Organometallics **2003,** *22,* 3921−3926

Yttrium Alkyl and Hydrido Complexes Containing a Tridentate-Linked Amido-Cyclopentadienyl Ligand

Peter Voth, Thomas P. Spaniol, and Jun Okuda[*,†]

Institut für Anorganische Chemie und Analytische Chemie,
Johannes Gutenberg-Universität Mainz, Duesbergweg 10-14, D-55099 Mainz, Germany

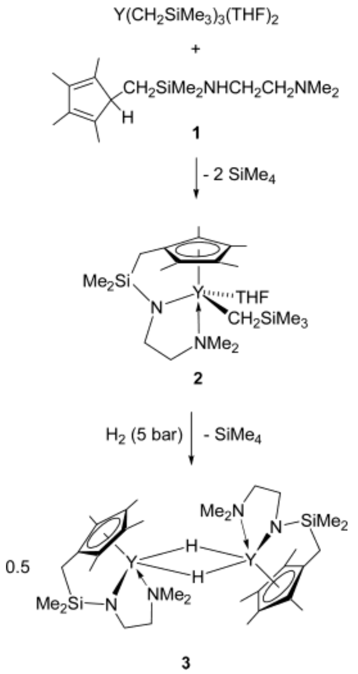
Received May 19, 2003

A tridentate-linked amido-cyclopentadienyl ligand $(C_5Me_4CH_2SiMe_2NCH_2CH_2NMe_2)^{2-}$ (L) was coordinated at yttrium to give the alkyl complex $[Y(L)(CH_2SiMe_3)(THF)]$ (**2**), which reacts with H_2 to give the THF-free dimeric hydride $[Y(L)(\mu\text{-}H)]_2$ (**3**). Styrene inserted into the yttrium−hydride bond of **3** at 60 °C to give the 1-phenylethyl complex $[Y(L)\{CH(CH_3)Ph\}]$ (**4**).

Introduction

Metallocene hydrido complexes of the rare-earth metals are interesting precursors for homogeneous catalysts in various olefin hydrometalations and polymerizations.[1] We have been exploring the synthesis of rare-earth metal hydrido complexes that contain a linked amido-cyclopentadienyl ("constrained geometry") ligand $(C_5Me_4SiMe_2NCMe_3)^{2-}$,[2] originally designed by Bercaw et al. as an ancillary ligand for scandium alkyl and hydrido complexes,[3,4] and that belong to the relatively unexplored class of rare-earth metal half-sandwich complexes.[5] In previously works we were not able to coordinate hemilabile tridentate variants of this ligand system[6] such as $(C_5Me_4SiMe_2NCH_2CH_2NMe_2)^{2-}$ due to cleavage of the bond between the ring carbon and silicon.[2b] Since the yttrium hydrido complex with a longer CH_2SiMe_2 bridge $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4CH_2SiMe_2NCMe_3)(THF)(\mu\text{-}H)]_2$ was recently found to be easily accessible,[7] we have explored the use of the longer CH_2SiMe_2 bridge to obtain yttrium complexes of the hemilabile tridentate ligand $(C_5Me_4CH_2SiMe_2NCH_2CH_2NMe_2)^{2-}$ (L).

Scheme 1



Results and Discussion

Following the procedure for the synthesis of $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4CH_2SiMe_2NCMe_3)(CH_2SiMe_3)(THF)]$,[7] we prepared the new alkyl complex $[Y(L)(CH_2SiMe_3)(THF)]$ (**2**) in 67% yield as hydrocarbon-soluble, colorless crystals by the reaction of the functionalized cyclopentadiene $(C_5Me_4H)CH_2SiMe_2NHCH_2CH_2NMe_2$ (**1**) with $[Y(CH_2SiMe_3)_3(THF)_2]$[8] in hexane at 0 °C (Scheme 1). Cyclopentadiene **1** could straightforwardly be prepared by reacting $(C_5Me_4H)CH_2SiMe_2Cl$ with $Li(NHCH_2CH_2NMe_2)$.

[†] New address: Institute of Inorganic Chemistry, Aachen University of Technology (RWTH), Prof.-Pirlet-Strasse 1, D-52056 Aachen, Germany.

(1) For a recent review, see: Molander, G. A. *Chem. Rev.* **2002**, *102*, 2161.

(2) (a) Hultzsch, K. C.; Spaniol, T. P.; Okuda, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 227. (b) Hultzsch, K. C.; Voth, P.; Beckerle, K.; Spaniol, T. P.; Okuda, J. *Organometallics* **2000**, *19*, 228. (c) Arndt, S.; Voth, P.; Spaniol, T. P.; Okuda, J. *Organometallics* **2000**, *19*, 4690. (d) Okuda, J. *Dalton Trans.* **2003**, 2367.

(3) (a) Shapiro, P J.; Bunel, E. E.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1990**, *9*, 867. (b) Piers, W. E.; Shapiro, P. J.; Bunel, E. E.; Bercaw, J. E. *Synlett* **1990**, 74. (c) Shapiro, P. J.; Cotter, W. D., Schaefer, W. P., Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 4623.

(4) (a) Mu, Y.; Piers, W. E.; MacQuarrie, D. C.; Zaworotko, M. J.; Young, V. G., Jr. *Organometallics* **1996**, *15*, 2720. (b) Mu, Y.; Piers, W. E.; MacDonald, M.-A.; Zaworotko, M. J. *Can. J. Chem.* **1995**, *73*, 2233. (c) Tian, S.; Arrendondo, V. M.; Stern, C. L.; Marks, T. J. *Organometallics* **1999**, *18*, 2568. (d) Arrendondo, V. M.; Tian, S.; McDonald, F. E.; Marks, T. J. *J. Am. Chem. Soc.* **1999**, *121*, 3633.

(5) Arndt, S.; Okuda, J. *Chem. Rev.* **2002**, *102*, 1953.

