Use of Alkane Elimination in the One-Step Synthesis of Organoscandium Complexes Containing a New Multidentate Cyclopentadienyl Ligand

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A new multidentate ligand, $CpH^{NMe}SiN(H)R$ (SiNR = $-SiMe_2N$-*tert*-butyl; NMe = 3-CH_2-CH_2NMe_2; **1**) was prepared in 71% yield as a mixture of 1,3 and 1,2 isomers (≈7:3) in one step from CpH^{NMe}, Me_2SiCl_2, and *tert*-butylamine. The ligand was attached to scandium in an efficient alkane elimination reaction by treatment of *in situ* generated $Sc(CH_2SiMe_3)_3$·-2THF with diproteo **1**, yielding the alkylscandium species $[(Cp^{NMe}SiNR)Sc(CH_2SiMe_3)]$, **2**, directly in 52% yield. The reaction was 100% diastereoselective for the (1*S*)-(R_{Sc})/(1*R*)-(S_{Sc}) pair of enantiomers. Treatment of **2** with dihydrogen gave two of four possible diastereomeric μ-dihydrides. The C_i symmetric 1*R*-*trans*-1′*S* diasteriomer **3a** was characterized crystallographically. Thermolysis of **2** at 70 °C for 3 days resulted in metalation of an *N*-methyl group and loss of Me_4Si. A mixture of two dimeric compounds with bridging methylene units was formed, one of which was identified as the C_i symmetric 1*R*-*trans*-1′*S* diasteriomer **4a** by X-ray crystallography.

Introduction

Incorporation of the ubiquitous cyclopentadienyl ancillary into a chelate array of donors via functionalization of the C_5 unit with pendant donors of various types is an effective means of altering the coordination environments of parent nonfunctionalized cyclopentadienyl compounds.[1] Previously, such ligands have been employed to explore the cyclopentadienyl chemistry of the main group elements[2] and as a means of gating access to vacant coordination sites in complexes of the later transition elements.[3] More recently, chelating cyclopentadienyl ligands with nitrogen- or oxygen-based pendant donors have been investigated in the context of ligand design for support of homogeneous olefin polymerization catalysts.

The most successful family of ligands in this regard have been the CpSiNR class,[4] in which a pendant (dimethylsilyl)amido donor provides a second uninegative, four electron ligand in a relatively constrained chelating arrangement.[5] The ease of synthesis of these ligand types, ever improving technologies for attachment to catalytically relevant metals,[6] and the unique properties of the polyolefins produced using the resulting catalysts have made these ligands an extremely important class of molecules.

In this paper we describe the synthesis and deployment of a derivative of the CpSiNR class of ligands in which a second pendant ligand, in this case a two electron amine donor, has been attached to the cyclopentadienyl ring. *A priori*, such a ligand was judged to be worth investigating for three reasons. First, it would be capable of donating a maximum of 12 electrons, which is equivalent to the electrons provided by two cyclopentadienyl ligands. Second, and in contrast to the bis(cyclopentadienyl) ligand set, the $Cp^{NMe}SiNR$ ligands would be expected, by virtue of their chelating nature, to occupy less space around the metal center, opening up the active site in a steric sense. Finally, with two different substituents on the cyclopentadienyl ring, an element of asymmetry is introduced and there is the possibility of effecting stereoselective reactions. Not all of these expectations have been realized at this point; however, some interesting coordination chemistry as well as a possibly general synthetic strategy for attachment of nitrogen-based ligands to group 3 metals have emerged from our initial studies.

Results and Discussion

Ligand Synthesis and Characterization. The new Cp−amido ligand incorporating a pendant amine

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(1) (a) du Plooy, K. E.; Moll, U.; Wocadlo, S.; Massa, W.; Okuda, J. *Organometallics* **1995**, *14*, 3129 and references therein. (b) Christoffers, J.; Bergman, R. G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2266.
(2) Jutzi, P.; Dahlhaus, J. *Coord. Chem. Rev.* **1994**, *137*, 179.
(3) Okuda, J. *Comments Inorg. Chem.* **1994**, *16*, 185.
(4) (a) Shapiro, P. J.; Bunel, E.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1990**, *9*, 867. (b) Shapiro, P. J.; Cotter, W. D.; Schaefer, W. P.; Labinger, J. A. Bercaw, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 4623. (c) Piers, W. E.; Shapiro, P. J.; Bunel, E.; Bercaw, J. E. *Synlett* **1990**, *1*, 74.
(5) (a) Stevens, J. C.; Timmers, F. J.; Wilson, D. R.; Schmidt, G. F.; Nickias, P. N.; Rosen, R. K.; Knight, G. W.; Lai, S. Y. European Patent Application EP-416-815-A2, March 13, 1991 (Dow). (b) Canich, J. A. PCT Application WO 91/04257, April 4, 1991 (Exxon). (c) Canich, J. A. U.S. Patent 5,026,798, 1991 (Exxon).
(6) (a) Hughes, A. K.; Meetsma, A.; Teuben, J. H. *Organometallics* **1993**, *12*, 1936. (b) Piers, W. E.; Mu, Y.; MacGillivray, L. R.; Zaworotko, M. J. *Polyhedron* **1995**, *14*, 1.

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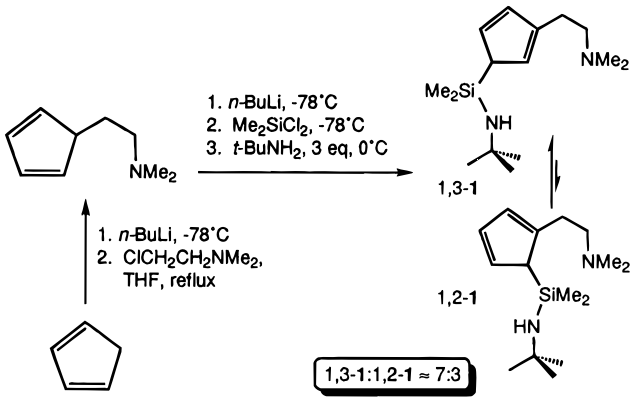
Scheme 1



