N-Alkoxy-*β*-ketoiminate Complexes of Groups 4 and 5: Synthesis and Characterization of the Complexes $[(\eta^5\text{-}C_5H_4R)M\{CH_3C(O)CHC(NCH_2CHR'O)CH_3\}Cl_n]$ (M = Ti, *n* = 1; M = Nb, *n* = 2; R = H, Me; R′ = H, Me), $[Ti\{CH_3C(O)CHC(NCH_2CHR'O)CH_3\}Cl_2(thf)]$, and $[Ti\{CH_3C(O)CHC(NCH_2CHR'O)CH_3\}_2]$

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The synthesis and characterization of a range of *N*-alkoxo *β*-ketoiminate complexes of groups 4 and 5 are reported. Reactions between the acylic *N*-hydroxyalkyl *β*-ketoimines $CH_3C(O)CH_2C(NCH_2CHR'OH)CH_3$ (R′ = H, Me) and $[(\eta^5\text{-}C_5H_4R)TiCl_3]$ (R = H, Me) in the presence of triethylamine afford the monocyclopentadienyl derivatives $[(\eta^5\text{-}C_5H_4R)Ti\{CH_3C(O)CHC(NCH_2CHR'O)CH_3\}Cl]$ (R = H, R′ = H, **2a**; R = Me, R′ = H, **2b**; R = H, R′ = Me, **2c**; R = Me, R′ = Me, **2d**). Complex **2a** adopts a square pyramidal coordination geometry with the Cp occupying the apical site and the terdentate ketoiminate and chloride occupying basal positions. Upon standing in thf, solutions of **2a**−**d** containing NEt_3HCl deposit deep orange crystals of $[Ti\{CH_3C(O)CHC(NCH_2CHR'O)CH_3\}Cl_2(thf)]$ (R′ = H, **3a**; R′ = Me, **3b**) via protonolysis of the Ti−Cp bond. Alternatively, compounds **3a** and **3b** can be prepared in near quantitative yield either from the reaction between $[TiCl_4(thf)_2]$ and the corresponding acylic *N*-hydroxyalkyl *β*-ketoimine, in the presence of NEt_3, or via a ligand exchange reaction between $[Ti(OPr^i)_2Cl_2]$ and the *N*-hydroxyalkyl *β*-ketoimine. Variable-temperature ^1H NMR studies of **3a** and **3b** have shown that stereoisomers of these complexes interchange via a dissociative dynamic process, involving the trigonal bypyramidal intermediate $[Ti\{CH_3C(O)CHC(NCH_2CHR'O)CH_3\}Cl_2]$. The free energy of activation associated with this exchange has been determined ($\Delta G^‡$ = 45.5 kJ mol^{-1}, **3a**; $\Delta G^‡$ = 47.0 kJ mol^{-1}, **3b**). Surprisingly, treatment of $[Ti(OPr^i)_4]$ with *N*-hydroxyalkyl *β*-ketoimine (1:1) results in complete alcoholysis to afford $[Ti\{CH_3C(O)CHC(NCH_2CHR'O)CH_3\}_2]$ (R′ = H, **4a**; R′ = Me, **4b**), which contain two meridianally coordinated terdentate ketoiminate ligands. The reactions between *N*-hydroxyalkyl *β*-ketoimine derivatives and $[(\eta^5\text{-}C_5H_4R)NbCl_4]$ afford $[(\eta^5\text{-}C_5H_4R)Nb\{CH_3C(O)CHC(NCH_2CHR'O)CH_3\}Cl_2]$ (R = H, R′ = H, **5a**; R = Me, R′ = H, **5b**; R = H, R′ = Me, **5c**; R = Me, R′ = Me, **5d**). A single-crystal X-ray study of **5a** revealed a structure based on an octahedral geometry, such that the nitrogen of the *mer*-terdentate ligand is trans to the Cp and the two chloro ligands mutually trans. The single-crystal X-ray structures of **2a**, **3a**, **3b**, **4a**·CH_2Cl_2, and **5a** are reported.

Introduction

Cyclic and acyclic multidentate ligands with varying combinations of donor atoms and charges have become an increasingly popular class of ligands for transition metals, lanthanides, and main group elements. In particular, group 4 transition metal complexes of such ligands have attracted considerable interest as possible alternatives to catalysts containing the bent metallocene fragment Cp_2M.[1] The majority of these complexes contain nitrogen- and/or oxygen-donor ligands such as diamides,[2] amidinates,[3] azamacrocycles,[4] tetradentate Schiff bases,[5] porphyrins,[6] alkoxides,[7] or donor-functionalized cyclopentadienyl ligands,[8] and the focus of attention has been their use as catalysts for α-olefin

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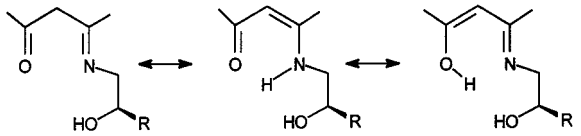
polymerization,[9] for the addition of nucleophiles to carbonyl groups,[10] and for various other carbon−carbon bond-forming processes.[11] Although nitrogen-donor ligands have dominated the development of non-metallocene chemistry, there have been relatively few reports that describe the coordination chemistry of bis-imines[12] and ketoimine[13] complexes of the early transition metals and lanthanides. This is somewhat surprising given that bis(iminates), $[CH_3C(NR)CHC(NR)CH_3]^-$, are potentially pseudo-isoelectronic with the cyclopentadienyl anion and that they are easily prepared from inexpensive and readily available starting materials. Moreover, through a judicious choice of primary amine and β-diketone used in their synthesis, the steric and electronic properties of this ligand type can be tuned and chirality and further functionalization readily introduced.[14] In an effort to develop novel reagents for Lewis-acid-promoted or -catalyzed asymmetric organic transformations, we are investigating the coordination chemistry of *N*-hydroxyalkyl-functionalized ketoimines such as **1a**,**b**[15] containing a pendant alcohol functionality, tautomeric forms of which are shown in Chart 1. These compounds are capable of coordinating to a metal center in a terdentate(−2) manner or as bidentate(−1) ketoiminates and as such offer a broad scope for the preparation of complexes with potential as catalysts for polymerization chemistry and/or for use in Lewis-acid-mediated asymmetric organic synthesis,[16] especially as chiral derivatives can be prepared and the number and type of donor atoms varied. Herein, we report the results of our preliminary studies in this area, including details of the synthesis and structural characterization of the mono(cyclopentadienyl) derivatives $[CpM(L)Cl_n]$ (M = Ti, *n* = 1; Nb, *n* = 2), which contain a terdentate *N*-alkoxy β-ketoiminate, with one (M = Ti) or two (M = Nb) M−Cl bonds available for further development of their reaction chemistry, and the noncyclopentadienyl derivatives $[Ti\{CH_3C(O)CHC(NCH_2CHR'O)CH_3\}Cl_2(thf)]$, which contain two Ti−Cl bonds and a labile thf ligand.

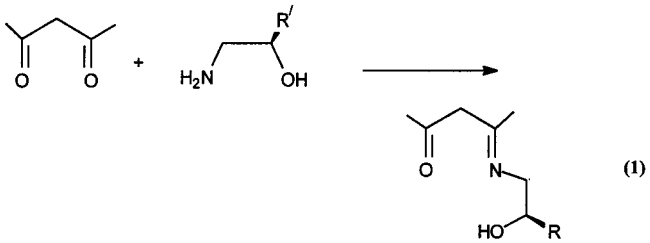
Chart 1[a]



[a] R= H, **1a**; R = Me, **1b**.

Results and Discussion

Synthesis and Characterization of $[(\eta^5\text{-}C_5H_4R)Ti\{CH_3C(O)CHC(NCH_2CHR'O)CH_3\}Cl_2]$ (2a−d). The addition of 1 equiv of $H_2NCH_2CH(R')OH$ (R′ = H, Me) to a dichloromethane solution of 2,4-pentanedione at room temperature results in the formation of the desired *N*-hydroxyalkyl β-ketoimine $CH_3C(O)CH_2C(NCH_2CHR'OH)CH_3$ (R′ = H, **1a**; Me, **1b**) in high yield as colorless crystals, after workup and crystallization (eq 1).



(1)

R′ = H, **1a**; R′ = Me, **1b**

Dropwise addition of a thf solution of **1a** and triethylamine into a thf solution of $[(\eta^5\text{-}C_5H_5)TiCl_3]$ results in a gradual color change from yellow to orange with the

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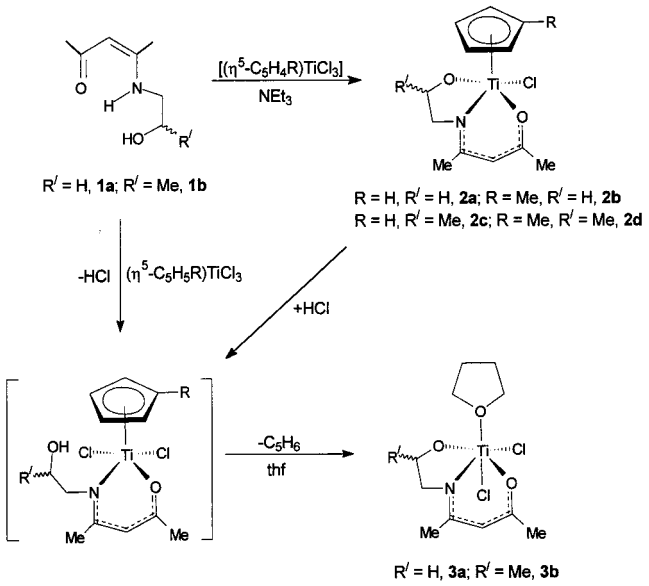
Scheme 1



formation of $[(\eta^5\text{-}C_5H_5)Ti\{CH_3C(O)CHC(NCH_2CH_2O)\text{-}CH_3\}Cl]$ (**2a**) in yields of up to 85% (Scheme 1). In a typical preparation, the reaction solution was filtered after stirring for 12 h, the remaining solid extracted exhaustively with thf, and the solvent removed to yield the product as a spectroscopically pure orange solid, which can be further purified by crystallization from thf/hexane or toluene/hexane mixtures. The ^{1}H NMR spectroscopic data for **2a**−**d** are readily interpreted, and a full spectroscopic assignment of the ^{1}H and ^{13}C NMR resonances has been obtained by using a combination of ^{1}H, ^{1}H−^{1}H COSY, and ^{1}H−^{13}C heteronuclear single-bond correlation studies. In the case of **2a** the methine proton appears as a sharp singlet at δ 5.30, while the methylene protons associated with the O*CH*$_2$*CH*$_2$N backbone appear as four distinct complex multiplets between δ 4.83 and 3.91, fully consistent with the structure shown in Scheme 1. In contrast, there are several noteworthy features in the ^{1}H NMR spectrum of **2c**, the first of which is the presence of two high-field doublets of equal intensity at δ 1.20 and 1.17 ($^3J_{HH}$ = 5.8 Hz), which belong to the OCH*Me*-methyl group. Second, six distinct multiplets ranging from δ 5.28 to 3.57 have been assigned to the methylene protons of the five-membered chelate ring. The complexity of this spectrum is not surprising since the generation of a chiral-at-metal complex from $[(\eta^5\text{-}C_5H_4R)TiCl_3]$ (R = H, Me) and *N*-hydroxyalkyl β-ketoimine racemate, derived from the condensation of (±)-1-amino-2-propanol with 2,4-pentanedione, is expected to afford a diastereoisomeric mixture of products. The stereoisomeric relationship between the two possible diastereoisomers and their corresponding enantiomers (**I**−**IV**) is shown in Chart 2. The ^{1}H NMR spectrum of the product isolated from the reaction between $[(\eta^5\text{-}C_5H_4Me)TiCl_3]$ and the β-ketoimine, derived from enantiomerically pure (*R*)-(+)-1-amino-2-propanol and 2,4-pentanedione, also contains two sets of equal intensity resonances associated with the OCH*Me*-methyl group of the five-membered chelate, indicating that there is no diastereoselectivity in the reaction between $[(\eta^5\text{-}C_5H_4R)TiCl_3]$ and (*R*)-(+)-$CH_3C(O)CH_2C(NCH_2CHMeOH)CH_3$. Attempts to separate diastereoisomers of **2c** and **2d** by fractional crystallization proved unsuccessful and in each case ^{1}H NMR spectroscopy revealed the presence of a 50:50 mixture of isomers.