(6) (a) du Plooy, K. E.; Moll, U.; Wocadlo, S.; Massa, W.; Okuda, J. *Organometallics* **1995**, *14*, 3129. (b) Okuda, J.; du Plooy, K. E.; Massa, W.; Kang, H.-C.; Rose, U. *Chem. Ber.* **1996**, *129*, 275 (c) Amor, F.; Spaniol, T. P.; Okuda, J. *Organometallics* **1997**, *16*, 4765. (d) Amor, F.; du Plooy, K. E.; Spaniol, T. P.; Okuda, J. *J. Organomet. Chem.* **1998**, *558*, 139. (e) Amor, F.; Butt, A.; du Plooy, K. E.; Spaniol, T. P.; Okuda, J. *Organometallics* **1998**, *17*, 5836. (f) Okuda, J.; Eberle, T.; Spaniol, T. P.; Piquet-Fauré, V. *J. Organomet. Chem.* **1999**, *591*, 127. For reviews on linked amido-cyclopentadienyl ligands, see: (g) Okuda, J.; Eberle, T. In *Metallocenes*; Halterman, R. L., Togni, A., Eds.; Wiley-VCH: Weinheim, 1998; p 415. (h) McKnight, A. L.; Waymouth, R. M. *Chem. Rev.* **1998**, *98*, 2587.

(7) Trifonov, A. A.; Spaniol, T. P.; Okuda, J. *Organometallics* **2001**, *20*, 4869.

(8) Lappert, M. F.; Pearce, R. *J. Chem. Soc., Chem. Commun.* **1973**, 126.

10.1021/om0303707 CCC: $25.00

Table 1. Experimental Data for the Crystal Structure Determinations of the Complexes 2, 3, and 4

	2	**3**	**4**
	Crystal Data		
empirical formula	$C_{24}H_{49}N_2OSi_2Y$	$C_{32}H_{62}N_4Si_2Y_2$	$C_{24}H_{39}N_2SiY$
fw	526.75	736.86	472.58
cryst color	colorless	colorless	yellow
cryst size, mm	0.58 × 0.31 × 0.25	0.69 × 0.44 × 0.37	0.56 × 0.31 × 0.25
cryst syst	orthorhombic	monoclinic	monoclinic
space group	$P2_12_12_1$ (No. 19)	$P2_1/c$ (No. 14)	$P2_1/c$ (No.14)
a, Å	9.2000(7)	10.8129(2)	18.10(2)
b, Å	17.677(1)	17.3648(5)	10.71(1)
c, Å	18.030(1)	21.0539(5)	13.89(2)
α, deg	90	90	90
β, deg	90	96.942(2)	102.14(2)
γ, deg	90	90	90
V, Å^3	2932.2(3)	3924.2(2)	2632(5)
Z	4	4	4
ρ_{calcd}, g cm^{-3}	1.193	1.247	1.192
μ, mm^{-1}	2.087	3.028	2.272
F(000)	1128	1552	1000
	Data Collection		
$2\theta_{\max}$, deg	57	57	50
index ranges	h, −12 to 12; k, −23 to 23; l, −23 to 24	h, −14 to 14; k, −18 to 23; l, −28 to 28	h, −21 to 16; k, −12 to 12; l, −16 to 16
	Solution and Refinement		
no. of reflns measd	26 773	29 344	13 632
no. of indep reflns	7241 [$R_{\text{int}} = 0.030$]	9716 [$R_{\text{int}} = 0.050$]	4701 [$R_{\text{int}} = 0.1551$]
no. of obsd reflns	6222 ($I > 2\sigma(I)$)	6297 ($I > 2\sigma(I)$)	1656 ($I > 2\sigma(I)$)
no. of params	292	423	262
GOF	0.967	0.934	0.743
final R indices R_1, wR_2 (obsd data)	0.0264/0.0532	0.0456/0.1074	0.0491/0.0988
final R indices R_1, wR_2 (all data)	0.0353/0.0544	0.0786/0.1165	0.1612/0.1366
largest e(max.)/e(min.), e·Å^{-3}	0.420/−0.306	1.011/−0.769	0.400/−0.253

Variable-temperature ^{1}H NMR spectra of **2** indicate fluxionality due to the presence of a labile THF ligand as well as the labile NMe_2 group of the amido side chain, resulting in an apparent mirror plane within the molecule at room temperature. At −60 °C, all pairs of equivalent signals are diastereotopic. Thus pairs of singlets for $SiMe_2$ (0.53, 0.72 ppm) and for NMe_2 (1.51, 1.70 ppm) as well as four distinct singlets (1.67, 1.99, 2.43, 2.54 ppm) for the C_5Me_4 moiety are recorded. AB patterns are observed for the methylene protons of the CH_2SiMe_3 group at −0.55 and −1.47 ppm with $^2J_{HH} = 8$ Hz and those of the CH_2SiMe_2 backbone at 2.31 and 2.40 ppm with $^2J_{HH} = 13.6$ Hz. The protons of the CH_2-CH_2 link are recorded as an ABCD multiplet, one of these multiplets being considerably shifted to higher field (1.83 versus 3.45, 3.30, and 3.19 ppm). The α-protons of the THF ligand are diastereotopic, and two broad singlets were detected at 2.83 and 3.07 ppm. These findings are in contrast to the *tert*-butylamido derivative $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4CH_2SiMe_2NCMe_3)(CH_2SiMe_3)(THF)]$, where no decoalescence of any of the diastereotopic signals was observed, even at −80 °C.[7] Notably, the nonequivalence of the NMe_2 signals at lower temperature indicates the intramolecular coordination of the side-chain donor. The diastereotopicity would not be apparent if the coordination is dissociatively labile (even if the THF coordination is rigid and the metal center chiral), as previously shown in detail for the isoelectronic group 4 metal complexes of the type $[M(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2NMe_2)(CH_2Ph)]^+$ (M = Ti, Zr, Hf).[6]

The structure derived from the trigonal-bipyramidal configuration was confirmed by a crystal structure analysis of **2**. Figure 1 shows an ORTEP diagram of **2**, and crystallographic data are compiled in Table 1. As expected the NMe_2 group is coordinated *trans* to the C_5Me_4 ring with a Y−N2 of 2.588(2) Å, while the amido group (Y−N1 2.241(2) Å), the THF ligand, and the alkyl ligand reside in the equatorial plane. When the metrical parameters of **2** are compared with those of $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4CH_2SiMe_2NCMe_3)(CH_2SiMe_3)(THF)]$,[7] an elongated Y−O bond distance of 2.462(1) Å as compared to 2.327(2) Å in $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4CH_2SiMe_2NCMe_3)(CH_2SiMe_3)(THF)]$ or 2.319(5) Å in $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(CH_2SiMe_3)(THF)]$ is found. This value is larger than the Y−O bond lengths found in other THF-