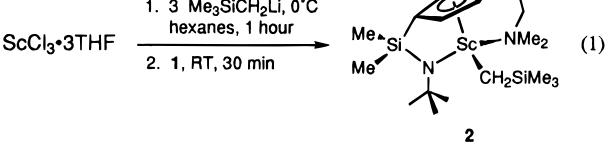
donor, $CpH^{NMe}SiN(H)R$ (SiNR = $-SiMe_2N$-*tert*-butyl; NMe = 3-$CH_2CH_2NMe_2$; **1**) was synthesized as shown in Scheme 1 in excellent yield from commercially available starting materials. (2-(Dimethylamino)ethyl)-cyclopentadiene was accessed via a literature synthesis (see Experimental Section) involving reaction of CpLi and 2-(dimethylamino)ethyl chloride and was distilled prior to the next step. The one-pot generation of **1** was accomplished via *in situ* deprotonation of the (2-(dialkylamino)ethyl)cyclopentadienes with *n*-butyllithium and treatment of the resulting cyclopentadienyllithium salt with dimethyldichlorosilane, followed by quenching the reaction with an excess of *tert*-butylamine. Workup via extraction and filtration yielded a viscous pale yellow liquid. Attempted purification via distillation or column chromatography led to extensive decomposition; therefore ligand attachment chemistry was carried out as described below using crude material which had been purged of *tert*-butylamine by prolonged exposure to dynamic vacuum.

The crude ligand's purity was difficult to assess in light of the complexity of the ^1H and ^{13}C NMR spectra obtained. For example, the ^1H NMR spectrum of **1** contained signals for at least eight chemically distinct *tert*-butyl groups. Two major signals, accounting for about 85% of the total mixture, were present in a 7:3 ratio, and we ascribe these to the 1,3-**1** and the 1,2-**1** compounds shown in Scheme 1. Kinetic product 1,3-**1** isomerizes to the observed mixture via the well-documented 1,5-silyl migration.[7] Consistent with this was the observation of coalescence of these two resonances in ^1H NMR spectra accumulated at higher temperatures (>60 °C).[8]

The other *tert*-butyl resonances, which comprised about 15% of the total product mixture, underwent separate temperature-dependent behavior under the same conditions. These peaks may be attributed to various isomers which arise from prototropic shifts. Such isomerizations have been invoked to account for the appearance of minor amounts (15%) of the 2- and 3-(trimethylsilyl)cyclopentadiene isomers in "pure" 1-(trimethylsilyl)cyclopentadiene.[9] The situation in **1** is somewhat more complex than this parent system because of the extra substitution on the cyclopentadienyl ring; for each of the 1,3- and 1,2-substituted ligands **1**, there are four possible isomers which could emanate from prototropic shifts. The observation of small overlapping, broad peaks in the region associated with ring protons bonded to sp^3 carbons ($\approx\delta$ 2.9−3.3)[10] indicates that the six minor products present belong to this family of isomers. The presence of this type of isomer is of little consequence with regard to the coordination chemistry of **1**; however, the ratio of 1,3 versus 1,2 substitution is important and must somehow be marshaled if pure transition metal compounds of these ligands are to be obtained in acceptable yields.

Conventional methods for coordination of Cp−amido type ligands to group 3 and 4 transition metals entail generation (and perhaps isolation) of an alkali metal salt of the ligand followed by reaction with a suitable metal halide starting material. Such protocols could not be adapted to suit $CpH^{NMe}SiN(H)R$, which partially decomposed via Si−N bond cleavage when treated with *n*-BuLi. Fortunately, recent advances in procedures for attachment of Cp−amido type ligands to metals suggested alternative strategies and permitted preparation of some scandium compounds supported by the Cp−amido−amine ligand array via alkane elimination procedures.[11]

Scandium Complexes. Amine elimination from $Y[N(SiMe_3)_2]_3$ has been shown to be an effective means of attaching ligands with amido donors to yttrium.[12] Although ligation of the NH functionality of the ligand occurs readily at room temperature, attachment of the Cp requires relatively high temperatures (>100 °C). Reaction between $CpH^{NMe}SiN(H)R$ and $Sc[N(SiMe_3)_2]_3$ was therefore unsuccessful since the conditions required caused the ligand to thermally decompose. We thus turned to alkane elimination as a milder means of affixing $CpH^{NMe}SiN(H)R$ to scandium. In a remarkably efficient procedure, the scandium alkyl complex [(Cp^{NMe}-SiNR)$Sc(CH_2SiMe_3)$], **2**, was prepared in 52% yield *in one pot from* $ScCl_3{\cdot}3THF$ (eq 1). *In situ* generation of



(1)

2

$Sc(CH_2SiMe_3)_3{\cdot}2THF$, which is stable in hexane solution at temperatures below 0 °C, followed by addition of 1 equiv of the diproteo ligand allows rapid preparation of gram quantities of **2**, eliminating three steps (each with its own problems) from the usual sequence of transformations required to prepare organoscandium compounds.[5c] Bearing in mind that a proportion of the ligand exists as the 1,2 substitutional isomer under

(7) (a) Cotton, F. A.; Marks, T. J. *Inorg. Chem.* **1970**, *9*, 2802. (b) Bonny, A.; Holmes-Smith, R. D.; Hunter, G.; Stobart, S. R. *J. Am. Chem. Soc.* **1982**, *104*, 1855. (c) McMaster, A. D.; Stobart, S. R. *J. Am. Chem. Soc.* **1982**, *104*, 2109.

(8) Additionally, certain procedures for attachment of **1** to zirconium lead to compounds supported by 1,2-**1**.[13b]

(9) Abel, E. W.; Dunster, M. O. *J. Organomet. Chem.* **1971**, *33*, 161.

(10) Flores, J. C.; Chien J. C. W.; Rausch, M. D. *Organometallics* **1994**, *13*, 4140.

(11) Alkane elimination procedures for Cp ligand attachment are not unprecedented: (a) Deacon, G. B.; Newham, R. H. *Aust. J. Chem.* **1985**, *38*, 1757. (b) Booij, M. Kiers, N. H.; Heeres, H. J.; Teuben, J. H. *J. Organomet. Chem.* **1989**, *364*, 79. (c) Deacon, G. B.; Forsyth, C. M.; Patalinghug, W. C.; White, A. H.; Deitrich, A.; Schumann, H. *Aust. J. Chem.* **1992**, *45*, 567. (d) Nickias, P. N.; Devore, D. D.; Wilson, D. R. PCT Application, WO 93/08199, 1993 (Dow).