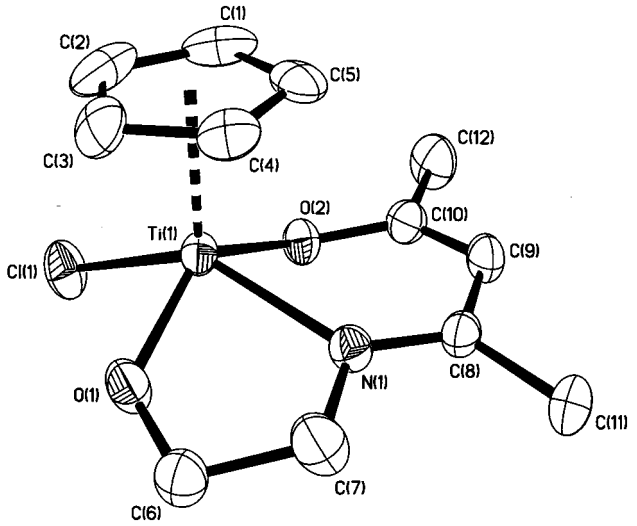
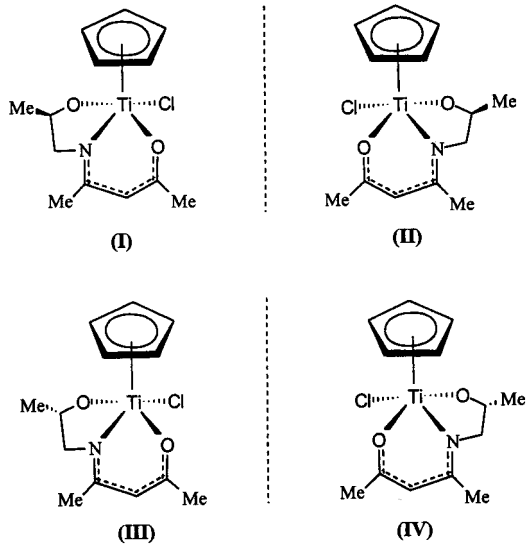


Figure 1. Molecular structure of $[CpTi\{CH_3C(O)CHC(NCH_2\text{-}CH_2O)CH_3\}Cl]$ (**2a**) illustrating the square pyramidal coordination geometry of the metal center. Ellipsoids are at 50% probability. H-atoms omitted for clarity.

Chart 2



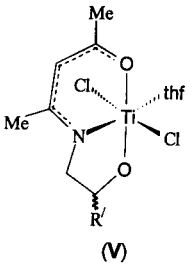
X-ray Structure of $[(\eta^5\text{-}C_5H_5)Ti\{CH_3C(O)CHC(NCH_2CH_2O)CH_3\}Cl]$ (2a). As no examples of early transition metal complexes of *N*-alkoxy-functionalized β-ketoiminates have previously been reported, a single-crystal X-ray study was undertaken to confirm the mode of binding and to provide precise structural details of the metal's coordination environment. A perspective view of the molecular structure together with the atomic numbering scheme is shown in Figure 1 and a selection of relevant bond lengths and angles listed in Table 1. The structure reveals **2a** to be monomeric with a coordination geometry best described as square-based pyramidal, with the centroid of the C_5H_5 ring occupying the apical site and the terdentate ketoiminate and a single chloride occupying the basal positions. The Ti−Cl(1) bond length of 2.3741(9) Å is substantially longer than those in $CpTiCl_3$ [2.201(5)−2.248(5) Å][17] and is similar to the Ti−Cl bond length of 2.3785(4) Å trans

Table 1. Selected Bond Distances (Å) and Angles (deg) for Compound 2a

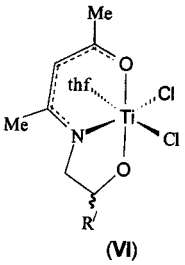
Ti(1)−C(1)	2.383(1)	Ti(1)−C(2)	2.364(16)
Ti(1)−C(3)	2.35(2)	Ti(1)−C(4)	2.390(8)
Ti(1)−C(5)	2.409(7)	Ti(1)−Cl(1)	2.3741(9)
Ti(1)−O(2)	1.924(2)	Ti(1)−N(1)	2.161(3)
Ti(1)−O(1)	1.844(2)	O(2)−C(10)	1.318(4)
C(9)−C(10)	1.355(5)	C(8)−C(9)	1.445(5)
N(1)−C(8)	1.296(4)		
O(2)−Ti(1)−Cl(1)	85.78(7)	N(1)−Ti(1)−Cl(1)	142.03(8)
O(1)−Ti(1)−Cl(1)	87.89(8)	O(1)−Ti(1)−O(2)	132.14(11)
O(2)−Ti(1)−N(1)	80.63(10)	O(1)−Ti(1)−N(1)	75.86(10)
C(8)−N(1)−Ti(1)	128.0(2)	C(7)−N(1)−Ti(1)	112.7(2)
C(8)−N(1)−C(7)	119.2(3)	C(6)−O(1)−Ti(1)	128.1(2)
C(10)−O(2)−Ti(1)	130.6(2)		

to the pyridyl group in $[CpTi\{NC_5H_4(CPr^i_2O)\text{-}2\}Cl_2]$.[18] A comparison of the Ti−O bond lengths reveals the titanium-alkoxide bond [Ti(1)−O(1) = 1.844(2) Å] to be considerably shorter than the titanium−ketoiminate bond [Ti(1)−O(2) = 1.924(2) Å]. The Ti(1)−O(1) bond length is comparable to those reported for other Ti(IV) and Ti(III) alkoxide complexes such as $Cp_2Ti(OC_2H_5)Cl]$ (1.855(2) Å) $[CpTi(OC_6H_2Bu^t_2\text{-}2,4\text{-}Ph\text{-}2)Me_2]$ (1.815(2) Å), and $[CpTi(OC_6HNp_2\text{-}2,6\text{-}Bu^t_2\text{-}3,5)Cl]_2$ (1.817(2) Å).[19] The bond length pattern within the six-membered ring system suggests significant localization of bonding electron density. For instance, the N(1)−C(8) bond length of 1.296(2) Å is close to that expected for a C−N double bond (∼1.30 Å), and the planar nature of N(1) [sum of angles at N(1) 359.9°] and the Ti(1)−N(1) length of 2.161(3) Å suggest that N−Ti pπ−dπ bonding is not significant and that Ti(1)−N(1) is a σ-dative bond involving a nitrogen atom with imine character. Additional noteworthy structural features include significantly different carbon−carbon bond lengths of 1.445(5) and 1.355(5) Å for C(8)−C(9) and C(9)−C(10), respectively (Δ = 0.09 Å), both of which are shorter than a normal C−C single bond (∼1.54 Å), and a C(10)−O(2) bond length of 1.318(4) Å, which is somewhat longer than expected for a C−O double bond (ca. ∼1.19 Å). This bond length pattern is consistent with the terdentate ligand binding to Ti(1) as an enolate, with N(1) coordinated through the sp^2 lone pair of the imine and through O(2) as a conventional alkoxide with O(pπ)−Ti(dπ) donation.

Synthesis and Characterization of $[Ti\{CH_3C(O)CHC(NCH_2CHR'O)CH_3\}Cl_2(thf)]$ (3a,b). Upon standing, thf/hexane solutions of the reaction mixture containing $[(\eta^5\text{-}C_5H_4R)TiCl_3]$ and $CH_3C(O)CH_2C(NCH_2CHR'OH)CH_3$ (R^1 = Me, racemic mixture) deposit deep orange-red crystals of $[Ti\{CH_3C(O)CHC(NCH_2CHR'O)CH_3\}Cl_2(thf)]$ (R′ = H, **3a**; R′ = Me, **3b**), identified in the first instance by ^1H and ^{13}C NMR spectroscopy and later structurally characterized by single-crystal X-ray crystallography (vide infra). At this stage we tentatively suggest that **3a**,**b** arise from inter- or intramolecular protonolysis of the Ti−Cp bond of an intermediate containing a bidentate or terdentate *N*-alkoxy β-ketominate (Scheme 1). Alternatively, compounds **3a**,**b** can be isolated in yields of up to 70% from the reaction between $[TiCl_4(thf)_2]$ and the corresponding *N*-hydroxyalkyl β-ketoimine in the presence of excess NEt_3. However, samples of **3a** and **3b** prepared in this manner are consistently contaminated with NEt_3HCl byproduct, which cannot be removed even after repeated crystallization. A more convenient route to analytically pure **3a** and **3b** involves the ligand exchange reaction between $[Ti(OPr^i)_2Cl_2]$ and the corresponding *N*-hydroxyalkyl β-ketoimine, generating propan-2-ol as the only byproduct. Dropwise addition of a thf solution of the ketoimine into a rapidly stirred solution of $[Ti(OPr^i)_2Cl_2]$ results in the immediate formation of an intense orange-red color followed by precipitation of the desired *N*-alkoxy β-ketoiminate complex as a microcrystalline solid. Spectroscopically pure **3a** and **3b** are obtained in near quantitative yield upon filtration, while analytically pure samples can be obtained by crystallization from a dichloromethane solution layered with hexane or from concentrated thf solutions. In the ^1H NMR spectrum of **3a** two broad triplets at δ 4.71 and 4.07 ($^3J_{HH}$ = 5.6 Hz) for the methylene protons of the OCH_2CH_2N backbone, a sharp singlet at δ 5.47 for the methine proton of the six-membered chelate ring, two sharp singlets of intensity 3H (δ 2.04 and 1.96) for the methyl groups, and two multiplets at δ 3.80 and 1.83 belonging to the coordinated thf are consistent with a C_2 symmetric complex containing a trans arrangement of chloro ligands (**V**, R = H) or a rapidly interconverting mixture of enantiomers with C_1 symmetry and cis chlorides (**VI**, R = H). The ^1H NMR spectrum of **3b** contains two doublets of doublets at δ 4.18 ($^2J_{HH}$ = 13.1 Hz; $^3J_{HH}$ = 5.1 Hz) and 3.78 ($^2J_{HH}$ = 13.1 Hz; $^3J_{HH}$ = 8.2 Hz) for the two methylene protons attached to the carbon atom adjacent to the imine nitrogen, a complex second-order multiplet at δ 5.23 associated with the methine proton on the carbon atom adjacent to the oxygen, C*H*Me, and two complex multiplets at δ 3.97 and 1.87 for the coordinated THF. The presence of only a single set of ligand resonances indicates that **3b** exists either as a mixture of enantiomers with a trans arrangement of chlorides (**V**, R = Me) or as two rapidly interconverting diastereoisomers with cis chloro ligands (**VI**, R = Me).



(V)



(VI)

X-ray Structures of $[Ti\{CH_3C(O)CHC(NCH_2CH_2O)CH_3\}Cl_2(thf)]$ (3a) and $[Ti\{CH_3C(O)CHC(NCH_2CHMeO)CH_3\}Cl_2(thf)]$ (3b). In view of the ambiguous ^1H NMR data for **3a** and **3b**, single-crystal X-ray analyses of both compounds were undertaken to unequivocally establish the stereochemistry at the metal center and the precise nature of the metal−ligand bonding. Perspective views of the molecular structures of **3a** and **3b** together with their numbering schemes

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(19) (a) Huffman, J. C.; Moloy, K. G.; Marsella, J. A.; Calulton, K. G. *J. Am. Chem. Soc.* **1980**, *102*, 3009. (b) Thorn, M. G.; Vilardo, J. S.; Fanwick, P. E.; Rothwell, I. P. *Chem. Commun.* **1998**, 2427. (c) Thorn, M. G.; Vilardo, J. S.; Fanwick, P. E.; Rothwell, I. P. *Chem. Commun.* **1998**, 2425.

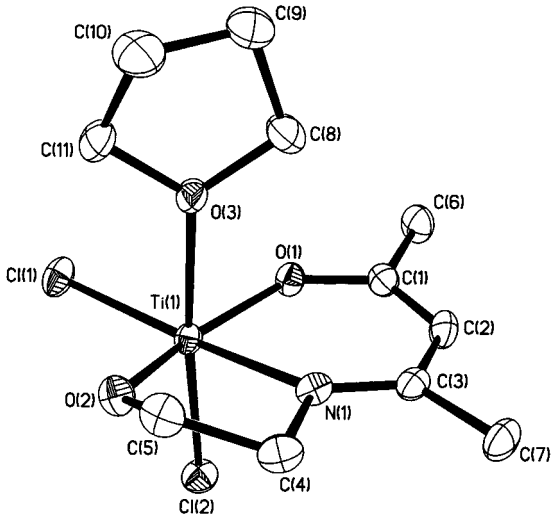

Figure 2. Molecular structure of [Ti{$CH_3C(O)CHC(NCH_2CH_2O)CH_3$}$Cl_2$(thf)] (**3a**). Ellipsoids are at 50% probability. H-atoms omitted for clarity.