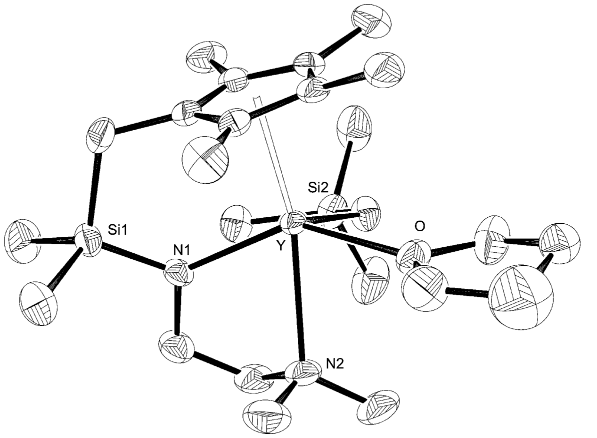


Figure 1. ORTEP diagram of the molecular structure of $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4CH_2SiMe_2NCH_2CH_2NMe_2)(CH_2SiMe_3)(THF)]$ (**2**). Thermal ellipsoids are drawn at the 50% probability level. The THF ligand is shown with one of both split positions (atoms C22a and C23a). Hydrogen atoms are omitted for the sake of clarity. Selected bond lengths (Å) and bond angles (deg): Y−N1 2.241(2), Y−N2 2.588(2), Y−C17 2.414(2), Y−O 2.462(1), Y−C_{ring} 2.642(2)−2.714(2), N1−Y−N2 70.24(6), C17−Y−N2 89.76(7), N1−Y−O 138.40(6), N1−Y−C17 109.93(7), C17−Y−O 92.09(7), O−Y−N2 75.21(6).

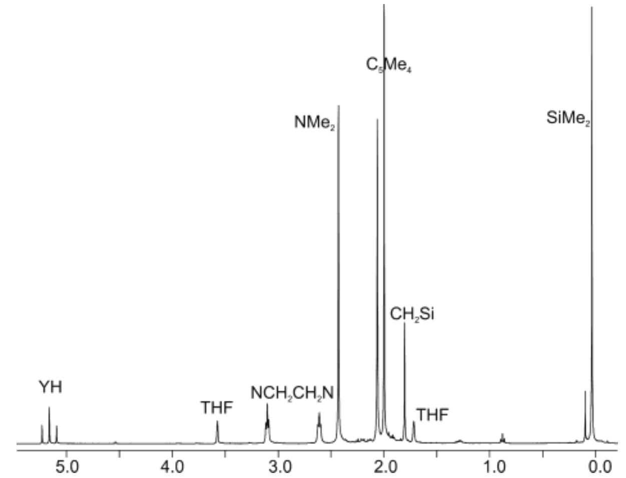


Figure 2. ^1H NMR spectrum of the hydride complex **3** in THF-d_8 at 25 °C.

coordinating yttrium complexes (usually in the range of 2.35−2.45 Å).[9] Also the Y−C_{ring} bond lengths (2.642(2)−2.714(2) Å) are somewhat longer than those found in [Y(η^5:η^1-$C_5Me_4CH_2SiMe_2NCMe_3$)(CH_2SiMe_3)(THF)] (2.593(2)−2.655(2) Å) and comparable to those observed in yttrocene complexes.[10] The larger bond lengths are due to the higher coordination number and to the increase in electron density by the NMe_2 group.

Hydrogenolysis of the alkyl complex **2** with dihydrogen in hexane (5 bar, 25 °C) resulted in clean formation of the dimeric hydrido complex [Y(L)(μ-H)]$_2$ (**3**), isolated as colorless microcrystals in high yield. Although the crude product contained nonstoichiometric amounts of THF, recrystallization from heptane afforded the analytically pure, THF-free hydrido complex **3**. The use of higher boiling hydrocarbon was required because residual THF from the mother liquor appeared to be included in the product.

Complex **3** is highly fluxional, and the ^1H NMR spectrum corresponds to a molecule that contains an internal mirror plane at room temperature. In THF-d_8 **3** preserves its dimeric structure, indicated by a sharp triplet at δ 5.16 ppm ($^1J_{YH}$ = 27.6 Hz). Sharp singlets are detected for the diastereotopic methyl groups of $SiMe_2$ (0.03 ppm), C_5Me_4 (2.00, 2.06 ppm), and NMe_2 (2.43 ppm) and for the protons of the methylene group attached to the silicon (1.80 ppm). For the CH_2 groups of the ethylene linkage bearing the additional donor two triplet-like resonances at 2.57 and 3.06 ppm are found with $^2J_{HH}$ = 5.2 Hz (Figure 2). Below −40 °C the fast interconversion between the different isomers is slowed, resulting in the loss of the internal mirror plane and a splitting of the signals.

In toluene-d_8 the hydride complex **3** shows one sharp triplet for the hydrido ligand at 5.44 ppm with J_{YH} = 30.4 Hz in the temperature range of +90 to 0 °C. At room temperature the resonances for the methyl groups of the C_5Me_4 ring are broadened. Below 0 °C, the fast interconversion between the two diastereomers is slowed, causing a broadening of the hydride triplet, and at −60 °C, three triplets in the intensity ratio 9:1:1 are observed. The resonances at δ 5.07 ppm ($^1J_{YH}$ = 33.6 Hz) and 5.35 ppm ($^1J_{YH}$ = 26.0 Hz) are assigned to the inequivalent hydrido ligands of the C_2-symmetric homochiral dimer, whereas the third resonance at δ 5.43 ppm ($^1J_{YH}$ = 30.4 Hz) is assigned to the centrosymmetric heterochiral diastereomer. At −60 °C all diastereotopic groups in both isomers should appear as separate signals, and therefore considerable broadening and overlapping of the methyl groups of the C_5Me_4 ring and of the NMe_2 group are observed (Figure 3).