(12) (a) Mu, Y.; Piers, W. E.; MacDonald, M.-A.; Zaworotko, M. J. *Can. J. Chem.* **1995**, *73*, 2233. (b) Lee, L.; Berg, D. J.; Bushnell, G. W. *Inorg. Chem.* **1994**, *33*, 5302.

Chart 1

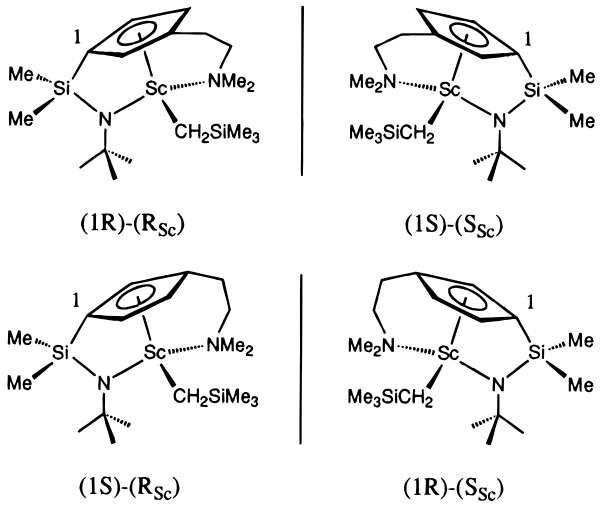
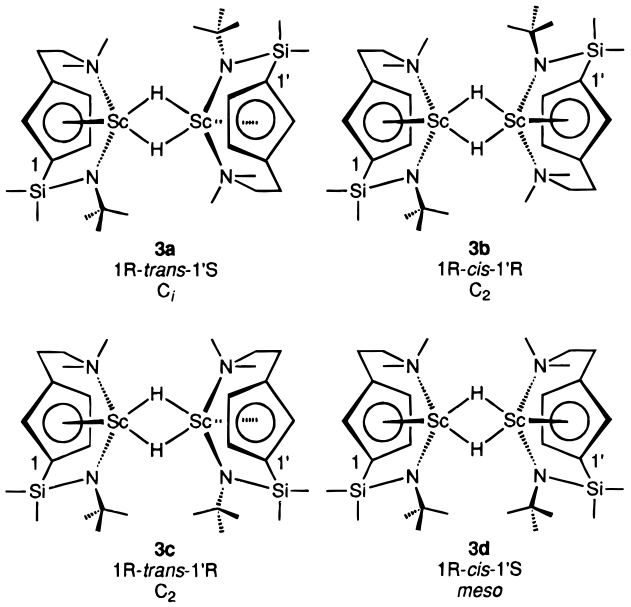


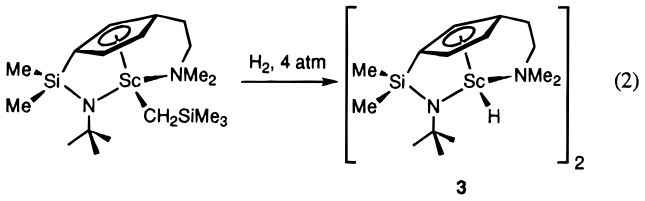
Chart 2



these conditions, the isolated yield of [(Cp^{NMe}SiNR)Sc(CH_2SiMe_3)] is ≈70% based on the amount of 1,3-substituted ligand present.[13]

Since the faces of the cyclopentadienyl ligand in **1** are enantiotopic and the resulting scandium center is a pseudotetrahedral center with four different substituents, two diastereomeric pairs of enantiomers are possible (Chart 1). Only one set of resonances for the Cp^{NMe}SiNR ligand was observed in the ^{1}H NMR spectrum, with each of the diastereotopic groups having identical connectivities (Si−Me, N−Me, Sc−CH_2) giving rise to separate peaks (Table 1). The reaction in eq 1 was therefore, within the detection limits of ^{1}H NMR spectroscopy, 100% diastereoselective for the (1*S*)-(R_{Sc})/(1*R*)-(S_{Sc})[14] (Chart 1, bottom) pair of enantiomers. Three lines of evidence support this assignment. Molecular models suggest that the (1*R*)-R_{Sc})/(1*S*)-(S_{Sc}) pair is unlikely because the aminoethyl side chain is not flexible or long enough to enable the amine to occupy the coordination site on the metal opposite to its position on the cyclopentadienyl ring. Consistent with this were nOe experiments that showed enhancement in *two* of the signals for ring protons (δ 6.74 and 6.63 ppm) upon irradiation of the three silyl methyl groups on the alkyl ligand; no enhancement in the other ring proton signal (δ 5.98 ppm) was observed. Thus, the alkyl ligand lies below the two adjacent ring protons as in the (1*S*)-R_{Sc})/(1*R*)-(S_{Sc}) enantiomers and not under the isolated ring proton as in the (1*R*)-R_{Sc})/(1*S*)-(S_{Sc}) pair. Furthermore, and perhaps most convincingly, the molecular structure found for a metalated decomposition product of [(Cp^{NMe}SiNR)Sc(CH_2SiMe_3)] (see below) was indicative of the assigned stereochemistry.

When treated with dihydrogen, Me_4Si was eliminated via hydrogenolysis of the Sc−C bond, affording a nearly equimolar mixture of two Cp−amido−amine ligand containing species (eq 2), as evidenced by both the ^{1}H



(2)

