{32}H_{28}Cl_2N_2O_4Zr$: C, 57.56; H, 4.19; N, 4.19. Found: C, 57.14; H, 4.30; N, 4.79.

Crystallography. The crystals selected for study were mounted in glass capillaries that were sealed under nitrogen. The reduced cells were obtained with use of TRACER.[30] Crystal data and details associated with data collection are given in Tables 1 and SI (supplementary material). Data were collected at room temperature (295 K) on a single crystal four-circle diffractometer. For intensities and background, the profile measurement technique[31] was used. The structure amplitudes were obtained after the usual Lorentz and polarization corrections,[32] and the absolute scale was established by the Wilson method.[33] The crystal quality was tested by ψ scans showing that crystal absorption effects could not be neglected for complexes **12**, **14**, and **16**. Data were corrected for absorption using the program ABSORB[34] for complex **12** and a semiempirical method[35] for complexes **14** and **16**. No absorption correction was applied for complex **11**. The function minimized during the least-squares refinement was $\Delta w|\Delta F|^2$ for **11**, **12**, and **14** and $\Delta w(\Delta F^2)^2$ for **16**. Weights were applied according to the scheme $w = k/[\sigma^2(F_o) + g|F_o|^2]$ for **11**, **12**, and **14** and $w = 1/[\sigma^2(F_o^2) + (0.0340P)^2]$ with $P = (F_o^2 + 2F_c^2)/3$ for **16**. Anomalous scattering corrections were included in the structure factor calculation.[36b] Scattering factors for neutral atoms were taken from ref 36a for non-hydrogen atoms and from ref 37 for H. Among the low-angle reflections, no correction for secondary extinction was deemed necessary. For complexes **11**, **12**, and **14** solution and refinement were based on the observed reflections. For complex **16** the structure solution was based on the observed reflections [$I > 2\sigma(I)$] while the structure refinement was based on all reflections.

Table 8. Selected Bond Distances (Å) and Angles (deg) for Complex **16**

Zr1−Cl1	2.452(3)	Zr1−N2	2.328(6)
Zr1−Cl2	2.440(3)	N1−C7	1.294(7)
Zr1−O1	1.992(3)	N1−C8	1.522(8)
Zr1−O3	1.986(4)	N2−C27	1.290(8)
Zr1−N1	2.317(5)	N2−C28	1.508(8)
N1−Zr1−N2	86.9(2)	Cl1−Zr1−O3	97.5(1)
O3−Zr1−N2	77.4(2)	Cl1−Zr1−O1	96.4(1)
O3−Zr1−N1	86.8(2)	Cl1−Zr1−Cl2	93.7(1)
O1−Zr1−N2	85.5(2)	Cl2−Zr1−N1	91.9(1)
O1−Zr1−N1	77.6(2)	Zr1−N1−C8	125.3(3)
O1−Zr1−O3	157.4(2)	Zr1−N1−C7	128.0(4)
Cl2−Zr1−N2	175.0(1)	C7−N1−C8	105.8(5)
Cl2−Zr1−O3	97.7(1)	Zr1−N2−C28	124.7(4)
Cl2−Zr1−O1	99.0(1)	Zr1−N2−C27	127.4(4)
Cl1−Zr1−N2	87.9(1)	C27−N2−C28	107.9(5)
Cl1−Zr1−N1	172.4(1)		

The structures were solved by the heavy atom method starting from a three-dimensional Patterson map for complexes **12** and **14**. For **11** the structure was solved using SHELX86;[38] for **16** SHELX76[39] was used for the early stages of resolution and SHELX92[40] for the structure refinement.

Refinement was first done isotropically for all the non-H atoms excepting those affected by disorder. The structures of complexes **11**, **12**, and **16** were refined straightforwardly. Some difficulties were encountered in the refinement of complex **14** owing to the disorder affecting the THF crystallization solvent molecule (C41−C45; no

---

(30) Lawton, S. L.; Jacobson, R. A. *TRACER, a cell reduction program*; Ames Laboratory, Iowa State University of Science and Technology: Ames, IA, 1965.

(31) Lehmann, M. S.; Larsen, F. K. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1974**, *A30*, 580.

(32) Data reduction, structure solution, and refinement were carried out on an ENCORE 91 computer and on an IBM AT personal computer equipped with an INMOS T88 transputer.