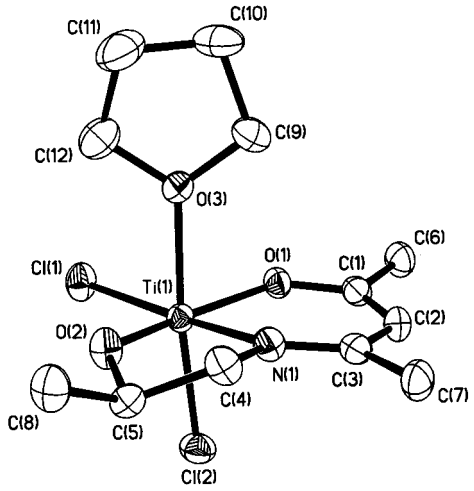

Figure 3. Molecular structure of [Ti{$CH_3C(O)CHC(NCH_2CHMeO)CH_3$}$Cl_2$(thf)] (**3b**). Ellipsoids are at 50% probability. H-atoms omitted for clarity.

are shown in Figures 2 and 3, respectively, and selected bond lengths and angles for both molecules are given in Table 2. For clarity, as the structures of **3a** and **3b** are essentially identical, the following discussion is based on the structure of **3a**, with the corresponding parameters for **3b** listed in Table 2. The structures show a cis arrangement of chloride ligands in **3a** and **3b**, which is clearly inconsistent with the ^{1}H NMR data reported in the previous section, unless a dynamic exchange process is occurring in solution. Complex **3a** is monomeric, based on a distorted octahedral geometry with the ketoiminate ligand occupying a meridianal coordination environment, two mutually cis chloro ligands, and a molecule of thf. While the Ti(1)−Cl(2) bond trans to O(3) [2.3276(6) Å (Å)] is markedly longer than that trans to N(1) [2.3161(6) Å], both are substantially shorter than the Ti−Cl bond length in **2a** [2.3741(9) Å] and are close to previously reported values of Ti−Cl bond lengths in noncyclopentadienyl complexes such as *cis*-[TiL_2Cl_2], where L is a (hydroxyphenyl)oxazoline ligand.[20a,c] The preference for a cis arrangement of chloride ligands is likely to be electronic in origin, especially since there are no geometrical constraints

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compounds 3a and 3b

compound **3a**		compound **3b**	
Ti(1)−Cl(1)	2.3161(6)	Ti(1)−Cl(1)	2.3251(8)
Ti(1)−O(1)	1.9060(14)	Ti(1)−O(1)	1.9010(17)
Ti(1)−N(1)	2.1421(17)	Ti(1)−N(1)	2.139(2)
Ti(1)−O(2)	1.8150(15)	Ti(1)−O(2)	1.8066(18)
Ti(1)−O(3)	2.1585(14)	Ti(1)−O(3)	2.1376(19)
Ti(1)−Cl(2)	2.3276(6)	Ti(1)−Cl(2)	2.3256(8)
O(1)−C(1)	1.313(2)	O(1)−C(1)	1.312(3)
C(1)−C(2)	1.358(3)	C(1)−C(2)	1.357(4)
C(2)−C(3)	1.429(3)	C(2)−C(3)	1.435(4)
C(3)−N(1)	1.310(3)	C(3)−N(1)	1.303(3)
O(1)−Ti(1)−Cl(1)	100.50(5)	O(1)−Ti(1)−Cl(1)	103.89(6)
N(1)−Ti(1)−Cl(1)	171.95(5)	Cl(1)−Ti(1)−N(1)	170.26(6)
O(2)−Ti(1)−Cl(1)	97.78(5)	Cl(1)−Ti(1)−O(2)	94.98(6)
O(3)−Ti(1)−Cl(1)	87.04(4)	Cl(1)−Ti(1)−O(3)	86.07(6)
Cl(1)−Ti(1)−Cl(2)	95.79(2)	Cl(1)−Ti(1)−Cl(2)	95.79(2)
O(1)−Ti(1)−N(1)	82.41(6)	O(1)−Ti(1)−N(1)	82.65(8)
O(2)−Ti(1)−O(1)	158.08(7)	O(2)−Ti(1)−O(1)	159.15(8)
O(1)−Ti(1)−Cl(2)	91.86(5)	O(1)−Ti(1)−Cl(2)	90.05(6)
O(1)−Ti(1)−O(3)	82.93(6)	O(1)−Ti(1)−O(3)	82.48(8)
N(1)−Ti(1)−O(3)	85.87(6)	N(1)−Ti(1)−O(3)	87.68(8)
O(2)−Ti(1)−N(1)	77.93(7)	O(2)−Ti(1)−N(1)	77.56(8)
N(1)−Ti(1)−Cl(2)	91.59(5)	N(1)−Ti(1)−Cl(2)	92.38(6)
O(2)−Ti(1)−O(3)	86.06(6)	O(2)−Ti(1)−O(3)	90.16(8)
O(2)−Ti(1)−Cl(2)	98.24(5)	O(2)−Ti(1)−Cl(2)	97.21(7)
O(3)−Ti(1)−Cl(2)	174.46(4)	O(3)−Ti(1)−Cl(2)	172.47(6)
C(1)−O(1)−Ti(1)	138.40(14)	C(1)−O(1)−Ti(1)	136.95(17)
C(5)−O(2)−Ti(1)	123.13(13)	C(5)−O(2)−Ti(1)	125.10(18)
C(3)−N(1)−Ti(1)	129.04(14)	C(3)−N(1)−Ti(1)	129.09(18)
C(4)−N(1)−Ti(1)	112.07(13)	C(4)−N(1)−Ti(1)	112.21(16)
C(3)−N(1)−C(4)	118.51(18)	C(3)−N(1)−C(4)	118.6(2)

imposed on **3a** or **3b** and no significant steric interactions within the metal's coordination sphere. Floriani has noted that dichloride derivatives of the type TiL_2Cl_2, where L is a bidentate Schiff base, can adopt either a cis or trans arrangement of chloride ligands.[20] In **3a**, the N(1)···O(1) six-membered chelate ring is nearly planar, Ti(1) being displaced by 0.241 Å from the plane containing the remaining five atoms toward Cl(2). The ethylene bridge adopts the usual gauche conformation with a O(2)−C(5)−C(4)−N(1) torsion angle of 37.0°. The ketoiminate nitrogen atom N(1) is close to planar (sum of the angles = 360(2)°), and the N(1)−C(3) bond distance of 1.310(3) Å is comparable to the C−N bond distance of 1.321(5) Å in the ketoiminate complex [Zr{$CH_3C(NPh)CH(O)CH_3$}$_2Cl_2$].[12a] The bonding within the terdentate ligand is highly localized, as evidenced by the difference in the C(1)−C(2) and C(2)−C(3) bond lengths of 0.071 Å, which is substantially larger than the comparable differences in the bis(iminate) and β-diketonate complexes [Zr{$CH_3C(NPh)CH(NPh)CH_3$}$_2Cl_2$] (0.005 Å)[12a] and [Ti{$CH_3C(O)CH(O)CH_3$}$(OPr^i_2)_3$]$_2$ (0.003 Å),[21] respectively. In addition, the titanium ketoiminate bond length Ti(1)−O(1) of 1.9060(14) Å is considerably longer than its alkoxide counterpart of 1.8150(15) Å for Ti(1)−O(2). Similar bond length patterns in β-diketonate derivatives of titanium alkoxide complexes have been noted, although the absolute differences in **3a** and **3b** are not as marked as those in [Ti{$CH_3C(O)CH(O)CH_3$}$(OPr^i_2)_3$]$_2$ (2.073(4) Å versus

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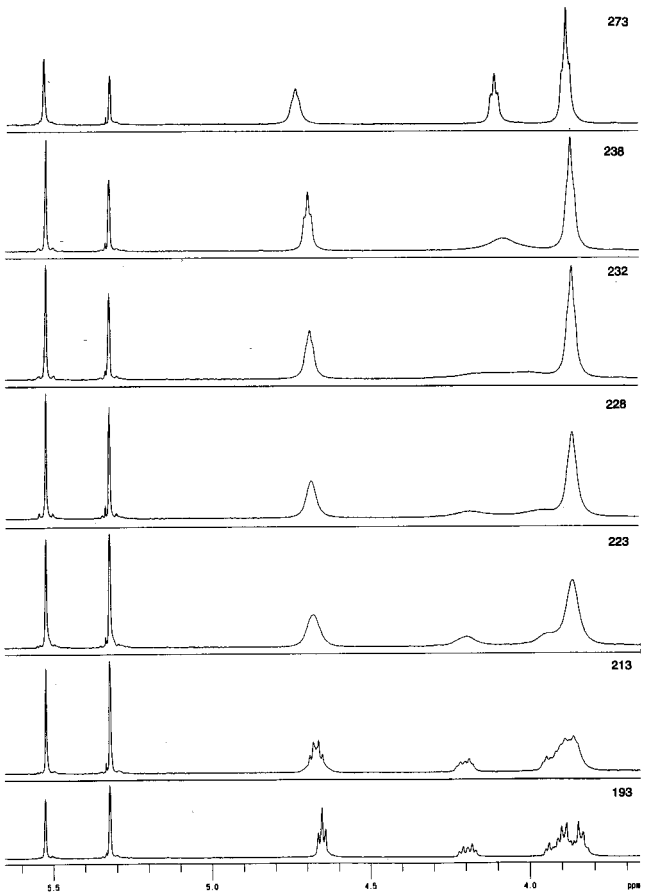


Figure 4. Variable-temperature ^{1}H NMR spectra of [Ti{$CH_3C(O)CHC(NCH_2CH_2O)CH_3$}$Cl_2$(thf)] (**3a**) recorded in CD_2Cl_2.

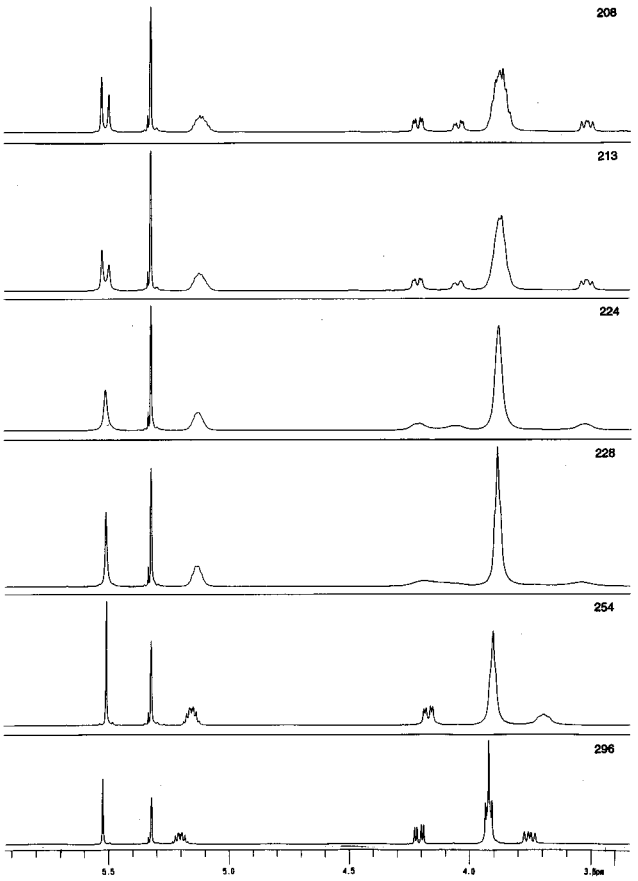
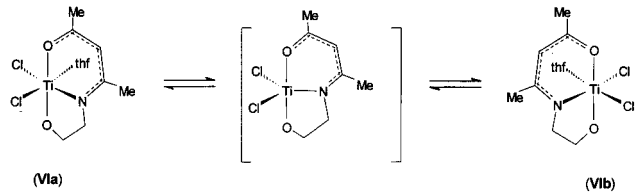


Figure 5. Variable-temperature ^{1}H NMR spectra of [Ti{$CH_3C(O)CHC(NCH_2CHMeO)CH_3$}$Cl_2$(thf)] (**3b**) recorded in CD_2Cl_2.

1.782(4) Å), presumably because localized bonding in the six-membered chelate of **3a**,**b** enables O(1) to compete for O(pπ) to Ti(dπ) bonding more effectively than in delocalized chelate rings in β-diketonate complexes.