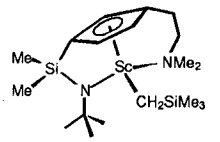
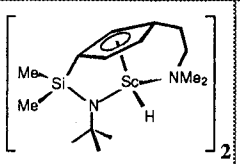
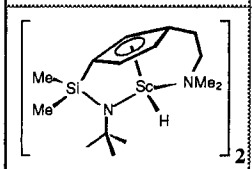
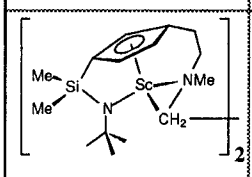
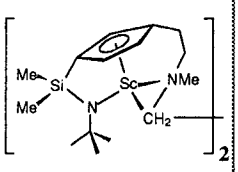
and $^{13}C\{^1H\}$ NMR spectra (Table 1). Crystals of one of these products, **3a**, grew preferentially from hexanes, and the compound was identified crystallographically as a dimeric scandium hydride, an ORTEP diagram of which is shown in Figure 1. In this C_i symmetric diastereomer, which is one of a possible four available upon dimerization of a kinetically formed monomeric hydrido species (Chart 2), the cyclopentadienyl moieties are found in a *trans* arrangement with respect to the Sc_2H_2 plane. The chirality symbols assignable to the highest priority cyclopentadienyl carbons (1 and 1′) are 1*R*-1′*S*. In this isomer, a *trans* arrangement of the *tert*-butyl amido groups (and also the dimethylamine donors) across the Sc_2H_2 core obtains, but since the *trans* placement of these donors relative to one another is dictated by which face of the cyclopentadienyl ring is bonded to the scandium, *trans* refers only to the disposition of the cyclopentadienyl rings across the Sc_2H_2 plane in our labeling of **3a** as the 1*R*-*trans*-1′*S* isomer. The other three diastereomers possible are thus the C_2 symmetric dimers **3b** (1*R*-*cis*-1′*R*) and **3c** (1*R*-*trans*-1′*R*) and the *meso* isomer **3d** (1*R*-*cis*-1′*S*), each illustrated in Chart 2.[15] We were unable to conclusively demonstrate which of these was the other diastereomer (**3′**) in the product mixture formed upon reaction of **2** with dihydrogen, but we favor the 1*R*-*cis*-1′*R* isomer (**3b**) for two reasons. First, molecular models suggest that placing the *tert*-butylamido ligands opposite each other,

(13) (a) In reactions carried out at lower temperatures (−20 °C), small quantities (≈5%) of what we believe to be a scandium complex of the 1,2-substituted ligand were observed. This compound could be disposed of via a second recrystallization. In related zirconium chemistry,[8,13b] complexes of 1,2-substituted ligand can be isolated and characterized when ligand attachment reactions are carried out at −78 °C. (b) Mu, Y.; Piers, W. E. Unpublished results.

(14) *R* and *S* symbols were designated according to Cahn−Ingold−Prelog rules as outlined in: (a) Schlögel, K. *Top. Stereochem.* **1967**, *1*, 39. (b) Sloan, T. E. *Top. Stereochem.* (c) Stanley, K.; Baird, M. C. *J. Am. Chem. Soc.* **1975**, *97*, 6598.

(15) Since there are four chiral centers in these dimers, 16 stereoisomers are possible, some of which are *meso* compounds. Half of them may be eliminated since the pseudocoordination site occupied by the bridging hydride ligands in each scandium coordination sphere can only lie beneath the two adjacent ring protons. The remaining stereoisomers are the three diastereomeric pairs of enantiomers and the *meso* compound shown in Chart 2.

Table 1. ^{1}H and ^{13}C{^{1}H} NMR Data for Isolated New Compounds[a]

		^{1}H NMR Data			^{13}C{^{1}H} NMR Data	
Compound	#	δ(ppm)	Assignment	J(Hz)	δ(ppm)	Assignment
	**2**	6.74, 6.63, 5.98 (m, 3H) 2.07-2.21 (m, 3H) 1.44 (ddd, 1H) 1.67, 1.46 (s, 6H) 1.31 (s, 9H) 0.70, 0.65 (s, 6H) 0.38 (s, 9H) -0.50, -0.73 (AB q, 2H)	Cp*H* NC*H*$_2$CH*H* NCH$_2$CH*H* (C*H*$_3$)$_2$N NC(C*H*$_3$)$_3$ Si(C*H*$_3$)$_2$ Si(C*H*$_3$)$_3$ ScC*H*$_2$Si	2.6, 2.2 12.4, 4.8, 2.2 10.8	130.0, 124.2, 124.1, 121.5, 114.9 65.3 54.4 48.3. 41.9 43.2 36.0 25.4 4.4 2.4, 2.1	 Cp*C* N*C*H$_2$ N*C*(CH$_3$)$_3$ (*C*H$_3$)$_2$NCH$_2$ Sc*C*H$_2$ NC(*C*H$_3$)$_3$ NCH$_2$*C*H$_2$ Si(*C*H$_3$)$_3$ Si(*C*H$_3$)$_2$
	**3a**	6.57, 6.52, 6.49 (m, 3H) 3.02, 2.42 (m, 2H) 2.46, 1.60 (m, 2H) 2.26, 1.91 (s, 6H) 1.40 (s, 9H) 0.72, 0.52 (s, 6H)	Cp*H* NC*H*$_2$ NCH$_2$*C*H$_2$ (*C*H$_3$)$_2$N NC(*C*H$_3$)$_3$ Si(*C*H$_3$)$_2$	2.6, 2.4	130.2, 123.5, 123.4 116.1, 112.8 63.8 55.4 51.5, 44.1 36.2 25.7 4.2, 2.9	 Cp*C* N*C*H$_2$ N*C*(CH$_3$)$_3$ (*C*H$_3$)$_2$NCH$_2$ NC(*C*H$_3$)$_3$ NCH$_2$*C*H$_2$ Si(*C*H$_3$)$_2$
	**3'**	6.74, 6.59, 6.48 (m, 3H) 2.90, 2.40 (m, 2H) 2.41, 1.60 (m, 2H) 2.23, 1.90 (s, 6H) 1.25 (s, 9H) 0.72, 0.54 (s, 6H)	Cp*H* NC*H*$_2$ NCH$_2$*C*H$_2$ (*C*H$_3$)$_2$N NC(*C*H$_3$)$_3$ Si(*C*H$_3$)$_2$	2.6, 2.4	130.6, 124.0, ---, 114.3, 112.3 63.6 55.5 51.1, 44.3 36.3 25.7 4.5, 2.8	 Cp*C* N*C*H$_2$ N*C*(CH$_3$)$_3$ (*C*H$_3$)$_2$NCH$_2$ NC(*C*H$_3$)$_3$ NCH$_2$*C*H$_2$ Si(*C*H$_3$)$_2$
	**4a**	6.33, 6.27, 6.16 (m, 3H) 2.85, 2.1-2.4 (m, 4H 1.97 (s, 3H) 1.23 (s, 9H) 0.76, 0.70 (s, 6H) **b**	Cp*H* NCH$_2$*C*H$_2$ (*C*H$_3$)N NC(*C*H$_3$)$_3$ Si(*C*H$_3$)$_2$ ScC*H*$_2$N		**c**	
	**4b**	6.35, 6.22, 6.05(m, 3H) 2.60, 2.25-2.32 (m, 4H) 2.07 (s, 3H) 1.18 (s, 9H) 0.74, 0.69 (s, 6H) **b**	Cp*H* NCH$_2$*C*H$_2$ (*C*H$_3$)N NC(*C*H$_3$)$_3$ Si(*C*H$_3$)$_2$ ScC*H*$_2$N	2.0, 2.6 7.6	133.6, 121.7, 116.7, 112.8, 109.1 67.1 56.3 (br) 54.7 48.3 36.4 26.4 4.5, 2.3	 Cp*C* N*C*H$_2$ ScC*H*$_2$N NC(*C*H$_3$)$_3$ (*C*H$_3$)NCH$_2$ NC(*C*H$_3$)$_3$ NCH$_2$*C*H$_2$ Si(*C*H$_3$)$_2$