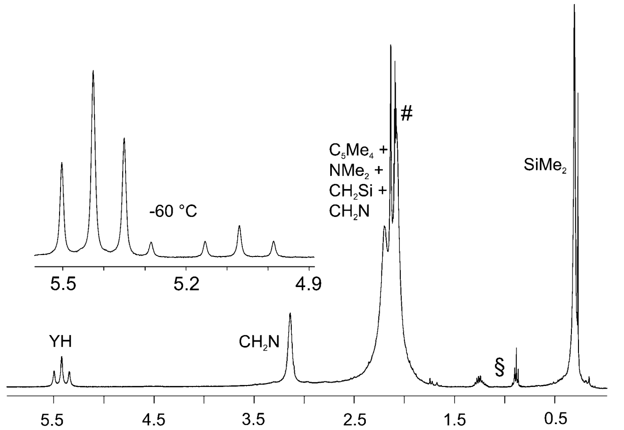


Figure 3. ^1H NMR spectra of the hydride complex **3** in toluene-d_8 at 25 °C. The inset shows the hydride region at −60 °C.

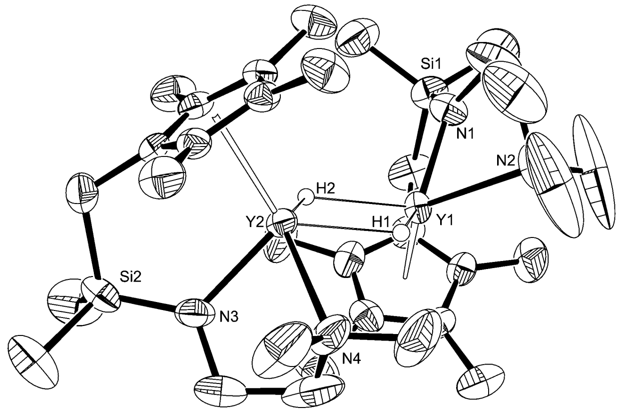


Figure 4. ORTEP diagram of the molecular structure of [Y(η^5:η^1:η^1-$C_5Me_4CH_2SiMe_2NCH_2CH_2NMe_2$)($\mu$-H)]$_2$ (**3**). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms, except for the two bridging hydrides H1 and H2, are omitted for the sake of clarity. Split positions of disordered atoms (C30b, C31b, and C32b) are omitted. Selected bond lengths (Å) and bond angles (deg): Y1−Y2 3.5995(4), Y1−H1 2.28(3), Y1−H2 2.19(3), Y1−N1 2.206(3), Y1−N2 2.557(3), Y1−C_{ring} 2.598(3)−2.652(3), Y2−H1 2.16(3), Y2−H2 2.13(3), Y2−N3 2.213(3), Y2−N4 2.546(3), Y2−C_{ring} 2.606(3)−2.648(3), Y1−H1−Y2 109(1), Y1−H2−Y2 113(1), H1−Y1−H2 68(1), H1−Y2−H2 71(1), N1−Y1−N2 73.0(1), N3−Y2−N4 73.2(1), $Cp_{Cent}1$−Y1−Y2−$Cp_{Cent}2$ 127.

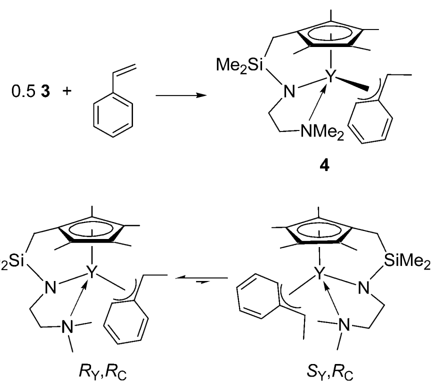
Crystallization by slow evaporation of the heptane solution at −30 °C afforded single crystals of **3**. The X-ray structure analysis confirms the dimeric structure with homochiral configuration at the metal centers with the ancillary ligands bonded in a tridentate fashion (Figure 4). The disposition of the two ring ligands is such that the dihedral angle $Cp_{cent.}$−Y−Y′−$Cp_{cent.}$′ is 127°, which is between 97° found for the benzene solvate of [Y(η^5:η^1-$C_5Me_4CH_2SiMe_2NCMe_3$)(THF)(μ-H)]$_2$[7] and 170°

---

(9) See 2b and references therein.

(10) (a) Evans, W. J.; Forster, S. E. *J. Organomet. Chem.* **1992**, *433*, 79. (b) Hultzsch, K. C.; Spaniol, T. P.; Okuda, J. *Organometallics* **1997**, *16*, 4845, and references therein.

Scheme 2



found for [Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$)(THF)(μ-H)]$_2$.[2a] Similar to [Y(η^5:η^1-$C_5Me_4CH_2SiMe_2NCMe_3$)(THF)(μ-H)]$_2$,[7] the dimerization of the two homochiral monomeric units results in a dimer structure with an arrangement that is intermediate between *cis* and *trans*. The dimerization of the monomeric units in the dimers of the type [Ln(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$)(L)(μ-X)]$_2$ (Ln = Sc, Y, Lu; L = THF, PMe_3; X = H, Cl) was found to critically depend on the nature of the ligands L and X.[2c] The Y$\cdots$Y distance of **3**, 3.5995(4) Å, is slightly shorter than the usual range of Y$\cdots$Y distances found in dimeric hydrido yttrium complexes (3.611(2)−3.7085(8) Å).[11]

The THF-free hydride complex **3** showed no or sluggish reactivity toward olefins such as 1-hexene and styrene at room temperature. Styrene, however, cleanly inserted at 60 °C into the Y−H bond in the secondary fashion, giving the yellow, hydrocarbon-soluble 1-phenylethyl complex [Y(L){CH(CH_3)Ph}] (**4**) (Scheme 2). No evidence for a primary insertion product [Y(L)(CH_2CH_2-Ph)] was found, nor did **4** react with excess styrene at elevated temperature, as was the case for other related complexes.[2b,7] The ^{1}H NMR spectrum of **4** shows the expected signals for an asymmetric molecule in the temperature range of −80 to +75 °C. For the methyl groups of the C_5Me_4 ring four singlets (1.86, 1.96, 2.19, 2.21 ppm) and for $SiMe_2$ group two singlets (0.25, 0.30 ppm) are detected. The protons of the CH_2Si backbone give rise to an AB pattern (2.05, 2.14 ppm, $^2J_{HH} = 5.6$ Hz) and those of the methylene groups of the sidearm to an ABCD pattern of four separated multiplets (1.59, 2.45, 2.89, 3.04 ppm). In the $^{13}C\{^1H\}$ NMR spectrum the methine carbon bonded to the yttrium atom appears as a doublet at 52.3 ppm with $^1J_{YH} = 19.6$ Hz, in agreement with a monomeric structure.