Variable-Temperature NMR Studies. As noted above, the room-temperature ^{1}H NMR spectrum of **3a** contains two broad triplets for the OCH_2CH_2N methylene protons, while that of **3b** contains a single complex AB multiplet for the diastereotopic protons of NC*HaHb*, spectroscopic characteristics that are inconsistent with their solid-state structures. To resolve this ambiguity, variable-temperature ^{1}H NMR spectra of **3a** and **3b** were obtained, the results of which are shown in Figures 4 and 5, respectively. Qualitatively both compounds exhibit similar line-broadening characteristics. For **3a**, a cis-arrangement of chlorides should render the methylene protons diastereotopic, yet at room temperature these protons appear as two broad triplets at δ 4.71 and 4.07, which suggests a structure with C_s symmetry. As the temperature was lowered (Figure 4), these two resonances start to broaden and at 193 K appear as a complex AB multiplet at δ 4.19 and 3.91, corresponding to diastereotopic NC*HaHb* protons, and a triplet at δ 4.65 for the protons attached to the carbon atom adjacent to the alkoxide oxygen, OC*HaHb*. Within the same temperature range the resonances associated with the coordinated thf broaden and eventually give rise to two sets of complex multiplets, one at δ 3.89 and 1.87, the other, a minor set of exchange-broadened signals at δ 3.63 and 1.76, those at higher field corresponding

Scheme 2

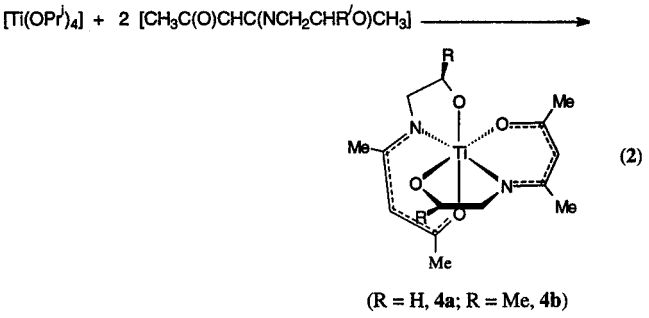


to uncoordinated thf in slow exchange with coordinated thf. While the low-temperature limiting spectrum of **3a** is consistent with the solid state structure, the temperature dependence of these resonances clearly shows that enantiomers **VIa** and **VIb** rapidly interconvert on the NMR time scale, most likely via dissociation of thf to generate the trigonal bipyramidal intermediate [Ti{$CH_3C(O)CHC(NCH_2CH_2O)CH_3$}$Cl_2$] (Scheme 2). These spectroscopic characteristics and the free energy of activation ($\Delta G^{\ddagger} = 46.0$ kJ mol^{-1}), determined from an analysis of the coalescence behavior in the temperature range 228−238 K, are consistent with the generation of time-averaged C_s symmetry by the dynamic process shown in Scheme 2. To demonstrate that **3a** exists in dissociative equilibrium with thf, a sample of **3a** in $CDCl_3$ was treated with 1 equiv of thf and as expected a shift of the ^{1}H NMR resonances was observed ($\Delta\delta$ = 0.16 ppm).

The room-temperature ^{1}H NMR spectrum of **3b** contains a single set of sharp well-resolved resonances, which, as the temperature is lowered, begin to broaden and decoalesce, eventually giving rise to two indepen-

dent sets of signals (Figure 5). The most distinctive features of the low-temperature limiting spectrum (203 K) of **3b** include two singlets at δ 5.63 and 5.60, associated with the ketoiminate methine proton, four doublets of doublets at δ 4.18, 4.01, 3.85, 3.49 (J_{HH} = 14.0, 4.60, 9.15, 13.7 Hz) for the diastereotopic methylene protons on the carbon atom adjacent to the imine nitrogen, and two doublets at δ 1.16 and 1.12 ($^3J_{HH}$ = 6.1 Hz) for the methyl group attached to the alkoxide carbon atom, CH*Me*. The signals associated with the ketoiminate methyl groups appear as three separate resonances in a 1:1:2 ratio, presumably as a result of accidental equivalence of two separate signals of equal intensity, while the methine proton, OC*H*Me, appears as two complex overlapping multiplets at δ 5.20. These two sets of resonances correspond to the two possible diastereoisomers of **3b**, **VII**−**VIII** and **IX**−**X** (Chart 3), their near equal abundance indicating that both are of similar energy. The free energy of activation, $\Delta G^{\ddagger} = 44.1$ kJ mol^{-1}, calculated from the coalescence behavior of the diastereotopic methylene signals at 233 K, is similar to that found for **3a**, which suggests that the same dynamic process is responsible for the line broadening associated with both compounds. In the case of **3a** the dynamic process shown in Scheme 2 interconverts enantiomers **VIa** and **VIb**, while the same process for **3b** interconverts **VII** and **VIII** with their diastereoisomeric counterparts **IX** and **X** (Chart 3).

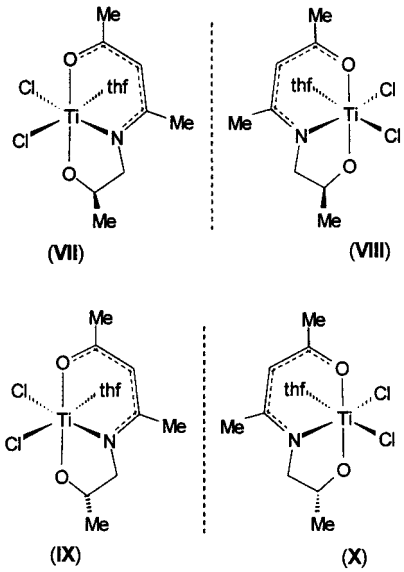
Synthesis and Characterization of [Ti{CH$_3$C(O)CHC(NCH$_2$CHR′O)CH$_3$}$_2$] (4a,b). While **3a**,**b** can most conveniently be prepared from the reaction between stoichiometric quantities of [Ti(OPr^i)$_2$Cl$_2$] and the *N*-hydroxyalkyl β-ketoimine, the corresponding reaction with [Ti(OPr^i)$_4$] results in complete alcoholysis to give [Ti{CH$_3$C(O)CHC(NCH$_2$CHR′O)CH$_3$}$_2$] (R′ = H, **4a**; R′ = Me, **4b**) (eq 2), as evidenced by the absence of signals



in the ^{1}H NMR spectrum associated with isopropyl groups. In the ^{1}H NMR spectrum of **4a**, an "apparent" triplet at δ 4.4 for the OCH_2 protons, a complex AB multiplet at δ 4.0 and 3.9 for the diastereotopic NC*HaHb* protons, and two singlets for the methyl groups (δ 1.90 and 2.05) are consistent with a C_2-symmetric complex containing two meridianally coordinated *N*-alkoxo β-ketoiminate ligands.

The ^{1}H NMR spectrum of **4b** is considerably more complex and clearly shows the presence of several species in solution, as evidenced by four equal intensity methine C−H resonances in the region δ 5.21−5.12, four sets of complex AB multiplets between 4.12 and 3.54, eight methyl resonances associated with the six-membered chelate ring (δ 1.98−1.81), and four doublets belonging to the OCH*Me* methyl groups (δ 1.13−1.11).

Chart 3



This is perhaps not surprising since **4b** was prepared from the exchange reaction between [Ti(OPr^i)$_4$] and a racemic mixture of *N*-hydroxyalkyl β-ketoimine. We would expect several diastereoisomers on the basis of an octahedral coordination geometry comprised of two meridianally coordinated *N*-alkoxy ketoiminate ligands. Since these ligands are geometrically constrained to coordinate in a meridianal manner, the total number of possible diastereoisomers is restricted to three, two of which have C_2 symmetry, the RR/SS, **XI/XII**, and SS/RR, **XIII/XIV** diastereoisomeric pairs, while the third, RS/SR, **XV/XVI**, has C_1 symmetry. A complete ^{1}H NMR spectroscopic assignment of **4b** has been achieved using a combination of ^{1}H, ^{1}H−^{1}H COSY, and ^{13}C−^{1}H heteronuclear single-bond correlation studies and a ^{1}H−^{1}H TOSCY experiment (Figure 6), the latter clearly showing two- and three-bond correlations that were not evident in the ^{1}H−^{1}H COSY spectrum. The three possible diastereoisomers and their corresponding enantiomers are shown in Chart 4.

Considering each enantiomeric pair in turn, C_2-symmetrical **XI** and **XII** are expected to give rise to a single set of resonances comprising an AB multiplet for the diastereotopic NC*HaHb* protons, a complex multiplet for the C*H*Me methine proton, two singlets of intensity three and one of intensity one for the methyl groups and methine protons, respectively, of the six-membered chelate ring, and a doublet for the methyl group, OCH*Me*. While an analogous ^{1}H NMR spectrum is expected for the other enantiomeric pair with C_2 symmetry, **XIII/XIV**, the remaining diastereoisomeic pair with C_1 symmetry, **XV/XVI**, gives rise to two sets of signals. As both RS/SR and SR/RS pairs are equivalent, the C_1 pair is twice as abundant as the RR/SS and SS/RR pairs. Thus, we suggest that two of the four sets of resonances in the ^{1}H NMR spectrum of **4b** correspond to diastereoisomers **XI**−**XII** and **XIII**−**XIV**, while the remaining two belong to **XV**−**XVI**, with a ratio consistent with the expected statistical distribution of 1:1:2 respectively, that is, there is no apparent diastereoselectivity in the reaction.

X-ray Structure of [Ti{CH$_3$C(O)CHC(NCH$_2$CH$_2$O)CH$_3$}$_2$] (4a·CH$_2$Cl$_2$). The solid-state structure of **4a**·

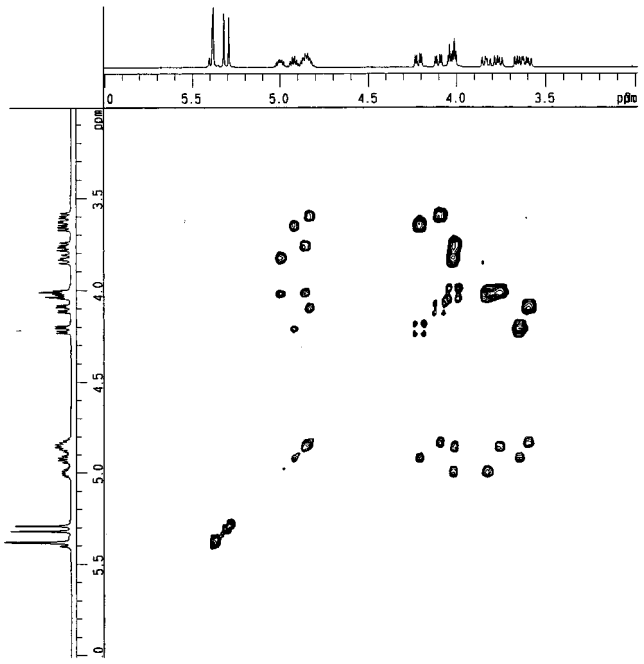
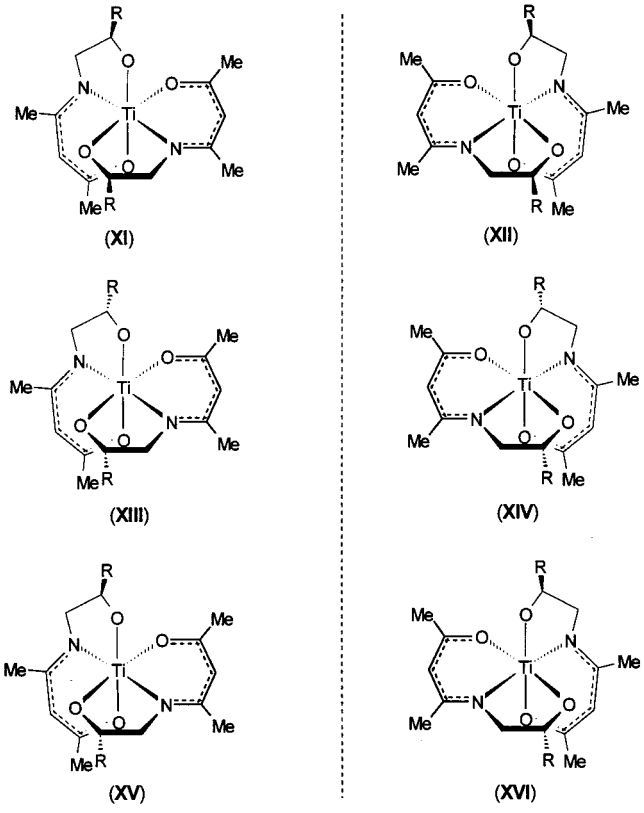


Figure 6. ^{1}H−^{1}H TOSCY spectrum of [Ti{$CH_3C(O)CHC(NCH_2$-$CHMeO)CH_3$}$_2$] (**4b**).