[a] ^{1}H NMR spectra were recorded in C_6D_6 at room temperature at 400 MHz. ^{13}C{^{1}H} NMR spectra were obtained in C_6D_6 at room temperature at 100 MHz. Spectra were referenced to solvent peaks. [b] Resonances broadened and obscured. [c] ^{13}C NMR data for the sparingly soluble **4a** was not obtained.

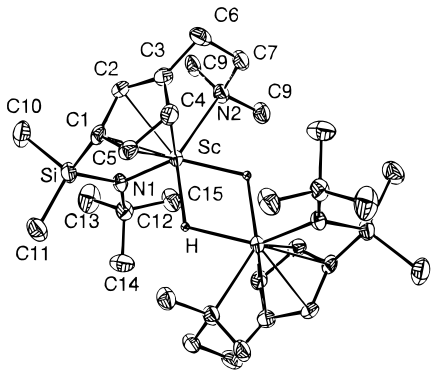


Figure 1. ORTEP diagram of 1*R-trans*-1′*S*-[(Cp^{NMe}SiNR)-ScH]$_2$, **3a**.

as in **3c**,**d**, results in unfavorable steric interactions.[16] Second, the ligand arrangement in **3b** is very similar to that found in the closely related (and crystallographically characterized) complex [(Cp*SiNR)Sc(PMe$_3$)]$_2$(μ-H)$_2$.[5a]

The observed ratio of the two diastereomers did not change appreciably over the range of 20−70 °C; however, slow interconversion between the two compounds was demonstrated by the equilibration of samples enriched in the less soluble diastereomer, **3a**. Samples which were ≈90% enriched in **3a** via fractional crystallization reverted back to the 1:1 mixture observed in the initial reaction over the course of about 4 h at room temperature. These observations suggest that small amounts of monomeric hydride are in equilibrium with the dimers observed[5b] but that dissociation of the dimers is slow. This accounts for the very slow reactions observed between hydrides **3** and α-olefins such as 1-hexene and 1-octene, which would presumably occur through a monomeric species. Even in neat olefin, these reactions were very slow and competitve decomposition processes of the metal alkyls formed as products of olefin insertion into the Sc−H bond precluded isolation of

(16) This is admittedly less of a problem in **3c**, where the *tert*-butyl groups are *trans* with repect to the Sc$_2$H$_2$ plane, and therefore, **3c** is also a credible candidate for **3′**.

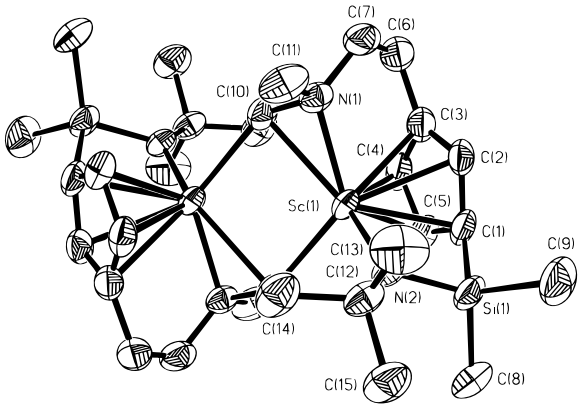
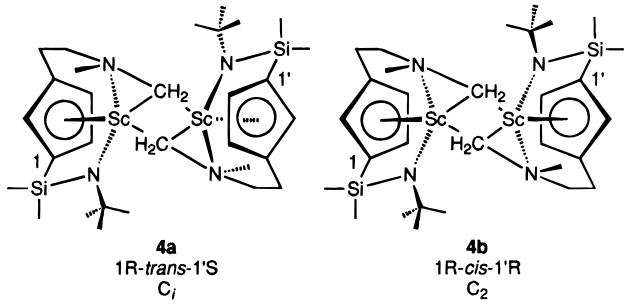


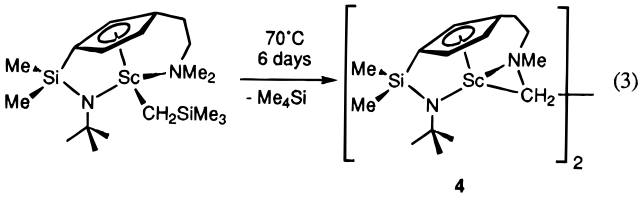
Figure 2. ORTEP diagram of 1*R-trans*-1′*S*-**4a**.

Chart 3



characterizable products. Also, no oligomerization of the substrates were observed. Since dissociation of trimethylphosphine to form highly active base-free monomers has been shown to be an important prerequisite to olefin polymerization by Bercaw's $[(Cp^*SiNR)ScR]_x$ system, a lack of activity in this regard for hydrides **3** is perhaps not surprising. The formation of the required active species via dissociation of the amine arm of the ligand in these compounds is entropically disfavored due to the chelate effect.

Alkyl complex **2** was observed by ^{1}H NMR spectroscopy to slowly decompose in solution with loss of Me_4Si to form a mixture of two products (eq 3). As was the



(3)

case for the hydrogenolysis reaction, one of the products was significantly less soluble than the other and X-ray-quality crystals were obtained directly from the NMR tube. The product thus characterized was the dimer **4a** (an ORTEP diagram is shown in Figure 2), which formed via a σ-bond metathesis reaction involving a C−H bond of one of the diastereotopic *N*-methyl groups.