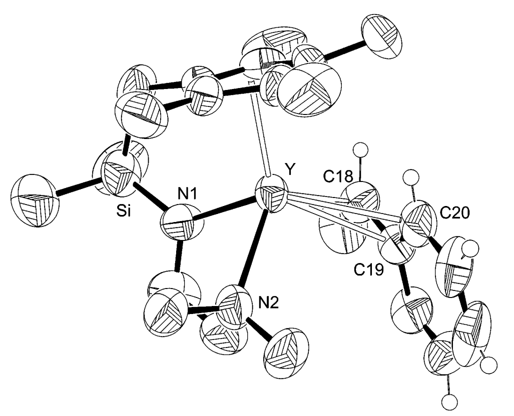


Figure 5. ORTEP diagram of the molecular structure of [Y(η^5:η^1-$C_5Me_4CH_2SiMe_2NCH_2CH_2NMe_2$)($CHMeC_6H_5$)] (**4**). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for the sake of clarity. Selected bond lengths (Å) and bond angles (deg): Y−C18 2.447(8), Y−C19 2.815(8), Y−C20 2.921(7), Y−N1 2.211(6), Y−N2 2.515(6), Y−C_{Ring} 2.609(7)−2.658(8), C18−C19 1.45(1), Y−C18−C19 88.6(4), N1−Y−N2 72.5(2), N1−Y−C18 103.9(3).

Variable-temperature NMR spectra reveal that the NMe_2 group coordination is fluxional with coalescence occurring at 25 °C. Two singlets are detected for the NMe_2 group at lower temperatures. For the phenyl protons in the 1-phenylethyl ligand one sharp (6.94 ppm) and one broad triplet (6.33 ppm) in the intensity ratio 2:3 are observed at room temperature. At −60 °C five inequivalent signals are detected, whereby the significant upfield shift of one of the ortho protons (doublet at 5.98 ppm) is diagnostic for an η^3-coordination of the 1-phenylethyl ligand as was found in [Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$){CH(CH_3)Ph}(THF)].[2b] An additional feature for the η^3-coordination is the reduced $^1J_{CH}$ value of 144 Hz for the ortho carbon resonance at 110.7 ppm in the ^{13}C NMR spectrum. Although the yttrium center becomes chiral at temperatures below 0 °C due to the coordination of the NMe_2 group, only one diastereomer was observed even at −80 °C, probably due to the unfavorable steric strain in one of the epimers (Scheme 2).

Recrystallization from toluene afforded yellow cubes, which were analyzed by X-ray diffraction. Crystallographic data are compiled in Table 1, and an ORTEP diagram of the structure of **4** is shown in Figure 5. Complex **4** is monomeric with a pseudotetrahedral coordination geometry similar to that found for [Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_2Et$){CH(CH_3)C_6H_4-4-^{t}Bu}(THF)]. The methyl group of the 1-phenylethyl ligand is oriented away from the cyclopentadienyl ring, similar to 1,3-diene ligands in linked *tert*-butylamido cyclopentadienyl titanium complexes that prefer the "supine" isomer (with the "cup" oriented toward the cyclopentadienyl ligand).[12] The Y−C18 and Y−C19 bond lengths of 2.447(8) and 2.815(8) Å as well as the Y−C_{ring} distances of

---

[11] (11) (a) [(C_5H_4Me)$_2$Y(THF)(μ-H)]$_2$: Y−H = 2.17(8), 2.19(8) Å, Y$\cdots$Y = 3.664(1) Å, see: Evans, W. J.; Meadows, J. H.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 2008. (b) [($C_5H_3Me_2$)$_2$Y(THF)(μ-H)]$_2$: Y−H = 2.03(7), 2.27(6) Å, see: Evans, W. J.; Drummond, D. K.; Hanusa, T. P.; Doedens, R. J. *Organometallics* **1987**, *6*, 2279. (c) [($MeOCH_2CH_2C_5H_4$)$_2$Y)(μ-H)]$_2$: Y−H = 2.02(6)−2.15(6) Å, Y$\cdots$Y = 3.611(2), 3.622(2) Å, see: Deng, D.; Jiang, Y.; Qian, C.; Wu, G.; Zheng, P. *J. Organomet. Chem.* **1994**, *470*, 99. (d) [{PhC($NSiMe_3$)$_2$}$_2$Y(μ-H)]$_2$: Y−H = 2.11(3)−2.19(3) Å, see: Duchateau, R.; van Wee, C. T.; Meetsma, A.; van Duijnen, P. T.; Teuben, J. H. *Organometallics* **1996**, *15*, 2279. (e) (*rac*)-[(*R,S*)-($C_{20}H_{12}O_2$)Si{C_5H_2-(CMe_3)($SiMe_3$)}$_2$)Y(μ-H)]$_2$: Y−H = 2.0(1), 2.4(1) Å, Y$\cdots$Y = 3.668(3) Å, see: Mitchell, J. P.; Hajela, S.; Brookhart, S. K.; Hardcastle, K. I.; Henling, L. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 1045. (f) [(2,4,7-$Me_3C_9H_4$)$_2$Y(μ-H)]$_2$: Y−H = 2.09(4)−2.14(7) Å, see: Kretschmer, W. P.; Troyanov, S. I.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Organometallics* **1998**, *17*, 284. (g) [{2,2′-bis((*tert*-butyldimethylsilyl)-amido)-6,6′-dimethylbiphenyl}Y(THF)(μ-H)]$_2$: Y−H = 2.22(4), 2.27(4) Å, Y$\cdots$Y = 3.6652(8) Å, see: Gountchev, T. I.; Tilley, T. D. *Organometallics* **1999**, *18*, 2896. (h) [Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$)(THF)(μ-H)]$_2$: Y−H = 1.98(6)−2.48(4) Å, Y$\cdots$Y = 3.672(1) Å, see ref 2a. (i) [Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$)(PMe_3)(μ-H)]$_2$: Y−H = 2.25(6)−2.28(6) Å, Y$\cdots$Y = 3.703(1) Å, see ref 2c. (j) [Y(η^5:η^1-$C_5Me_4CH_2SiMe_2NCMe_3$)(THF)(μ-H)]$_2$: Y−H = 2.03(4)−2.30(4) Å, Y$\cdots$Y = 3.7085(8) Å, see ref 7. (k) [Y_2(μ-{Me_2Si(2-Me-C_9H_5)$_2$})$_2$(μ-H)$_2$]: Y−H = 2.09(3)−2.13(3) Å, Y$\cdots$Y = 3.6524(3) Å, see: Kimbel, M. G.; Sirsch, P.; Scherer, W.; Anwander, R. *Angew. Chem., Int. Ed.* **2003**, *42*, 574.