Chart 4



CH_2Cl_2 has been confirmed by single-crystal X-ray crystallography. The molecular structure together with the atomic numbering scheme is shown in Figure 7, and a selection of bond lengths and angles is given in Table 3. The structure is based on a distorted octahedron in which the O−Ti(1)−N angles involving the *N*-alkoxy *β*-ketoiminate ligand are distorted significantly from 90° (O(1)−Ti(1)−N(1) = 82.04(9); O(2)−Ti(1)−N(1) = 77.54-(9); O(3)−Ti(1)−N(2) = 81.59(9); O(4)−Ti(1)−N(2) = 77.30(9)°). The two six-membered chelate rings O(1)···N(1) and O(2)···N(2) are nearly planar, the titanium atom being displaced by 0.276 and 0.363 Å, respectively, from the plane containing the remaining five atoms. The ethylene bridges C(6)−C(7) and C(13)−C(14) adopt the usual gauche conformation, with torsion angles of 40.7° and 34.1° for N(1)−C(6)−C(7)−O(2) and N(2)−C(13)−C(14)−O(4), respectively. As for **2a**, **3a**, and **3b**, the bonding in the six-membered chelate rings is localized and can most aptly be described as a *N*-hydroxyalkyl imine-enolate. The two six-membered rings are close to perpendicular with a dihedral angle of 82.6°.

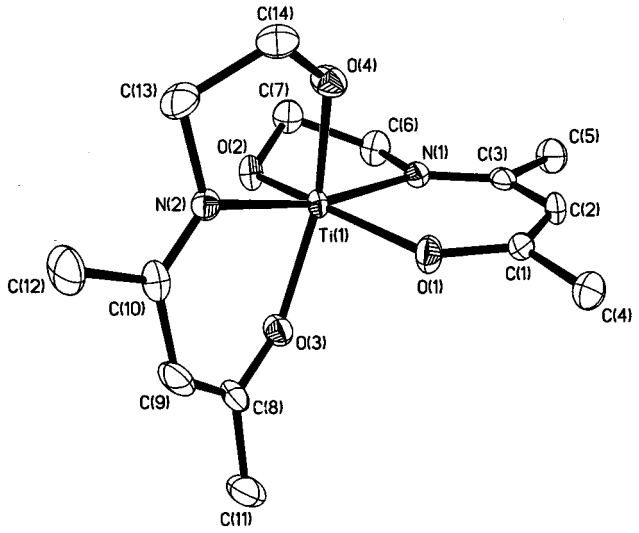


Figure 7. Molecular structure of [Ti{$CH_3C(O)CHC(NCH_2$-$CH_2O)CH_3$}$_2$] (**4a·CH_2Cl_2**) illustrating the octahedral geometry of the metal center. Ellipsoids are at 50% probability. H-atoms and solvent molecules omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) for Compound 4a·CH_2Cl_2

Ti(1)−O(1)	1.956(2)	Ti(1)−O(2)	1.857(2)
Ti(1)−O(3)	1.940(2)	Ti(1)−O(4)	1.858(2)
Ti(1)−N(1)	2.175(2)	Ti(1)−N(2)	2.160(2)
O(1)−C(1)	1.301(3)	C(1)−C(2)	1.361(4)
C(2)−C(3)	1.416(4)	C(3)−N(1)	1.309(4)
O(3)−C(8)	1.299(3)	C(8)−C(9)	1.358(4)
C(9)−C(10)	1.424(4)	C(10)−N(2)	1.303(4)
O(1)−Ti(1)−N(2)	101.65(9)	O(2)−Ti(1)−O(1)	156.86(9)
O(1)−Ti(1)−N(1)	82.04(9)	O(3)−Ti(1)−O(1)	86.32(9)
O(4)−Ti(1)−O(1)	94.13(9)	O(2)−Ti(1)−N(2)	100.49(9)
N(2)−Ti(1)−N(1)	168.55(9)	O(4)−Ti(1)−N(2)	77.30(9)
O(3)−Ti(1)−N(2)	81.59(9)	O(2)−Ti(1)−N(1)	77.54(9)
O(2)−Ti(1)−O(3)	90.34(9)	O(2)−Ti(1)−O(4)	97.22(9)
O(4)−Ti(1)−O(3)	158.53(9)	O(3)−Ti(1)−N(1)	109.59(9)
N(1)−Ti(1)−O(4)	91.69(9)	C(7)−O(2)−Ti(1)	118.87(16)
C(8)−O(3)−Ti(1)	136.24(19)	C(14)−O(4)−Ti(1)	125.2(2)
C(3)−N(1)−Ti(1)	129.3(2)	C(10)−N(2)−Ti(1)	129.24(19)
C(13)−N(2)−Ti(1)	111.41(7)	C(10)−N(2)−C(13)	119.4(2)

Synthesis and Characterization of [(η^5-C_5H_4R)-Nb{$CH_3C(O)CHC(NCH_2CHR'O)CH_3$}$Cl_2$] (5a−d). Following a procedure similar to that used to prepare **2a**−**d**, the reaction between [(η^5-C_5H_4R)$NbCl_4$] and **1a** gave high yields of [(η^5-C_5H_4R)Nb{$CH_3C(O)CHC(NCH_2CH_2O)$-CH_3}Cl_2] (**5a**) as an orange crystalline material. In the ^{1}H NMR spectrum the methine proton of the six-membered chelate ring appears as a singlet at δ 5.31, while that associated with the Cp ring is high-field shifted (δ 6.70). Surprisingly, in contrast to the complex multiplets associated with the methylene protons of the terdentate ligand in **2a**, those in **5a** appear as two triplets at δ 4.61 and 4.08 ($^3J_{HH}$ = 5.5 Hz). If the

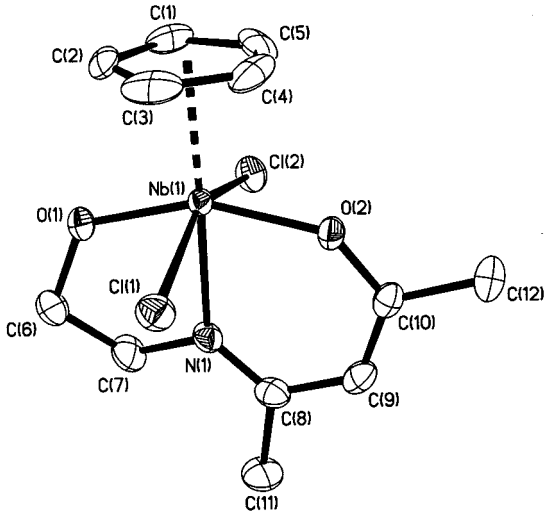
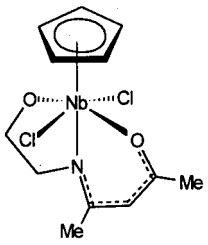
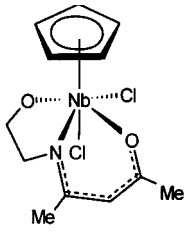


Figure 8. Molecular structure of [CpNb{$CH_3C(O)CHC(NCH_2CH_2O)CH_3$}$Cl_2$] (**5a**) illustrating the trans arrangement of chloride ligands and the octahedral coordination geometry of the metal center. Ellipsoids are at 50% probability. H-atoms omitted for clarity.

ketoimine is assumed to bind in a terdentate manner, we would expect two possible isomers, **XVII** and **XVIII**, which should be readily distinguishable by ^{1}H NMR spectroscopy, since the former contains trans chlorides and the latter a cis arrangement of chloride ligands. We are confident that the ^{1}H NMR spectrum of **5a** corresponds to **XVII**, since **XVIII** has C_1 symmetry, for which resonances corresponding to four nonequivalent methylene protons would be expected, the presence of only two triplet resonances being consistent with the C_s symmetry of **XVII**.



(XVII)



(XVIII)

The structure of **5a** has been confirmed by a single-crystal X-ray study, the result of which is shown in Figure 8, with selected bond lengths and angles listed in Table 4. The molecular structure reveals **5a** to be monomeric and based on a distorted octahedral geometry. The cyclopentadienyl ligand occupies one site, while the terdentate ligand adopts a meridianal arrangement with the nitrogen atom trans to the Cp ligand and chlorides occupying the two remaining trans sites. There are two essentially identical molecules in the unit cell, both with 2-fold disorder in the Cp rings. There are a number of noteworthy similarities between the structures of **2a** and **5a**. In the first instance, the bond length pattern within the six-membered ketoiminate chelate ring is similar to that in **2a**, the short N(1)−C(8) and C(6)−C(7) bond lengths of 1.303(3) and 1.355(3) Å, respectively, indicating a significant contribution from the enolate tautomer. By comparison, reported C−N bond lengths in bisiminate complexes of group 4 are slightly longer (~1.33 Å), presumably due to delocalization within the π-system of these ligands. The sum of the angles at N(1) (359.8°) is consistent with sp^2 hybridization, which, together with the short N(1)−C(8) bond, is suggestive of imine coordination. The Nb(1)−Cl(1) and Nb(1)−Cl(2) bond lengths, 2.4999(6) and 2.4689(6) Å, respectively, are similar to that in the 18-electron complex [(η^5-C_5H_5)$_2$NbCl(NBu^t)PMe$_3$].[23] As **5a** is a 16-electron compound, the unexpectedly long Nb−Cl bond length is most likely the result of competitive ligand(pπ)−M(dπ) bonding between the Cp−Nb, alkoxide−Nb, and chloride−Nb bonds. As is common in cyclopentadienyl compounds of niobium,[24] the Cp ring is distorted away from a symmetrical η^5-geometry with bond lengths that range from 2.394(15) to 2.479(11) Å. Although approximated to octahedral coordination, Nb(1) lies 0.476 Å out of the mean plane defined by C1(1), O(1), Cl(2), and O(2) toward the Cp ring.

Table 4. Selected Bond Distances (Å) and Angles (deg) for Compound 5a

molecule **a**		molecule **b**	
Nb(1)−C(1)	2.429(12)	Nb(2)−C(13)	2.446(14)
Nb(1)−C(2)	2.479(10)	Nb(2)−C(14)	2.433(10)
Nb(1)−C(3)	2.479(11)	Nb(2)−C(15)	2.458(10)
Nb(1)−C(4)	2.457(15)	Nb(2)−C(16)	2.45(2)
Nb(1)−C(5)	2.394(15)	Nb(2)−C(17)	2.43(2)
Nb(1)−Cl(1)	2.4999(6)	Nb(2)−Cl(3)	2.4974(6)
Nb(1)−Cl(2)	2.4689(6)	Nb(2)−Cl(4)	2.4825(6)
Nb(1)−O(1)	1.9142(15)	Nb(2)−O(3)	1.9164(15)
Nb(1)−O(2)	1.9884(14)	Nb(2)−O(4)	1.9918(15)
Nb(1)−N(1)	2.2395(18)	Nb(2)−N(2)	2.2351(18)
O(1)−C(6)	1.411(3)	O(3)−C(18)	1.416(3)
C(6)−C(7)	1.492(3)	C(18)−C(19)	1.512(3)
C(7)−N(1)	1.479(3)	C(20)−C(21)	1.432(3)
N(1)−C(8)	1.303(3)	N(2)−C(20)	1.303(3)
C(1)−C(2)	1.380(11)	C(13)−C(14)	1.382(9)
C(2)−C(3)	1.385(11)	C(14)−C(15)	1.405(11)
C(3)−C(4)	1.385(11)	C(15)−C(16)	1.380(11)
C(4)−C(5)	1.396(11)	C(16)−C(17)	1.388(11)
C(1)−C(5)	1.392(11)	C(13)−C(17)	1.417(10)
O(2)−Nb(1)−Cl(1)	85.97(5)	O(4)−Nb(2)−Cl(3)	85.02(5)
O(1)−Nb(1)−O(2)	156.07(6)	O(3)−Nb(2)−O(4)	155.64(7)
O(2)−Nb(1)−Cl(2)	85.81(5)	O(4)−Nb(2)−Cl(4)	87.16(5)
O(2)−Nb(1)−N(1)	80.39(6)	O(4)−Nb(2)−N(2)	80.01(7)
Cl(2)−Nb(1)−Cl(1)	153.96(2)	Cl(3)−Nb(2)−Cl(4)	154.84(2)
N(1)−Nb(1)−Cl(1)	77.51(5)	Cl(3)−Nb(2)−N(2)	77.66(5)
O(1)−Nb(1)−N(1)	75.83(7)	O(3)−Nb(2)−N(2)	75.81(7)
Cl(2)−Nb(1)−N(1)	76.77(5)	Cl(4)−Nb(2)−N(2)	77.45(5)
O(1)−Nb(1)−Cl(1)	86.39(5)	O(3)−Nb(2)−Cl(3)	86.89(5)
O(1)−Nb(1)−Cl(2)	91.25(5)	O(3)−Nb(2)−Cl(4)	90.52(5)
Nb(1)−O(2)−C(10)	138.45(14)	C(22)−O(4)−Nb(2)	137.46(15)
Nb(1)−O(1)−C(6)	123.27(13)	C(18)−O(3)−Nb(2)	123.72(14)
Nb(1)−N(1)−C(7)	110.83(14)	C(20)−N(2)−Nb(2)	129.65(15)
Nb(1)−N(1)−C(8)	129.67(15)	C(19)−N(2)−Nb(2)	110.70(14)
C(8)−N(1)−C(7)	119.29(19)	C(20)−N(2)−C(19)	119.64(19)