Interestingly, the less soluble isomer **4a** is of the same topology as crystallographically characterized **3a**; that is, it is the 1*R-trans*-1′*S* diastereomeric pair of enantiomers (Chart 3). Unlike the dihydride dimers, however, isomers in which the (dimethylamino)ethyl groups are *cis* to one another (*i.e.* analogous to **3c** and the *meso* isomer **3d**) are likely precluded in this series by the structural constraints of the ligand. We thus assign the more soluble species produced in the thermolysis of

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for 3a

		Distances	
Sc−N1	2.075(4)	$ScCp_{cent}$	2.1635(18)
Sc−N2	2.452(5)	Sc−H1	2.02(5)
Sc−C1	2.406(5)	Sc−H1′	2.05(4)
Sc−C2	2.436(5)	H1−Sc′	2.05(4)
Sc−C3	2.535(6)	Sc−Sc′	3.359(3)
Sc−C4	2.533(6)	Si−N1	1.717(5)
Sc−C5	2.462(6)	Si−C1	1.851(6)
		Angles	
N1−Sc−N2	111.74(17)	Si−N1−C8	127.0(3)
N1−Sc−H1	91.2(13)	Sc−N2−C13	105.5(3)
N1−Sc−H1a	137.0(13)	Si−C1−C2	115.2(4)
N2−Sc−H1	142.0(13)	Si−C1−C5	130.1(4)
N2−Sc−H1a	74.1(13)	C2−C3−C12	123.5(6)
H1−ScH1a	68.6(18)	C4−C3−C12	127.6(6)
N1−Si−C1	95.39(23)	C3−C12−C13	111.6(5)
N1−Si−C6	116.1(3)	N2−C13−C12	113.9(4)
Sc−N1−C8	128.1(3)	Sc−H1−Sca	111.4(21)
Cp_{cent}−Sc−N1	101.82(14)	Cp_{cent}−Sc−N2	98.71(14)

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for 4a

		Distances	
Sc1−N2	2.104(3)	Sc1−C10	2.476(4)
Sc1−N1	2.223(3)	Sc1−C10′	2.410(4)
Sc1−C1	2.414(4)	Sc1−Sc1′	3.3351(13)
Sc1−C2	2.441(4)	Si1−N2	1.731(3)
Sc1−C3	2.525(4)	Si1−C1	1.865(4)
Sc1−C4	2.533(4)	C7−N1	1.484(5)
Sc1−C5	2.466(4)	N1−C11	1.463(5)
		N1−C10	1.495(5)
		Angles	
N2−Sc1−N1	116.41(12)	C4−C5−C1	108.6(4)
N2−Sc1−C10′	92.66(13)	C3−C6−C7	110.1(4)
N1−Sc1−C10′	127.20(13)	N1−C7−C6	113.2(4)
N2−Sc1−C10	142.55(14)	C11−N1−C7	110.2(4)
N1−Sc1−C10	36.61(12)	C11−N1−C10	111.1(4)
C10′−Sc1−C10	93.92(13)	C7−N1−C10	113.8(3)
N2−Si1−C1	96.5(2)	C11−N1−Sc1	117.0(3)
C5−C1−C2	106.0(3)	C7−N1−Sc1	120.5(3)
C5−C1−Si1	126.2(3)	C10−N1−Sc1	80.9(2)
C1−C1−Si1	117.5(3)	C12−N2−Si1	123.6(2)
C3−C2−C1	109.8(4)	C12−N2−Sc1	134.5(2)
C2−C3−C4	107.6(4)	Si1−N2−Sc1	101.9(2)
C2−C3−C6	124.2(4)	N1−C10−Sc1′	141.8(3)
C4−C3−C6	127.0(4)	N1−C10−Sc1	62.4(2)
C3−C4−C5	108.1(4)	Sc1′−C10−Sc1	86.08(13)
Cp_{cent}−Sc−N2	102.2	Cp_{cent}−Sc−N1	99.5

$[(Cp^{NMe}SiNR)Sc(CH_2SiMe_3)]$ to be the C_2 symmetric 1*R-cis*-1′*R*/1*S-cis*-1′*S* enantiomeric pair. Similar to what was observed for the hydrides **3a** and **3′**, enriched samples of the poorly soluble **4a** slowly converted to a mixture of diastereomers, indicating that dissociation of the dimers occurs in solution to a limited degree.

X-ray Structures of 3a and 4a. Selected bond distances and angles for **3a** and **4a** are provided in Tables 2 and 3, respectively. As we have already alluded, these compounds are structurally related to μ-hydride and μ-alkyl dimers containing the simpler Cp*SiNR ligand.[5] The metrical parameters associated with the Cp−amido portion of our ligand do not differ significantly from those found for scandium complexes containing the Cp*SiNR ligand. Our two structures allow for some assessment of the coordinating properties of the Cp^{NMe}SiNR ligand compared with Cp*SiNR/PMe_3. Since the stabilizing Lewis base is chelating, it is more constrained than the PMe_3 ligand in Bercaw's compounds and the ligand assumes a pseudofacial coordination mode and occupies a hemispherical region of space around the scandium centers. This indeed results in a

more open environment about the alkyl/hydride coordination site as originally predicted; however, the effect was not an increase in reactivity but rather more tightly connected dimeric structures.

Comparison of the $Cp_{cent}-Sc-N$ angles in **3a** and **4a** shows that, despite the greater flexibility of the (dimethylamino)ethyl arm of the ligand, the $Cp_{cent}-Sc-N_{amido}$ angles (**3a**, 101.5°; **4a**, 102.2°) are greater than the $Cp_{cent}-Sc-N_{amine}$ (98.5 and 99.5°) angles in both complexes. This is another manifestation of the previously noted similarity between $SiMe_2$ and ethylene bridges (for example in *ansa*-metallocenes) in terms of their steric properties.[17]

Not unexpectedly, there are marked differences in the $Sc-N_{amido}$ and $Sc-N_{amine}$ bond distances in both complexes, although the variance between the two in **3a** (Δ = 0.377 Å) is significantly larger than that in **4a** (0.119 Å). This observation is a consequence of metalation of the *N*-methyl group, which draws the N_{amine} into closer proximity to the scandium center in **4a**. Even so, the $Sc-N_{amine}$ distance of 2.452(5) Å appears anomolously long compared to calculated values based on ionic or covalent radii considerations (2.205 Å[18]) for six-coordinate scandium centers[19] and to previously reported experimental values for $Sc-N(sp^3)$ lengths. In the ammine complex $[Sc\{OCH(CF_3)_2\}_3(NH_3)_2]_2$[20] the average Sc−N distance was 2.32(1) Å, and the $Sc-N(sp^3)$ linkage in $Cp^*_2ScNH_2NC(CH_3)CN(H)$[21] was 2.277(4) Å.[22] The length of the $Sc-N_{amine}$ bond in **3a** may be due to the constraints of the ligand structure.

