

Table IV. Final Fractional Coordinates ($\times 10^5$ for Pt and I, $\times 10^4$ for Others) with Estimated Standard Deviations in Parentheses

atom	x	y	z
Me ₂ Pt(pz ₂ CH ₂)I ₂ (1)			
Pt	16712 (5)	25000	832 (3)
I(1)	30046 (12)	25000	18774 (6)
I(2)	840 (11)	25000	-16285 (6)
N(1)	3364 (8)	1384 (6)	-530 (5)
N(2)	4939 (9)	1572 (6)	-674 (6)
C(1)	96 (11)	1379 (6)	600 (7)
C(2)	5670 (17)	2500	-264 (11)
C(3)	5640 (13)	835 (9)	-1199 (7)
C(4)	4464 (18)	134 (7)	-1394 (8)
C(5)	3109 (14)	520 (7)	-968 (7)
Me ₂ Pt[(Me ₂ pz) ₂ CH ₂]I ₂ (2)			
Pt	11279 (4)	25000	23304 (3)
I(1)	35340 (9)	25000	4249 (8)
I(2)	-10304 (13)	25000	44310 (7)
N(1)	-725 (6)	1445 (3)	962 (4)
N(2)	-1658 (6)	1669 (3)	-489 (4)
C(1)	2815 (9)	1511 (5)	3612 (7)
C(2)	-1231 (11)	2500	-1244 (8)
C(3)	-2862 (7)	999 (4)	-1067 (6)
C(4)	-2686 (8)	303 (4)	46 (7)
C(5)	-1359 (8)	604 (4)	1284 (6)
C(6)	-4085 (8)	1050 (5)	-2635 (6)
C(7)	-789 (9)	107 (5)	2798 (7)

revealed all hydrogen atoms; these were allowed for (in geometrically idealized positions with C-H = 0.95 Å and an overall U_{iso} was refined in each case) in subsequent calculations. For 1, refinement converged at $R = 0.034$ and $R_w = (\sum \omega \Delta^2 / \sum \omega F_o^2)^{1/2}$

= 0.043; for 2, the final R and R_w values were 0.036 and 0.038 respectively. In the least-squares calculations, scattering factors for Pt, I, N, and C were taken from ref 29; those for hydrogen were from ref 30, and allowance was made for anomalous dispersion.³¹ Weights in the refinement were based on counting statistics [$\omega = 1/\sigma^2(F)$], and final difference syntheses were devoid of any significant features.

Final fractional coordinates for 1 and 2 are in Table IV. Thermal parameters, calculated hydrogen coordinates, and structure factor listings are available as supplementary material.

Acknowledgment. H.C.C. and G.F. are grateful to NSERC Canada for grants in aid of research.

Registry No. 1, 84987-14-4; 2, 84987-15-5; Me₂Pt[(Me₂pz)₂CH₂](NO₃)₂, 84987-16-6; Me₂P(N \overline{N} N)I₂ (N \overline{N} N = bis-(2-pyridyl)methane), 84987-17-7; Me₂Pt(N \overline{N} N)I₂ (N \overline{N} N = 2,2'-bipyridyl), 85027-40-3; Me₂Pt(N \overline{N} N)I₂ (N \overline{N} N = 2,2-bis(1-pyrazolyl)propane), 84987-18-8.

Supplementary Material Available: Tables of thermal parameters, calculated hydrogen coordinates, and structure factors (9 pages). Ordering information is given on any current masthead page.

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(α -Haloethyl)silanes Optically Active at Carbon and at Silicon. Synthesis and Absolute Configuration

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Received December 15, 1982

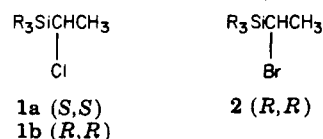
A synthetic sequence that is stereospecific at silicon was utilized to prepare 1-naphthylphenylmethyl(1-chloroethyl)silane, 1, and 1-naphthylphenylmethyl(1-bromoethyl)silane, 2, as a mixture of diastereomers. Crystallization from hexane gave 1 and 2 as pure diastereomers, the structures of which were determined by X-ray analysis.