Conclusion

A range of d^0 chiral-at-metal complexes of groups 4 and 5 containing *N*-alkoxy β-ketoiminates have been prepared in high yield and characterized by X-ray crystallography and a range of NMR techniques. In each case the β-ketoiminate appears to coordinate as a β-imino enolate, rather than as its β-ketoamide tau-

(22) Williams, D. N.; Mitchell, J. P.; Poole, A. D.; Siemeling, U.; Clegg, W.; Hockless, D. C. R.; O'Neil, P. A.; Gibson, V. C. *J. Chem. Soc., Dalton Trans.* **1992**, 739.
(23) Green, M. L. H.; James, J. T.; Sanders, J. F. *Chem. Commun.* **1996**, 1343.
(24) Gibson, V. C. *J. Chem. Soc., Dalton Trans.* **1994**, 1607.

tomer (Chart 1), possibly reflecting the differing π-donor ability of OR compared with NR_2.[24] The terdentate ligand in these compounds might therefore be described as an asymmetric imine−bisalkoxide. As enantiomeric derivatives of these and related terdentate ligands with variable charge and number/type of donor atoms are readily synthesized, complexes of this type offer interesting possibilities for use in stoichiometric and catalytic organic transformations. In this regard, we are currently investigating the coordination chemistry and the synthesis of alkyl, alkoxide, and amide derivatives of these compounds, including their cationic derivatives.

Experimental Section

General Procedures. Unless otherwise stated all manipulations were carried out in an inert atmosphere glovebox or by using standard Schlenk line techniques. Diethyl ether and hexane were distilled from Na/K alloy, toluene from Na, tetrahydrofuran from potassium, and dichloromethane from CaH_2. $CDCl_3$ was predried over freshly ground calcium hydride and vacuum transferred and stored over 4 Å molecular sieves. NMR samples were prepared in the drybox in 5 mm Wilmad tubes equipped with a Young's Teflon valve. $TiCl_4$ was purchased from Aldrich and used with out further purification, $[(\eta^5\text{-}C_5H_4R)TiCl_3]$[25] and $[TiCl_4(thf)_2]$[26] were prepared according to published procedures, and $[Ti(OPr^i)_2Cl_2]$ was prepared by mixing equimolar amounts of $[Ti(OPr^i)_4]$ with $[TiCl_4]$ in toluene.

$[(\eta^5\text{-}C_5H_5)Ti\{CH_3C(O)CHC(NCH_2CH_2O)CH_3\}Cl]$ (2a). A solution of $[CH_3C(O)CH_2C(NCH_2CH_2OH)CH_3]$ (0.36 g, 2.52 mmol) and triethylamine (0.52 mL, 3.8 mmol) in thf (20 mL) was added over 1 h to a stirred solution of $[(\eta^5\text{-}C_5H_5)TiCl_3]$ (0.55 g, 2.52 mmol) in thf (40 mL). During the addition the reaction mixture changed color from yellow and an orange precipitate appeared. The resulting deep orange suspension was stirred for 5 h and then filtered. The remaining solid was extracted with thf (3 × 10 mL) and the solvent removed to yield the desired product as a spectroscopically pure orange solid. Crystallization from thf/hexane at room temperature yielded orange crystals of **2a** in 73% yield (0.53 g). ^{1}H NMR (500.1 MHz, $CDCl_3$, δ): 6.37 (s, 5H, C_5H_5), 5.30 (s, 1H, C−*H* methine), 4.83 (ddd, $^2J_{HH}$ = 10.1 Hz, $^3J_{HH}$ = 6.4 Hz, $^3J_{HH}$ = 8.2 Hz, 1H, OC*Ha*Hb), 4,59 (ddd, $^2J_{HH}$ = 10.1 Hz, $^3J_{HH}$ = 4.9 Hz, $^3J_{HH}$ = 7.0 Hz, 1H, OHa*Hb*), 4.22 (br m, 1H, N*Hc*Hd), 3.91 (ddd, $^2J_{HH}$ = 11.3 Hz, $^3J_{HH}$ = 4.6 Hz, $^3J_{HH}$ = 6.4 Hz, 1H, NHc*Hd*), 2.00 (s, 3H, CH_3), 1.97 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, δ): 177.4 (s, O*C*CH$_3$), 168.1 (s, N*C*CH$_3$), 117.9 (s, C_5H_5), 104.6 (s, *C*−H methine), 76.7 (s, O*C*H$_2$), 61.8 (s, N*C*H$_2$), 23.7 (s, *C*H$_3$), 22.8 (s, *C*H$_3$). Anal. Calcd for $C_{12}H_{16}ClO_2NTi$: C, 49.91: H, 5.55; N, 4.87. Found: C, 49.53; H, 5.57; N, 4.80.

Compounds **2b**−**d** were prepared using a procedure similar to that described above for **2a.**

$[(\eta^5\text{-}C_5H_4Me)Ti\{CH_3C(O)CHC(NCH_2CH_2O)CH_3\}Cl]$ (2b). **2b** was obtained as orange crystals in 80% yield from thf/hexane at room temperature. ^{1}H NMR (500.1 MHz, $CDCl_3$, δ): 6.29 (br m, 1H, C_5H_4Me), 6.10 (br m, 3H, C_5H_4Me), 5.29 (s, 1H, C−*H* methine), 4.80 (ddd, $^3J_{HH}$ = 6.7 Hz, $^3J_{HH}$ = 9.2 Hz, $^3J_{HH}$ = 6.6 Hz, 1H, OC*Ha*Hb), 4.60 (ddd, $^2J_{HH}$ = 10.9 Hz, $^3J_{HH}$ = 4.4 Hz, $^3J_{HH}$ = 6.7 Hz, 1H, OCHa*Hb*), 4.19 (br m, $^2J_{HH}$ = 13.1 Hz, $^3J_{HH}$ = 7.9 Hz, 1H, NC*Hc*Hd), 3.90 (dd, $^3J_{HH}$ = 13.1 Hz, $^3J_{HH}$ = 4.4 Hz, 1H NCHc*Hd*), 2.28 (s, 3H, C_5H_4Me), 2.0 (s, 3H, CCH_3), 1.98 (s, 3H, CCH_3). ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, δ): 177.2 (s, O*C*CH$_3$), 168.1 (s, N*C*CH$_3$), 133.2 (C_5H_4Me), 119.3 (s, C_5H_4Me), 118.5 (s, C_5H_4Me), 117.0 (s, C_5H_4Me), 117.3 (s, C_5H_4Me), 104.3 (s, *C*−H methine), 76.7 (s, O*C*H$_2$), 61.8 (s, N*C*H$_2$), 23.9 (s, *C*H$_3$), 22.8 (s, *C*H$_3$), 15.7 (s, C_5H_4*Me*). Anal. Calcd for $C_{13}H_{18}ClO_2NTi$: C, 51.55: H, 5.95; N, 4.65. Found: C, 51.02; H, 5.65; N, 4.47.

$[(\eta^5\text{-}C_5H_5)Ti\{CH_3C(O)CHC(NCH_2CHMeO)CH_3\}Cl]$ (2c). **2c** was obtained as orange crystals in 72% yield from thf/hexane at room temperature. ^{1}H NMR (500.1 MHz, $CDCl_3$, δ): 6.35 (s, 5H, C_5H_5), 6.33 (s, 5H, C_5H_5), 5.30 (s, 1H, C−*H* methine), 5.25 (s, 1H, C−*H* methine), 5.28 (m, $^3J_{HH}$ = 5.2, $^3J_{HH}$ = 5.8, $^3J_{HH}$ = 6.4 Hz, 1H, C*H*CH$_3$), 4.89 (ddq, $^3J_{HH}$ = 6.4, $^3J_{HH}$ = 6.4 Hz, $^3J_{HH}$ = 4.5 Hz, 1H, C*H*Me), 4.30 (dd, $^2J_{HH}$ = 13.4 Hz, $^3J_{HH}$ = 6.4 Hz, 1H, NC*Ha*Hb), 3.90 (ABd, $^2J_{HH}$ = 12.5 Hz, $^3J_{HH}$ = 5.2 Hz, 1H, NC*Hc*Hd), 3.86 (ABd, $^2J_{HH}$ = 12.5 Hz, $^3J_{HH}$ = 11.0 Hz, 1H, NCHc*Hd*), 3.57 (dd, $^2J_{HH}$ = 13.4 Hz, $^3J_{HH}$ = 4.5 Hz, 1H, NCHa*Hb*), 1.99 (s, 3H, CH_3), 1.98 (s, 3H, CH_3), 1.97 (s, 3H, CH_3), 1.95 (s, 3H, CH_3), 1.20 (d, $^3J_{HH}$ = 6.4 Hz, 3H, OCH*Me*), 1.17 (d, $^3J_{HH}$ = 5.8 Hz, OCH*Me*). ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, δ): 177.7 (s, O*C*CH$_3$), 177.4 (s, O*C*CH$_3$), 168.2 (s, N*C*CH$_3$), 167.4 (s, N*C*CH$_3$), 117.8 (s, C_5H_5), 117.7 (s, C_5H_5), 104.5 (s, *C*−H methine), 104.1 (s, *C*−H methine), 85.4 (s, OCH_2), 83.0 (s, OCH_2), 68.9 (s, NCH_2), 67.4 (s, NCH_2), 25.6 (s, *C*H$_3$), 23.8 (s, *C*H$_3$), 22.9 (s, *C*H$_3$), 22.8 (s, *C*H$_3$), 22.7 (s, *C*H$_3$), 21.4 (s, *C*H$_3$). Anal. Calcd for $C_{13}H_{18}ClO_2NTi$: C, 51.55: H, 5.95; N, 4.65. Found: C, 51.43; H, 5.87, N, 4.44.

$[(\eta^5\text{-}C_5H_4Me)Ti\{CH_3C(O)CHC(NCH_2CHMeO)CH_3\}Cl]$ (2d). **2d** was obtained as orange crystals in 78% yield from thf/hexane at room temperature. ^{1}H NMR (500.1 MHz, $CDCl_3$, δ): 6.3−7.30 (m, 10H, C_5H_5), 5.3 (s, 1H, *C*−H, methine), 5.26 (s, 1H, C−*H* methine), 5.24 (m, $^3J_{HH}$ = 6.1 Hz, $^3J_{HH}$ = 5.1 Hz, $^3J_{HH}$ = 11.3 Hz, 1H, C*H*CH$_3$), 4.90 (ddq, $^3J_{HH}$ = 4.6 Hz, $^3J_{HH}$ = 6.8 Hz, $^3J_{HH}$ = 6.1 Hz, 1H, C*H*CH$_3$), 4.32 (dd, $^2J_{HH}$ = 13.4 Hz, $^3J_{HH}$ = 6.8 Hz, 1H, C*H*aHb), 3.94 (ABd, $^2J_{HH}$ = 12.5 Hz, $^3J_{HH}$ = 5.1 Hz, 1H, CHa*Hb*), 3.87 (ABd, $^2J_{HH}$ = 12.5 Hz, $^3J_{HH}$ = 12.0 Hz, 1H, CHa*Hb*), 3.56 (dd, $^3J_{HH}$ = 13.4 Hz, $^3J_{HH}$ = 4.6 Hz, 1H, CHa*Hb*), 2.30 (s, 3H, C_5H_4*Me*), 1.99 (s, 3H, CH_3), 1.98 (s, 3H, CH_3), 1.96 (s, 3H, CH_3), 1.95 (s, 3H, CH_3), 1.17 (d, $^3J_{HH}$ = 6.1 Hz, 6H, CH*Me*). ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, δ): 177.0 (s, O*C*CH$_3$), 176.7 (s, O*C*CH$_3$), 168.0 (s, N*C*CH$_3$), 167.3 (s, N*C*CH$_3$), 132.7 (s, C_5H_4Me), 131.9 (s, C_5H_4Me), 119.2 (s, C_5H_4Me), 118.4 (s, C_5H_4Me), 117.6 (S, C_5H_4Me), 117.4 (s, C_5H_4-Me), 116.8 (s, C_5H_4Me), 116.7 (s, C_5H_4Me), 116.0 (s, C_5H_4Me), 104.1 (s, *C*−H methine), 103.7 (s, *C*−H methine), 84.6 (s, OCH_2), 82.2 (s, OCH_2), 68.8 (s, NCH_2), 67.1 (NCH_2), 23.6 (s, *C*H$_3$), 23.5 (s, *C*H$_3$), 22.6 (s, *C*H$_3$), 21.3 (s, *C*H$_3$), 15.6 (s, *C*H$_3$), 15.4 (s, *C*H$_3$). Anal. Calcd for $C_{14}H_{20}ClO_2NTi$: C, 53.08; H, 6.36; N, 4.42. Found: C, 52.97; C, 6.21; N, 4.51.