[12] (12) Devore, D. D.; Timmers, F. J.; Hasha, D. L.; Rosen, R. K.; Marks, T. J.; Deck, P. A., Stern, C. L. *Organometallics* **1995**, *14*, 3132.

2.609(7)−2.658(8) Å are comparable within the standard error with those in $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_2Et)\{CH(CH_3)C_6H_4\text{-}4\text{-}{}^tBu\}(THF)]$. The short Y−N1 bond distance of 2.211(6) Å is remarkable, being one of the shortest yttrium amido bond distances reported so far.[9] The η^3-coordination is manifested by a short Y−C20 bond length (2.921(7) Å, compared to 3.078(7) Å in $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_2Et)\{CH(CH_3)C_6H_4\text{-}4\text{-}{}^tBu\}(THF)]$ and 3.28 in $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4CH_2SiMe_2NCMe_3)\{CH(CH_3)Ph\}(THF)]$). The Y−C18−C19 angle of 88.6(4)° is significantly smaller than those found in η^1-benzyl ligands.[9]

Experimental Section

General Considerations. All operations were performed under an inert atmosphere of argon using standard Schlenk-line or glovebox techniques. The solvents were purified by distillation from sodium/triglyme benzophenone ketyl. Anhydrous yttrium trichloride (ALFA or Strem) was used as received. $[Y(CH_2SiMe_3)_3(THF)_2]$,[2c,8] $Li(NHCH_2CH_2NMe_2)$, and $(C_5Me_4H)CH_2SiMe_2Cl$[13] were prepared according to published procedures. All other chemicals were commercially available and used after appropriate purification. NMR spectra were recorded on a Bruker DRX 400 spectrometer (^1H, 400 MHz; ^{13}C, 101 MHz; ^{89}Y, 19.6 MHz) in C_6D_6 at 25 °C, unless otherwise stated. Chemical shifts for ^1H and ^{13}C spectra were referenced internally using the residual solvent resonances and reported relative to tetramethylsilane. ^{89}Y spectra were referenced externally to a 1 M solution of YCl_3 in D_2O. Elemental analyses were performed by the Microanalytical Laboratory of this department.

$(C_5Me_4H)CH_2SiMe_2NHCH_2CH_2NMe_2$ (1). A suspension of $Li(NHCH_2CH_2NMe_2)$ (3.34 g, 35.5 mmol) in 70 mL of hexane was cooled to −78 °C and treated with $(C_5Me_4H)CH_2SiMe_2Cl$ (8.11 g, 35.4 mmol) in 20 mL of hexane. After allowing the reaction mixture to warm to room temperature and stirring overnight, the reaction mixture was filtered and the solvent was removed from the filtrate in vacuo. Distillation under reduced pressure (78 °C, 2×10^{-2} mbar) gave an extremely moisture-sensitive, yellow oil; yield 8.36 g (84%). ^1H NMR δ: 0.09 (s, 6 H, $SiMe_2$), 1.03 (dd, $^2J_{HH} = 18.2$ Hz, $^3J_{HH} = 7.6$ Hz, 2 H, CH_2Si), 1.77, 1.79, 1.81, 1.84 (s, 3 H, C_5Me_4), 2.05 (s, 6 H, NMe_2), 2.16 (br t, $^3J_{HH} = 6.1$ Hz, 2 H, $C\mathit{H}_2NMe_2$), 2.48 (m, 1 H, $C_5Me_4\mathit{H}$), 2.73 (m, 2 H, CH_2NH). $^{13}C\{^1H\}$ NMR δ: −1.2, −1.0, −0.8 ($SiMe_2$), 11.3, 11.4, 11.8, 11.9, 12.6, 14.3, 14.8, 14.9 (C_5Me_4), 17.1, 17.9 (CH_2Si), 39.7 (ring C attached to CH_2), 45.4 (NMe_2), 51.4, 51.7, 63.1 ($NCH_2CH_2NMe_2$), 131.9, 134.4, 134.5, 134.6, 136.3, 136.5, 137.9, 140.0 (ring C, C_5Me_4). EI MS *m/z* (%): 280 (1%, M^+), 193 (4%, $C_5MeCH_2SiMe_2^+$), 145 (70%, $Me_2SiNHCH_2CH_2NMe_2$), 135 (53%, $C_5Me_4CH_2^+$), 121 (13%, $C_5Me_4H^+$), 88 (11%, $NHCH_2CH_2NMe_2$), 58 (16%, $SiMe_2$), 57 (100%, $CH_2NMe_2^+$). Anal. Calcd for $C_{16}H_{32}N_2Si$: C, 68.50; H, 11.50; N, 9.99. Found: C, 67.49; H, 11.39; N, 8.53.