(33) Wilson, A. J. C. *Nature* **1942**, *150*, 151.

(34) Ugozzoli, F. ABSORB, a program for F_o Absorption Correction. *Comput. Chem.* **1987**, *11*, 109.

(35) North, A. C. T.; Phillips, D. C. Mathews, F. S. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 351.

(36) (a) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 99. (b) *Ibid.*, p 149.

(37) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(38) Sheldrick, G. *SHELX-86: A FORTRAN-77 Program for the Solution of Crystal Structure from Diffraction Data*; University of Cambridge: Cambridge, England, 1986.

(39) Sheldrick, G. M. *SHELX-76: Program for Crystal Structure Determination*; University of Cambridge: Cambridge, England, 1976.

(40) Sheldrick, G. M. *SHELX-92: Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1992.

Table 9. Comparison of Structural Parameters for complexes **11**, **12**, and **14**

	complex **11**		complex **12**			complex **14**	
				mol A	mol B		
dist of atoms from the best equatorial plane, Å (excluding M)	O1	0.028(2)	Cl1	−0.007(2)	0.006(2)	N2	0.002(3)
	Cl1	−0.003(1)	O3	0.041(4)	−0.045(5)	Cl1	−0.001(2)
	N1′	−0.031(2)	N2	−0.080(6)	0.058(6)	N1	0.003(4)
	O1′	0.029(2)	O1	0.037(4)	−0.023(4)	O5	−0.002(3)
	Ti	−0.084(1)	Ti	0.036(1)	−0.089(1)	V	−0.009(1)
angle between M−N1−O1 and M−N2−O3 planes, deg		89.2(1)		84.9(2)	83.1(2)		11.9(2)
folding[a] along the N1···O1 line, deg		16.1(1)		9.2(2)	10.3(2)		12.2(2)
folding along the N2···O3 line, deg				3.2(2)	3.2(2)		11.7(2)
angle between the OC3N planes, deg		72.7(1)		76.4(2)	78.1(2)		14.8(2)
angle between the N1, C7, O2, C8, C9 and C1···C6 rings		7.4(1)		4.5(2)	2.1(2)		5.3(2)
angle between the N2, C27, O4, C28, C29 and C21···C26 rings				7.2(2)	5.7(2)		6.0(2)

[a] The folding is defined as the dihedral angle between the MNO and OC_3N planes of a six-membered chelation ring.

possibility to distinguish between oxygen and carbon), which was considered to be disordered over two positions (A and B). These atoms were refined isotropically with a site occupation factor of 0.5. During the refinement of complex **12**, the aromatic rings were constrained to be regular hexagons (C−C = 1.395 Å), resulting in a final esd's of 0.006 Å.

For all complexes the hydrogen atoms were located from difference Fourier maps. They were introduced in the subsequent refinement as fixed atom contributions with isotropic U's fixed at 0.08 Å^2 for **11**, **12**, and **16** and 0.10 Å^2 for **14**. Hydrogen atoms related to the disordered THF solvent molecules in complex **14** were ignored.

Since the space group in complex **12** is polar, the crystal chirality was tested by inverting all the coordinates ($x, y, z \rightarrow -x, -y, -z$) and refining to convergence again. The resulting R values ($R = 0.050$, $R_G = 0.052$ *vs* $R = 0.051$, $R_G = 0.053$) indicated that the original choice should be considered the correct one.

The absolute configuration of the ephedrine ligands in complex **16** was unambiguously determined on the basis of known chirality of the starting material and confirmed by the structure refinement ($R = 0.033$ *vs* 0.034; $wR2 = 0.078$ *vs* 0.079 for the correct and the "inverted" structures respectively).

The final difference map showed no unusual feature, with no significant peak above the general background. Final atomic coordinates are listed in Tables 2−5 for non-H atoms and in Tables SII-SV[41] for hydrogens. Thermal parameters are given in Tables SVI−SIX,[41] and bond distances and angles in Tables SX-SXIII.[41]

Acknowledgment. We thank the Fonds National Suisse de la Recherche Scientifique (Grant No. 20-40268.94) for financial support.

Supplementary Material Available: Tables giving crystal data and details of the structure determination, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom locations for complexes **11**, **12**, **14**, and **16** (18 pages). Ordering information is given on any current masthead page.

IC9414740

---

(41) See paragraph at end of paper regarding supplementary material.