The Sc_2H_2 core of **3a** is similar to that in $[(Cp^*SiNR)Sc(PMe_3)]_2(\mu\text{-}H)_2$[5a] and undeserving of further comment. In **4a**, however, the central portion of the molecule is not as symmetrical in that the distance separating the Sc and C10 atoms is slightly longer (2.476(4) Å) than the Sc-C10′ distance of 2.410(4) Å. These distances fall outside the range of Sc−C distances (2.320−2.372 Å) found in dimeric Cp*SiNR scandium alkyl complexes, likely a factor of the metalated nature of the μ-alkyl groups in **4a**.

Conclusions. In summary, we have prepared a new ligand type and developed procedures for attaching it to scandium via efficient an efficient alkane elimination reaction from *in situ* generated $Sc(CH_2SiMe_3)_3\cdot 2THF$. When treated with dihydrogen, the resulting alkyl complex can be converted to robust dimeric hydrides. The olefin chemistry of these dihydrides is limited, suggesting that ligand **1** has little promise as an auxillary; however, we believe the procedure for its attachment to scandium has potential as a general method for binding ligands with −NH functionality to early transition metals.[23] For example, we have prepared dialkyl derivatives of scandium containing pyrazolylborate ligands via alkane elimination through reaction of $Sc(CH_2SiMe_3)_3\cdot 2THF$ with $[HB(pyz)_3]^-[H]^+$ type reagents.[24] It is conceivable that known Cp*SiNR,[5] porphyrin,[25] or benzamidate[26] alkyl complexes of scandium could be prepared directly using this methodology, avoiding preparation of ligand salts and sequential salt elimination reactions for ligand and alkyl attachment to scandium.

Experimental Section

General Methods. General techniques, drying of solvents, and analytical tools employed were as described previously. All materials were purchased from Aldrich and used as recieved or purified by standard procedures.[27] $Sc(CH_2SiMe_3)_3\cdot 2THF$[28] and $CpCH_2CH_2NMe_2$[11] were synthesized according to published procedures.

Synthesis of $CpH^{NMe}SiN(H)R$, 1. $CpCH_2CH_2NMe_2$ (11.0 g, 80.2 mmol) was dissolved in 65 mL of THF. *n*-Butyllithium (51 mL of a 1.6 M solution in hexanes, 81.6 mmol) was added at −78 °C. The mixture was allowed to warm to room temperature and stirred for 30 min. Me_2SiCl_2 (10 mL, 82.4 mmol) was then added at −78 °C, and the mixture was warmed to room temperature and stirred for further 30 min. Solvents and excess Me_2SiCl_2 were removed *in vacuo,* and the residue was redissolved in 65 mL of THF. To the solution was added 20 mL of *t*-$BuNH_2$ (190.3 mmol) at −78 °C, and the mixture was stirred at room temperature for 1 h. Solvent was removed *in vacuo*, and the residue was extracted with 2 × 100 mL of hexane. After the hexanes were removed *in vacuo*, the pale yellowish oil was exposed to dynamic vacuum for several hours. The remaining material (15.1 g, 71%) was used without further purification. ^{1}H NMR (C_6D_6; δ): 6.95−6.00 (m, ring H on sp^2 C), 3.30−2.90 (m, ring H on sp^3 C); 2.70−2.50, 2.15−2.10 (m, CH_2CH_2N); 2.18 (s), 2.15 (s, major), 2.11 (s), 2.09 (s) ($N(CH_3)_2$); 1.19 (s), 1.16 (s), 1.10 (s), 1.08 (s, major) ($NC(CH_3)_3$); 0.30 (s), 0.29 (s), 0.20 (s), 0.05 (s), 0.03 (s, major), 0.02 (s, major) ($Si(CH_3)_2$). $^{13}C\{^1H\}$ NMR (C_6D_6) for major isomer: δ 134.5, 132.7, 128.4, 126.2 (ring sp^2 C), 60.6 (CH_2CH_2N), 55.8 ($NC(CH_3)_3$), 53.6 (ring sp^3 C), 45.5 ($N(CH_3)_2$), 33.8 ($NC(CH_3)_3$), 29.0 (CH_2CH_2N), 0.19, 0.05 ($Si(CH_3)_2$).

Synthesis of $[(Cp^{NMe}SiNR)ScCH_2SiMe_3]$, 3. A 2.61 g amount of $ScCl_3(THF)_3$ (7.1 mmol) and 2.0 g of $TMSCH_2Li$ (21.3 mmol) were combined with 60 mL of hexane at −78 °C. The mixture was stirred at 0 °C for 2 h and then filtered to remove LiCl. To the filtrate was added a solution of **1** (1.90 g, 7.1 mmol) in 10 mL of hexane at 0 °C. The reaction solution was stirred at room temperature for 30 min and then reduced in volume to 15 mL, during which period a large amount of off-white crystalline solid formed. The solid product (1.47 g, 3.7 mmol, 52%) was collected on a frit, washed with hexane, and dried under vacuum. Anal. Calcd for $C_{19}H_{39}N_2Si_2Sc$: C, 57.53; H, 9.91; N, 7.06. Found: C, 57.60; H, 10.03; N, 6.76.