$[Y(\eta^5{:}\eta^1{:}\eta^1\text{-}C_5Me_4CH_2SiMe_2NCH_2CH_2NMe_2)(CH_2SiMe_3)(THF)]$ (2). To a solution of $[Y(CH_2SiMe_3)_3(THF)_2]$ (1.88 g, 3.8 mmol) in pentane (60 mL) was added **1** (1.07 g, 3.8 mmol) at 0 °C. Over a period of 2 h the bath temperature was allowed to rise to room temperature. The reaction mixture was concentrated in vacuo, and the product crystallized at −30 °C as colorless crystals; yield 1.34 g (67%). ^1H NMR δ: −1.06 (br d, 2 H, YCH_2), 0.41 (s, 9 H, $SiMe_3$), 0.44 (s, 6 H, $SiMe_2$), 1.18 (br s, 4 H, THF), 1.73 (s, 6 H, NMe_2), 2.00, 2.15 (s, 6 H, C_5Me_4), 2.21 (s, 2 H, CH_2Si), 2.60 (br s, 2 H, CH_2NMe_2), 3.17 (br t, 2 H, CH_2N), 3.30 (br s, 4 H, THF). $^{13}C\{^1H\}$ NMR δ: 1.9 ($SiMe_3$), 5.4 ($SiMe_2$), 11.8, 12.0 (C_5Me_4), 16.0 (CH_2Si), 23.5 (d, $^1J_{YC} = 45$ Hz, YCH_2), 25.1 (THF), 44.5, 62.7 ($NCH_2CH_2NMe_2$), 44.6 (NMe_2), 69.6 (THF), 112.5, 114.2 (ring C, C_5Me_4), 124.5 (ring C attached to CH_2). ^1H NMR (toluene-d_8, −60 °C) δ: −1.47, −0.55 (d, $^2J_{HH} = 8.0$ Hz, 2 × 1 H, YCH_2), 0.53, 0.72 (s, 2 × 3 H, $SiMe_2$), 0.62 (s, 9 H, $SiMe_3$), 0.95 (br s, 4 H, THF), 1.51, 1.70 (br s, 2 × 3 H, NMe_2), 1.67, 1.99, 2.43, 2.54 (s, 3 H, C_5Me_4), 1.83, 3.19, 3.30, 3.45 (m, 1 H, $NCH_2CH_2NMe_2$), 2.31, 2.40 (d, $^2J_{HH} = 13.6$ Hz, 1 H, CH_2Si), 2.83, 3.07 (m, 1 H, THF). Anal. Calcd for $C_{24}H_{49}N_2OSi_2Y$: C, 54.73; H, 9.38; N, 5.32. Found: C, 54.66; H, 9.38; N, 5.47.

$[Y(\eta^5{:}\eta^1{:}\eta^1\text{-}C_5Me_4CH_2SiMe_2NCH_2CH_2NMe_2)(\mu\text{-}H)]_2$ (3). A solution of **2** (1.07 g, 2.0 mmol) in pentane (30 mL) was loaded in a thick-walled 100 mL glass reactor. At room temperature dihydrogen was charged (5 bar), and the reaction mixture was stirred vigorously for 8 h. After the removal of the solvent in vacuo, the residue was recrystallized from heptane to give colorless crystals; yield 615 mg (82%). ^1H NMR δ: 0.34 (s, 6 H, $SiMe_2$), 2.03, 2.23 (br s, 8 H, C_5Me_4, CH_2NMe_2, CH_2Si), 2.19 (s, 6 H, NMe_2), 3.15 (br s, 2 H, CH_2N), 5.44 (t, $^1J_{YH} = 30.4$ Hz, 1 H, YHY). $^{13}C\{^1H\}$ NMR δ: 2.8 ($SiMe_2$), 11.0, 13.0 (C_5Me_4), 16.7 (CH_2Si), 45.1, 61.4 ($NCH_2CH_2NMe_2$), 47.0 (NMe_2), 114.5, 116.6 (ring C, C_5Me_4), 125.9 (ring C attached to CH_2). ^1H NMR (THF-d_8) δ: 0.03 (s, 6 H, $SiMe_2$), 1.77 (s, 2 H, CH_2Si), 1.96, 2.02 (s, 6 H, C_5Me_4), 2.39 (s, 6 H, NMe_2), 2.57, 3.06 (t, 2 H, $^3J_{HH} = 5.2$ Hz, $NCH_2CH_2NMe_2$), 5.12 (t, $^1J_{YH} = 27.6$ Hz, 1 H, YHY). $^{13}C\{^1H\}$ NMR (THF-d_8) δ: 2.6 ($SiMe_2$), 12.6, 13.2 (C_5Me_4), 16.5 (CH_2Si), 45.6, 66.8 (NCH_2CH_2N), 48.6 (NMe_2), 113.4, 114.7 (C_5Me_4), 125.3 (ring C attached to CH_2). ^1H NMR (toluene-d_8, 80 °C): 0.25 (s, 6 H, $SiMe_2$), 2.08, 2.16 (s, 10 H, $C_5Me_4 + NMe_2 + CH_2Si$), 2.58, 3.18 (br s, 2 H, NCH_2CH_2N), 5.45 (t, $^1J_{YH} = 30.4$ Hz, 1 H, YHY). ^1H NMR (toluene-d_8, −60 °C): *major isomer* δ: 0.26, 0.39 (s, 3 H, $SiMe_2$), 1.64, 2.92, 3.07, 3.37 (m, 1 H, NCH_2CH_2N), 1.77, 1.91, 2.03, 2.10, 2.38, 2.40 (s, 3 H, C_5Me_4, NMe_2), 2.13, 2.22 (d, $^2J_{HH} = 21.6$ Hz, 1 H, CH_2Si), 5.43 (t, $^1J_{YH} = 30.4$ Hz, 1 H, YHY); *minor isomer* δ: 0.44, 0.56 (s, 1.2 H, $SiMe_2$), 1.80, 1.84, 2.07, 2.34, 2.55 (s, 1.2 H, C_5Me_4, NMe_2), 2.80, 3.11, 3.29 (m, 0.4 H, NCH_2CH_2N), 5.08 (t, $^1J_{YH} = 33.6$ Hz, 0.2 H, YHY), 5.38 (t, $^1J_{YH} = 25.2$ Hz, 0.2 H, YHY); resonances for the CH_2Si, C_5Me_4, and NCH_2CH_2N are covered by signals of the major isomer. $^{89}Y\{^1H\}$ NMR (toluene-d_8) δ: 271.4. Anal. Calcd for $C_{32}H_{62}N_4Si_2Y_2$: C, 52.16; H, 8.48; N, 7.60. Found: C, 52.01; H, 8.36; N, 7.58.