$[Ti\{CH_3C(O)CHC(NCH_2CH_2O)CH_3\}Cl_2(thf)]$ (3a). A solution of $[CH_3C(O)CH_2C(NCH_2CH_2OH)CH_3]$ (0.36 g, 2.5 mmol) in thf (20 mL) was added dropwise to a stirred solution of $[TiCl_2(OPr^i)_2]$ (0.60 g, 2.5 mmol) in thf (40 mL) over 1 h, during which time a deep red microcyrstalline solid was deposited. The resulting suspension was stirred for an additional 3 h, the volume reduced to approximately 15 mL, and the solid isolated by filtration. After washing with hexane the solid was dried in vacuo to give analytically pure **3a** in 86% yield (0.57 g). X-ray quality crystals were grown from a concentrated thf solution at room temperature. ^{1}H NMR (500.1 MHz, $CDCl_3$, 298 K δ): 5.47 (s, methine C−H), 4.71 (br, 2H, OCH_2), 4.52 (br, 2H, NCH_2), 3.80 (t, $^3J_{HH}$ = 6.4 Hz, 4H, OC$_4$H$_8$), 2.04 (s, 3H, CH$_3$), 1.96 (s, 3H, CH$_3$), 1.83 (m, 4H, OC$_4$H$_8$). ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, δ): 178.8 (s, O*C*CH$_3$), 170.6 (s, N*C*CH$_3$), 109.0 (s br, methine *C*−H), 78.1 (s, O*C*HMe), 73.9 (s, OC$_4$H$_8$), 62.1 (s, s, NCH_2), 27.3 (s, OC$_4$H$_8$), 25.0 (s, CH$_3$), 24.5 (s, CH$_3$). Anal. Calcd for $C_{11}H_{19}Cl_2NO_3Ti$: C, 39.88; H, 5.78; N, 4.23. Found: C, 39.96; C, 6.11; N, 4.51.

$[Ti\{CH_3C(O)CHC(NCH_2CHMeO)CH_3\}Cl_2(thf)]$ (3b). **3b** was prepared using a procedure similar to that described above for **3a**. X-ray quality crystals were grown from a dichloromethane solution layered with hexane. ^{1}H NMR (500.1 MHz, $CDCl_3$, 298 K, δ): 5.60 (s, 1H, methine C−H), 5.23 (ddt, $^3J_{HH}$ = 6.1 Hz, $^3J_{HH}$ = 5.2 Hz, $^3J_{HH}$ = 8.2 Hz, 1H, OC*H*Me), 4.18 (dd, $^3J_{HH}$ = 5.2 Hz, $^2J_{HH}$ = 13.1 Hz, 1H, NC*Ha*Hb), 3.97 (br, t,

(25) Cardoso, A. M.; Clark, R. J. H.; Moorhouse, S. *J. Chem. Soc., Dalton Trans.* **1980**, 1156.
(26) *Inorg. Synth.* **1987**, *21*, 137.

Table 5. Summary of Crystal Data and Structure Determination for Compounds 2a, 3a, 3b, 4a, and 5a

	2a	3a	3b	4a	5a
mol form	$C_{12}H_{16}ClNO_2Ti$	$C_{11}H_{19}Cl_2NO_3Ti$	$C_{12}H_{21}Cl_2NO_3Ti$	$C_{14}H_{22}N_2O_4Ti{\cdot}CH_2Cl_2$	$C_{12}H_{16}Cl_2NO_2Nb$
fw	289.61	332.07	346.10	415.16	370.07
radiation and wavelength, Å	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073	Cu Kα, 1.54184	Mo Kα, 0.71073
temp, K	173	160	160	160	190
cryst size, mm	0.35 × 0.30 × 0.22	0.26 × 0.19 × 0.14	0.42 × 0.21 × 0.10	0.29 × 0.27 × 0.23	0.65 × 0.50 × 0.24
cryst color	orange	orange	red	yellow	orange
cryst syst	monoclinic	monoclinic	orthorhombic	triclinic	triclinic
space group	$P2_1/c$	$P2_1/c$	$Pbca$	$P\bar{1}$	$P\bar{1}$
a, Å	12.5279(9)	8.7435(5)	14.4022(9)	7.995(3)	7.8414(5)
b, Å	6.7169(5)	11.6855(8)	14.6208(9)	11.264(5)	13.0378(8)
c, Å	15.4844(12)	14.3168(9)	14.8973(9)	11.580(5)	14.4708(9)
α, deg	90	90	90	79.44(3)	104.134(2)
β, deg	96.677(2)	91.346(2)	90	72.290(19)	94.292(2)
γ, deg	90	90	90	74.96(2)	98.097(2)
V, Å^3	1294.15(17)	1462.37(16)	3136.9(3)	953.2(7)	1411.10(15)
Z	4	4	8	2	4
D_{calcd}, g cm^{-3}	1.486	1.508	1.466	1.446	1.742
μ, mm^{-1}	0.856	0.950	0.889	6.569	1.224
F(000)	600	688	1440	432	744
reflns for cell refinement; θ range, deg	6211; 2.6−28.8	6340; 2.2−28.8	11095; 2.4−28.6	36; 24.6−27.4	9044; 2.4−28.7
θ range for data collection, deg	2.6−28.8	2.2−28.8	2.4−28.8	4.0−55.0	1.5−28.7
max indices: h, k, l	16, 8, 20	11, 15, 19	18, 18, 20	8, 11, 12	10, 17, 19
reflns measd	8043	9084	18642	4297	10419
no. of unique reflns	3063	3479	3764	2392	6299
no. of reflns with $F^2 > 2\sigma(F^2)$	2718	2837	3024	2334	5761
transmission coeff range	0.862 to 0.750	0.928 to 0.751	0.862 to 0.690	0.313 to 0.252	0.564 to 0.403
R_{int} (on F^2)	0.0213	0.0316	0.0424	0.0591	0.0175
weighting parameters[a] a, b	0.0709, 3.2732	0.0460, 0.5759	0.0354, 4.6646	0.0418, 1.0776	0.0360, 0.7602
extinction coefficient x[b]				0.0038(4)	0.0070(4)
R [$F^2 > 2\sigma(F^2)$][c]	0.0585	0.0383	0.0457	0.0390	0.0267
$wR2$ [all data][d]	0.1546	0.0954	0.1037	0.0972	0.0714
no. of refined params	202	165	184	232	422
GOF[e]	1.062	1.055	1.070	1.039	1.073
max, min in diff map, e Å^{-3}	2.320, −0.784	0.605, −0.418	0.831, −0.680	0.736, −0.481	0.594, −0.730

[a] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = (F_o^2 + 2F_c^2)/3$. [b] $F_c' = F_c\,(1 + 0.001xF_c^2\lambda^3/\sin 2\theta)^{-1/4}$. [c] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [d] $wR2 = \{\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2\}^{1/2}$. [e] GOF = $[\sum w(F_o^2 - F_c^2)^2/$(no. of unique reflections − no. of parameters)$]^{1/2}$.

4H, OC_4H_8), 3.78 (dd, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 13.1 Hz, 1H, NCHa*Hb*), 2.03 (s, 3H, CH_3), 1.99 (s, 3H, CH_3), 1.23 (d, $^3J_{HH}$ = 6.1 Hz, 3H, OCH*Me*). $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, δ): 176.9 (s, O*C*CH$_3$), 168.1 (s, N*C*CH$_3$), 107.3 (s, methine *C*−H), 83.0 (s, O*C*HMe), 72.6 (s, O*C*$_4$H$_8$), 67.3 (s, N*C*H$_2$), 25.5 (s, O*C*$_4$H$_8$), 23.6 (s, *C*H$_3$), 22.8 (s, *C*H$_3$), 20.4 (s, *C*H$_3$). Anal. Calcd for $C_{12}H_{21}Cl_2NO_3Ti$: C, 41.62; H, 6.11; N, 4.04. Found: C, 41.96; C, 6.23; N, 4.31.

[Ti{CH$_3$C(O)CHC(NCH$_2$CH$_2$O)CH$_3$}$_2$] (4a). A solution of [CH$_3$C(O)CH$_2$C(NCH$_2$CH$_2$OH)CH$_3$] (1.01 g, 7.70 mmol) in toluene was added to a solution of [Ti(OPr^i)$_4$] (1.0 g, 3.53 mmol) in toluene, with rapid stirring. The addition of *N*-hydroxyalkyl β-ketoimine was accompanied by the appearance of a pale yellow coloration. After stirring overnight the solvent was removed to leave a yellow solid reside, which was recrystallized from *n*-hexane to give **4a** in 96% yield (1.13 g). ^1H NMR (200.0 MHz, $CDCl_3$, 298 K, δ): 5.20 (s, 1H, methine C−H), 4.4 (t, $^3J_{HH}$ = 5.2 Hz, 2H, OC*H*$_2$), 4.0 (ABt, $^3J_{HH}$ = 5.2 Hz, $^3J_{HH}$ = 5.2 Hz, $^2J_{HH}$ = 5.2 Hz 1H, NC*Ha*Hb), 3.9 (ABt, $^3J_{HH}$ = 5.2 Hz, $^3J_{HH}$ = 5.2 Hz, $^2J_{HH}$ = 5.2 Hz 1H, NCHa*Hb*), 2.05 (s, 3H, C*H*$_3$), 1.90 (s, 3H, C*H*$_3$). $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$, δ): 176.0 (s, O*C*CH$_3$), 169.4 (s, N*C*CH$_3$), 103.0 (s, methine *C*−H), 71.6 (s, O*C*H$_2$), 60.3 (s, N*C*H$_2$), 24.6 (s, *C*H$_3$), 22.8 (s, *C*H$_3$). Anal. Calcd for $C_{14}H_{22}N_2O_4Ti.0.35CH_2Cl_2$: C, 47.93; H, 6.36; N, 7.79. Found: C, 47.98; C, 6.42; N, 7.80.