Synthesis of $[(Cp^{NMe}SiNR)ScH]_2$, 3a and 3′. $[(Cp^{NMe}SiNR)ScCH_2SiMe_3]$ (165 mg, 0.42 mmol) was dissolved in 10

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(23) An yttrium complex of **1** could be generated in an analogous fashion via reaction of diproteo **1** and *in situ* prepared $Y(CH_2SiMe_3)_3\cdot x$THF. Due to the larger size of yttrium, THF adducts were formed. Removal of THF via heating under vacuum was to a degree successful; however, at least two metalation reactions were also facile under these conditions leading to a complex mixture of products. This ligand thus appears less suited for preparing stable alkyl derivatives of yttrium.
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Table 4. Summary of Data Collection and Structure Refinement Details for 3a and 4a

	3a	4a
formula	$C_{18}H_{32}ScSiN_2$	$C_{15}H_{27}ScSiN_2$
fw	349.50	308.44
cryst syst	triclinic	monoclinic
a, Å	8.667(4)	10.3832(7)
b, Å	9.989(3)	8.5974(6)
c, Å	13.098(4)	18.751(1)
α, deg	103.75(4)	
β, deg	93.32(6)	92.813(1)
γ, deg	112.49(3)	
V, Å^3	1003.6(6)	1671.9(2)
space group	$P\bar{1}$	$P2_1/c$
Z	2	4
F(000)	378.69	664
d_{calc}, Mg m^{-3}	1.157	1.225
μ, mm^{-1}	0.42	0.502
R	0.053	
R_w	0.047	
*R*1		0.0602
w*R*2		0.1275
gof	2.17	1.11

mL of benzene and loaded in a 50 mL thick-walled reactor bomb. The bomb was sealed under 1 atm of H_2 at −196 °C and then heated to 70 °C for 12 h. The solvent was removed to leave a white solid, which was washed with hexane and dried *in vacuo*. Yield: 105 mg, 82%. Single crystals of **3a** were obtained from C_6D_6 solutions of mixtures of **3a** and **3′** at room temperature. Anal. Calcd for $C_{30}H_{58}N_4Si_2Sc_2$: C, 58.03; H, 9.42; N, 9.02. Found: C, 57.91; H, 9.56; N, 8.78.

Reaction of 3a/3′ with CH_2=CHR (R = C_4H_9, C_6H_{13}). A 1:1 mixture of diastereomers **3a** and **3′** (5−10 mg) was loaded into a small reactor bomb and dissolved in 2−3 mL of 1-hexene or 1-octene. The mixtures were stirred for 24 h at room temperature; removal of olefin led to recovery of the hydride dimers. When these reactions were carried out over similar time periods at 60−80 °C, removal of olefin left small amounts (<50 mg) of gummy material which was not analyzed further.

Thermolysis of [(Cp^{NMe}SiNR)ScCH$_2$SiMe$_3$]. [(Cp^{NMe}SiNR)ScCH$_2$SiMe$_3$] (20 mg, 0.05 mmol) was loaded into a sealable NMR tube and dissolved in 0.8 mL of C_6D_6. The solution was heated at 60 °C, and the reaction was monitored by ^{1}H NMR. The clear white crystals formed were collected when the starting material was no longer present, and crystals suitable for X-ray analysis were obtained directly from the NMR tube. The remainder of the material (≈5 mg) was redissolved in C_6D_6. Over the course of 2 h at room temperature, the 1:1 mixture of **4a** to **4b** was reestablished.

X-ray Structure Determination of [(Cp^{NMe}SiNR)ScH]$_2$, 3a. Single crystals suitable for X-ray crystallography were mounted in thin-walled glass capillaries and optically centered in the X-ray beam of an Enraf Nonius CAD-4 diffractometer. Unit cell dimensions were determined via least-squares refinement of the setting angles of 24 high-angle reflections, and intensity data were collected using the $\omega-2\theta$ scan mode. Data were corrected for Lorentz, polarization, and absorption effects but not for extinction. Pertinent data collection and structure refinement parameters are presented in Table 4. All structures were solved using direct methods. All non-hydrogen atoms were refined with anisotropic thermal parameters. Aryl and methylene hydrogens were placed in calculated positions (D_{C-H} = 1.00 and 1.08 Å, respectively). Hydride and methyl hydrogen atoms were located via inspection of difference Fourier maps. The hydride thermal parameters were refined isotropically whereas the remaining hydrogen atoms were given isotropic temperature factors based upon the atom to which they are bonded and fixed during least-squares refinement. A weighting scheme based upon counting statistics was used with the weight modifier *k* in kF_o^2 being determined via evaluation of variation in the standard reflections that were collected during the course of data collection. Neutral atom scattering factors were taken from ref 29. Values of *R* and R_w are given by $R = (F_o - F_c)/EF_o$ and $R_w = [E(w(F_o - F_c))^2/E(wF_o^2)]^{1/2}$. All crystallographic calculations were conducted with the PC version of the NRCVAX program package[30] locally implemented on an IBM-compatible 80486 computer.

X-ray Structure Determination of 4a. A crystal of **4a** was attached to a glass fiber and mounted on the Siemens SMART system for a data collection at 173(2) K. An initial set of cell constants was calculated from reflections harvested from three sets of 30 frames. Final cell constants were calculated from a set of 8192 strong reflections from the actual data collection. See Table 4 for additional crystal and refinement information.

In the hemisphere collection technique employed here a randomly oriented region of reciprocal space is surveyed to the extent of 1.3 hemispheres to a resolution of 0.84 Å. Three major swaths of frames are collected with 0.30° steps in ω. This collection strategy provides a high degree of redundancy in the data, providing good ψ input in the event an empirical absorption correction is applied (see Table 4). Frames were 45 s in duration.

The space group $P2_1/c$ was determined on the basis of systematic absences and intensity statistics. A successful direct-methods solution was calculated which provided most non-hydrogen atoms from the *E*-map. Several full-matrix least-squares difference Fourier cycles were performed which located the remainder of the non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. Half of the dimer is unique, the remainder being generated by symmetry. All hydrogen atoms were placed in ideal positions and refined as riding atoms with individual (or group if appropriate) isotropic displacement parameters. Two peaks were found near C(10) in the difference Fourier map that correspond to methylene hydrogens with sp^3 hybridization. These hydrogen atoms were refined isotropically. The final agreement for the refinement was R = 0.0602. All calculations were preformed using SGI INDY R4400-SC or Pentium computers using the SHELXTL V5.0 suite of programs.[31]

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Supporting Information Available: Tables of data collection parameters, complete positional and thermal parameters, and bond distances and angles (17 pages). Ordering information is given on any current masthead page.

OM9600856

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