$[Y(\eta^5{:}\eta^1{:}\eta^1\text{-}C_5Me_4CH_2SiMe_2NCH_2CH_2NMe_2)\{CH(CH_3)Ph\}]$ (4). A solution of complex **3** (150 mg, 0.2 mmol) in hexane (5 mL) was treated with styrene (50 μL, 0.4 mmol) and the mixture heated to 60 °C for 3 h. The reaction mixture was cooled to room temperature, and the volume of the solvent was reduced in vacuo to 2 mL. Cooling overnight at −30 °C afforded yellow crystals (101 mg), yield 52%. ^1H NMR (toluene-d_8) δ: 0.25, 0.30 (s, 3 H, $SiMe_2$), 1.59, 2.45, 2.89, 3.04 (m, 1 H, NCH_2CH_2N), 1.64 (d, $^3J_{HH} = 5.6$ Hz, 3 H, $CHC\mathit{H}_3$), 1.86, 1.96, 2.19, 2.21 (s, 3 H, C_5Me_4), 2.05, 2.14 (d, $^2J_{HH} = 14.6$ Hz, 1 H, CH_2Si), 6.33 (br t, $^3J_{HH} = 7.0$ Hz, 3 H, 2-, 4-, 6-C_6H_5), 6.94 (t, $^3J_{HH} = 7.6$ Hz, 2 H, 3-, 5-C_6H_5). $^{13}C\{^1H\}$ NMR (toluene-d_8) δ: 0.6, 3.8 ($SiMe_2$), 10.0, 11.8, 12.1, 12.5 (C_5Me_4), 14.1 ($CH\mathit{C}H_3$), 16.5 (CH_2Si), 43.1, 60.1 (NCH_2CH_2N), 44.3 (br s, NMe_2), 52.8 (d, $^1J_{YC} = 19.6$ Hz, $\mathit{C}HCH_3$), 113.3, 114.5 (ring C), 115.5 (2-C_6H_5, 4-C_6H_5, 6-C_6H_5), 125.0 (ring C attached to CH_2Si), 129.2 (3-C_6H_5, 5-C_6H_5), 155.5 (1-C_6H_5). ^1H NMR (toluene-d_8, −60 °C) δ: 0.39, 0.47 (s, 3 H, $SiMe_2$), 0.79, 1.49 (s, 3 H, NMe_2), 1.35, 2.41, 2.86, 3.04 (m, 1 H, NCH_2CH_2N), 1.81 (d, $^3J_{HH} = 5.6$ Hz, 3 H, $CHC\mathit{H}_3$), 1.88, 1.99, 2.27, 2.34 (s, 3 H, C_5Me_4), 2.18, 2.26 (d, $^2J_{HH} = 14.6$ Hz, 1 H, CH_2Si), 5.98 (d, $^3J_{HH} = 7.6$ Hz, 1 H, 2-C_6H_5), 6.42 (br t, $^3J_{HH} = 7.2$ Hz, 1 H, 4-C_6H_5), 6.73 (d, $^3J_{HH} = 8.0$ Hz, 1 H, 6-C_6H_5), 6.86 (t, $^3J_{HH} = 7.6$ Hz, 1 H, 3-C_6H_5), 7.08 (t, $^3J_{HH} = 7.6$ Hz, 1 H, 5-C_6H_5). ^{13}C NMR (toluene-d_8, −60 °C) δ: 1.3, 4.5 (q, $SiMe_2$), 10.1, 12.1, 12.5, 12.9 (q, C_5Me_4), 14.6 (q, $^1J_{CH} = 123.8$ Hz, $CH\mathit{C}H_3$), 16.2 (t, CH_2Si), 43.0, 58.8 (t, NCH_2CH_2N), 43.1, 44.6 (q, NMe_2), 52.3 (dd, $^1J_{YC} = 19.2$ Hz, $^1J_{CH} = 134.9$ Hz, $\mathit{C}HCH_3$), 110.8 (d, $^1J_{CH} = 144.4$ Hz, 2-C_6H_5), 115.7 (dt, $^1J_{CH} = 153.7$ Hz, 4-C_6H_5), 120.9 (dt, $^1J_{CH} = 154.3$ Hz, 6-C_6H_5), 133.2 (dd, $^1J_{CH} = 155.6$ Hz, 3-C_6H_5), 133.8 (dd, $^1J_{CH} = 155.6$ Hz, 5-C_6H_5), 155.1 (s, 1-C_6H_5). Anal. Calcd

---

(13) Eberle, T. Doctoral Thesis, University of Mainz, Germany, 1999.

for $C_{24}H_{39}N_2SiY$: C, 61.00; H, 8.32; N, 5.93. Found: C, 61.05; H, 8.34; N, 5.81.

Crystal Structure Analysis of 2, 3, and 4. Relevant crystallographic data for **2**, **3**, and **4** are summarized in Table 1. Single crystals suitable for X-ray crystal structure analysis were obtained by cooling concentrated pentane and heptane solutions of **2** and **3**, respectively, to −30 °C. Single crystals of **4** were obtained by recrystallization with toluene at −30 °C. The data collections were carried out with a Bruker AXS diffractometer; the data reduction as well as the correction for absorption was carried out using the program system SMART.[14] The structures were solved by Patterson and difference Fourier syntheses (SHELXS-86).[15] All non-hydrogen atoms were refined with anisotropic thermal parameters. For compound **2**, split positions were introduced due to disorder within the THF ligand. For compound **3**, split positions were introduced to resolve disorder within a CH_2NMe_2 unit. The hydrogen atoms of **2**, **3**, and **4** were included in calculated positions with isotropic thermal parameters. The hydrogen atoms of the methyl groups were allowed for torsional refinement. The hydrogen atoms of the Y_2H_2 core in **3** were localized in a Fourier difference map and were refined in their positions with isotropic thermal parameters. From the measured reflections, all independent reflections were used, and the parameters were refined by full-matrix least-squares against all F_o^2 data (SHELXL-97)[16] and refined with anisotropic thermal parameters. Compound **2** crystallized in the noncentrosymmetric space group $P2_12_12_1$. The structure solution gave an absolute structure parameter of −0.024(3), indicating the correct assignment of the chirality.[17] For the graphical representation the program ORTEP-III was used as implemented in the program system WINGX.[18]

Acknowledgment. Generous financial support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

Supporting Information Available: Tables of all crystal data and refinement parameters, atomic parameters including hydrogen atoms, thermal parameters, and bond lengths and angles for **2**, **3**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0303707

---

[14] *ASTRO*, *SAINT*, and *SADABS*, Data Collection and Processing Software for the SMART System; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1996.

[15] Sheldrick, G. M. *SHELXS-86*, *Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1986.

[16] Sheldrick, G. M. *SHELXL-97*, *Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

[17] Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876.

[18] Farrugia, L. J. WinGX−Version 1.64.02, An Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single-crystal X-Ray Diffraction Data. *J. Appl. Crystallogr.* **1999**, *32*, 837.