[Ti{CH$_3$C(O)CHC(NCH$_2$CHMeO)CH$_3$}$_2$] (4b). Prepared using a procedure similar to that described above for **4a** and crystallized from dichloromethane/hexane at room temperature. ^1H NMR (500.1 MHz, $CDCl_3$, δ): 5.21 (s, 1H, methine C−*H*), 5.19 (s, 1H, methine C−*H*), 5.16 (s, 1H, methine C−*H*), 5.12 (s, 1H, methine C−*H*), 4.74−4.90 (multiplet, 4H, OC*H*Me), 4.12 (dd, $^2J_{HH}$ = 13.1 Hz, $^3J_{HH}$ = 5.2 Hz, 1H, C*Ha*Hb), 3.99 (dd, $^2J_{HH}$ = 13.4 Hz, $^3J_{HH}$ = 5.2 Hz, 1H, C*Ha*Hb), 3.90 (dd, $^2J_{HH}$ = 13.4 Hz, $^3J_{HH}$ = 5.2 Hz, 1H, C*Ha*Hb), 3.87 (dd, $^2J_{HH}$ = 13.4 Hz, $^3J_{HH}$ = 4.9 Hz, 1H, C*Ha*Hb), 3.77 (dd, $^2J_{HH}$ = 13.1 Hz, $^3J_{HH}$ = 8.6 Hz, 1H, CHa*Hb*), 3.70 (dd, $^2J_{HH}$ = 13.1 Hz, $^3J_{HH}$ = 7.6 Hz, 1H, CHa*Hb*), 3.56 (dd, $^2J_{HH}$ = 13.1 Hz, $^3J_{HH}$ = 6.4 Hz, 1H, CHa*Hb*), 3.54 (dd, $^2J_{HH}$ = 13.4 Hz, $^3J_{HH}$ = 7.3 Hz, 1H, CHa*Hb*), 1.98 (s, 3H, C*H*$_3$), 1.97 (s, 3H, C*H*$_3$), 1.96 (s, 3H, C*H*$_3$), 1.94 (s, 3H, C*H*$_3$), 1.85 (s, 3H, C*H*$_3$), 1.84 (s, 3H, C*H*$_3$), 1.81 (s, 3H, C*H*$_3$), 1.13 (d, $^3J_{HH}$ = 6.1 Hz, 3H, OCH*Me*), 1.12 (d, $^3J_{HH}$ = 6.1 Hz, 3H, OCH*Me*), 1.11 (d, $^3J_{HH}$ = 6.1 Hz, 6H, OCH*Me*). $^{13}C\{^1H\}$ NMR (125.65 MHz, CD_2Cl_2, δ): 176.0 (s, O*C*CH$_3$), 175.9 (s, O*C*CH$_3$), 175.7 (s, O*C*CH$_3$), 169.1 (s, N*C*CH$_3$), 169.0 (s, N*C*CH$_3$), 169.0 (s, N*C*CH$_3$), 168.8 (s, N*C*CH$_3$), 102.6 (s, methine *C*−H), 102.2 (s, methine *C*−H), 102.0 (s, methine *C*−H), 101.8 (s, methine *C*−H), 77.9 (s, O*C*H$_2$), 77.4 (s, O*C*H$_2$), 77.0 (s, O*C*H$_2$), 76.9 (s, O*C*H$_2$), 67.7 (s, N*C*H$_2$), 67.0 (s, N*C*H$_2$), 66.8 (s, N*C*H$_2$), 66.6 (s, N*C*H$_2$), 24.6 (s, *C*H$_3$), 24.5 (s, *C*H$_3$), 24.2 (s, *C*H$_3$), 24.1 (s, *C*H$_3$), 22.8 (s, *C*H$_3$), 22.7 (s, *C*H$_3$), 22.6 (s, *C*H$_3$), 22.5 (s, *C*H$_3$), 21.4 (s, *C*H$_3$), 21.2 (s, *C*H$_3$), 21.1 (s, *C*H$_3$), 20.7 (s, *C*H$_3$). Anal. Calcd for $C_{16}H_{26}N_2O_4$-Ti: C, 53.62; H, 7.31; N, 7.81. Found: C, 53.46; C, 7.41; N, 7.79.

[(η^5-C$_5$H$_5$)Nb{CH$_3$C(O)CHC(NCH$_2$CH$_2$O)CH$_3$}Cl$_2$] (5a). A solution of [CH$_3$C(O)CH$_2$C(NCH$_2$CH$_2$OH)CH$_3$] (0.286 g, 2.0 mmol) and triethylamine (0.41 mL, 3.0 mmol) in THF (20 mL) was added over 2 h to a stirred suspension of [(η^5-C$_5$H$_5$)NbCl$_4$] (0.60 g, 2.0 mmol) in THF (40 mL). The reaction mixture was allowed to stir overnight, during which time the color changed from red to golden-yellow orange. The reaction mixture was filtered, the remaining solid extracted with thf (3 × 10 mL), and the solvent removed in vacuo to yield a golden yellow solid. Crystallization of the crude product from thf/hexane at room temperature gave **5a** as yellow crystals in 57% yield (0.42 g). ^1H NMR (500.1 MHz, $CDCl_3$, δ): 6.70 (s, 5H, C$_5$H$_5$), 5.31 (s, 1H, C−*H* methine), 4.61 (t, $^3J_{HH}$ = 5.5 Hz, 2H, OC*H*$_2$), 4.08 (t, $^3J_{HH}$ = 5.5 Hz, 2H, NC*H*$_2$), 2.06 (s, 3H, CH$_3$), 1.82 (s, 3H, CH$_3$).

$^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, δ): 169.2 (s, O*C*HCH$_3$), 164.7 (s, N*C*HCH$_3$), 122.4 (s, C_5H_5), 105.4 (s, *C*−H methine), 76.1 (s, O*C*H$_2$), 57.4 (s, N*C*H$_2$), 24.7 (s, *C*H$_3$), 23.5 (s, *C*H$_3$). Anal. Calcd for $C_{12}H_{16}Cl_2NONb$: C, 39.03: H, 4.37; N, 3.79. Found: C, 39.05; H, 4.17; N, 3.71.

Compounds **5b**−**d** were prepared using a procedure similar to that described above for **5a**.

[(η^5-C$_5$H$_4$Me)Nb{CH$_3$C(O)CHC(NCH$_2$CH$_2$O)CH$_3$}Cl$_2$] (5b). **5b** was obtained as yellow-orange crystals in 54% yield from thf/hexane at room temperature. ^1H NMR (500.1 MHz, $CDCl_3$, δ): 6.53 (t, $^3J_{HH}$ = 2.7 Hz, 2H, C_5H_4Me), 6.47 (t, $^3J_{HH}$ = 2.7 Hz, 2H, C_5H_4Me), 5.31 (s, 1H, C−*H*, methine), 4.64 (t, $^3J_{HH}$ = 5.5 Hz, 2H, OC*H*$_2$), 4.07 (t, $^3J_{HH}$ = 5.5 Hz, 2H, NC*H*$_2$), 2.26 (s, 3H, C*H*$_3$), 2.06 (s, 3H, C*H*$_3$), 1.85 (s, 3H, C$_5$H$_4$*Me*). $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, δ): 168.8 (s, O*C*HCH$_3$), 164.2 (s, N*C*HCH$_3$), 133.3 (s, C_5H_5Me), 123.9 (s, C_5H_5Me), 120. 7 (s, C_5H_5Me), 106.9 (s, *C*−H methine), 75.7 (s, O*C*H$_2$), 67.7 (s, N*C*H$_2$), 24.2 (s, *C*H$_3$), 23.9 (s, *C*H$_3$), 14.8 (s, C$_5$H$_5$*Me*). Anal. Calcd for $C_{13}H_{18}Cl_2NONb$: C, 40.74; H, 4.73; N, 3.65. Found: C, 40.51; H, 4.34; N, 3.31.

[(η^5-C$_5$H$_5$)Nb{CH$_3$C(O)CHC(NCH$_2$CHMeO)CH$_3$}Cl$_2$] (5c). **5c** was obtained as orange crystals in 63% yield from thf/hexane at room temperature. ^1H NMR (500.1 MHz, $CDCl_3$, δ): 6.45 (s, 5H, C_5H_5), 5.06 (s, 1H, C−*H* methine), 4.48 (ddq, $^3J_{HH}$ = 6.5 Hz, $^3J_{HH}$ = 4.6 Hz, $^3J_{HH}$ = 8.8 Hz, 1H, C*Ha*Hb), 3.82 (dd, $^2J_{HH}$ = 13.4 Hz, $^3J_{HH}$ = 4.6 Hz, 1H, CHa*Hb*), 3.61 (dd, $^2J_{HH}$ = 13.4 Hz, $^3J_{HH}$ = 8.8 Hz, 1H, CHa*Hb*), 1.80 (s, 3H, C*H*$_3$), 1.57 (s, 3H, C*H*$_3$), 0.93 (d, $^3J_{HH}$ = 6.5 Hz, CH$_3$). $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, δ): 169.9, (s, O*C*HCH$_3$), 164.5 (s, N*C*HCH$_3$), 122.7 (s, C_5H_4), 105.9 (s, *C*−H methine), 83.2 (s, O*C*H$_3$), 71.2 (s, N*C*H$_2$), 25.0 (s, *C*H$_3$), 24.0 (s, *C*H$_3$). Anal. Calcd for $C_{13}H_{18}Cl_2NONb$: C, 40.74; H, 4.73; N, 3.65. Found: C, 41.03; H, 4.84; N, 3.79.

[(η^5-C$_5$H$_4$Me)Nb{CH$_3$C(O)CHC(NCH$_2$CHMeO)CH$_3$}Cl$_2$] (5d). **5d** was obtained as orange crystals in 71% yield from thf/hexane at room temperature. ^1H NMR (500.1 MHz, $CDCl_3$, δ): 6.5 (m, 2H, C_5H_4Me), 6.48 (m, 1H, C_5H_4Me), 6.45 (m, 1H, C_5H_4Me), 5.29 (s, 1H, C−*H* methine), 4.74 (ddq, $^3J_{HH}$ = 6.1 Hz, $^3J_{HH}$ = 4.6 Hz, $^3J_{HH}$ = 8.9 Hz 1H, C*H*Me), 4.07 (dd, $^2J_{HH}$ = 13.5 Hz, $^3J_{HH}$ = 4.6 Hz, 1H, C*Ha*Hb), 3.85 (dd, $^2J_{HH}$ = 13.5 Hz, $^3J_{HH}$ = 9.2 Hz, 1H, CHa*Hb*), 2.24 (s, 3H, C*H*$_3$), 2.03 (s, 3H, C*H*$_3$), 1.83 (s, 3H, C*H*$_3$), 1.12 (d, $^3J_{HH}$ = 6. 1 Hz, OCH*Me*). $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, δ): 168.8, (s, O*C*HCH$_3$), 163.4 (s, N*C*HCH$_3$), 131.8 (s, C_5H_4Me), 124.2 (s, C_5H_4Me), 123.9 (s, C_5H_4Me), 120.4 (s, C_5H_4Me), 120. 3 (s, C_5H_4Me), 104.7 (s, *C*−H methine), 82.0 (s, O*C*HMe), 63.2 (s, *NCH*$_2$), 25.3 (s, *C*H$_3$), 23.9 (s, *C*H$_3$), 19.4 (s, O*C*HMe), 14.7 (s, C$_5$H$_4$*Me*). Anal. Calcd for $C_{14}H_{20}Cl_2NONb$: C, 42.32; H, 5.07; N, 3.52. Found: C, 42.33; H, 4.84; N, 3.39.

Crystal Structure Determination of 2a, 3a, 3b, 4a·CH$_2$Cl$_2$, and 5a. Measurements for **2a**, **3a**, **3b**, and **5a** were made on a Bruker AXS SMART CCD area-detector diffractometer using narrow frame exposures (0.3° in ω). Cell parameters were refined from the observed ω angles of all strong reflections in each data set. Intensities were corrected semiempirically for absorption, based on symmetry-equivalent and repeated reflections. No significant intensity decay was observed. Measurements for **4a·CH$_2$Cl$_2$** were made on a Stoe-Siemens 4-circle diffractometer using on-line profile fitting.[27] Accurate cell parameters were determined from the setting angles of reflections measured on both sides of the direct beam to avoid zero-point errors. A semiempirical absorption correction was made using ψ scan data. Intensity decay of 2.5% was monitored by five check reflections remeasured each hour, and a correction was made using a least-squares fit. Structure solution was by direct methods for **3a**, **4a·CH$_2$Cl$_2$**, and **5a** and by Patterson synthesis for **2a** and **3b**. Refinement was on F^2 values for all unique data by full-matrix least-squares. Table 5 gives further details. All non-H atoms were refined anisotropically. H atoms were constrained with a riding model; U(H) was set to 1.2 (1.5 for methyl groups) times U_{eq} for the parent atom. Twofold disorder was modeled with restraints for atoms C(5) in **3b** and C(14) in **4a·CH$_2$Cl$_2$**, and for the Cp rings in **2a** and **5a**. Programs used were SHELXTL[28] for structure solution, refinement, and molecular graphics, Bruker AXS SMART (control) and SAINT (integration),[29] Stoe DIF4 (control), and local programs.

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Supporting Information Available: For **2a**, **3a**, **3b**, **4a·CH$_2$Cl$_2$**, and **5a** details of the structure determination (Tables S1, S6, S11, S16, and S21), non-hydrogen atomic positional parameters (Tables S2, S7, S12, S17, and S22), full listings of bond lengths and angles (Tables S3, S8, S13, S18, and S23), anisotropic displacement parameters (Tables S4, S9, S14, S19, and S24), hydrogen atomic coordinates (Tables S5, S10, S15, S20, and S25). This material is available free of charge via the Internet at http://pubs.acs.org.

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