Introduction

The interest in α -halo organosilanes has come from the synthetic organic chemists due to their being precursors to α -metalated organosilanes, useful in the Peterson olefination reaction² and more recently as synthons for aldehydes or ketones as shown by the Magnus group.³ In addition the mechanistic organosilicon chemists have studied the intramolecular rearrangements in these systems under a variety of conditions in order to better understand these processes, which, although they have syn-

thetic potential, have not been exploited in this way as yet.

We have recently become interested in the possibility of utilizing carbofunctional organosilanes optically active at silicon in order to better understand the mechanistic routes of certain reactions of carbofunctional organosilanes and to be able to investigate the potential of a chiral silyl group in asymmetric induction. We wish to report herein on the preparation of (*S*)-Si(*S*)-1-naphthylphenylmethyl-(α -chloroethyl)silane, 1a (*R*)-Si(*R*)-1-naphthylphenylmethyl-(α -chloroethyl)silane, 1b, and (*R*)-Si(*R*)-1-naphthylphenylmethyl(α -bromoethyl)silane, 2, and their absolute configurations.



R₃Si = 1-NpPhMeSi

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Table I. Some Key NMR Data (δ)

entry	compd	α -CH	β -CH ₃	SiCH ₃	α -C	β -C	SiCH ₃	²⁹ Si
1	4	5.88		0.93	61.8		-5.1	-4.43
2	10	5.94, 5.91		0.97	48.8, 48.7		-4.6	-4.49, -4.53
3	12	5.85		0.98	33.5		-4.2	-4.40
4	6	3.25		0.80	29.7		-4.0	
5	5		2.2	0.96	34.9	80.6	-3.4	
6	11		2.4	0.98	36.3	70.7, 70.6	-2.9	-3.2, -3.4
7	13		2.7	1.0		58.5	-2.5	
8	1 ^a	4.20 4.13	1.62 1.45	0.85 0.82	20.77	43.85 43.68	-4.96	-5.95 -6.20
9	1 ^b	4.20	1.46	0.82	20.82	43.85	-4.96	-5.95
10	2 ^a	4.14 4.10	1.79 1.64	0.87 0.83	21.4	34.5 34.4	-4.30	-5.9 -6.2
11	2 ^c	4.14	1.63	0.85	21.4	34.4	-4.30	-5.88

^a An equimolar mixture of diastereomers. ^b Only the *S,S* stereoisomer. ^c Only the *R,R* stereoisomer.

yielding only return of starting material. Likewise it proved to be inert to freshly sublimed aluminum chloride in dichloromethane at reflux and only reacted slightly with this reagent in refluxing cyclohexane.¹¹ Attempts to form the Grignard reagent and quench it with a variety of electrophiles (Me₃SiCl, CH₃I, D₂O, PhCHO) all gave 8 as the only observed product. In a like manner, treatment of 1a sequentially with *sec*-butyllithium and trimethylchlorosilane gave only 8, metal-chlorine exchange apparently being preferred over the metal-hydrogen exchange observed by Magnus and co-workers with the trimethylsilyl system.³

Discussion

Table I shows some of the key NMR signals for several of the compounds prepared. Of particular interest is that, where mixtures of diastereomers exist, two signals are observed in at least some of the key nuclei. For example, 10 (entry 2) shows two resonances for the α -hydrogen, two for the α -carbon, and two resonances for the silicon nucleus, although only one silicon methyl is seen in both the ¹H and the ¹³C spectra. This is also the case for its methyl derivative 11. The diastereomeric mixtures of 5 or 13 were readily discernible from either the C-CH₃ doublet or the silyl methyl singlet. The CH₃ doublets at ca. 1.5 ppm are especially well separated in these systems. In addition the ²⁹Si or ¹³C NMR spectra can be used to check homogeneity in such systems as seen from the data.

The fact that no asymmetric induction was seen in the reduction of the dihalides 4 and 12 probably reflects the effect of the rather long C-Si bonds and the small steric difference between the α -naphthyl and phenyl groups. However, it was gratifying to note that it is indeed possible to use an optically active silicon to create and separate diastereomers optically active at carbon as well. We are aware of only one other related example.¹² This observation could be important in systems wherein the silicon-carbon bond can be stereoselectively cleaved as well as in mechanistic studies of carbonyl silanes.

Structure Description. Although chemical transformations of the carbon side chain necessarily involving retention at silicon could be employed to assure the stereochemistry at silicon, this would not aid us in the de-

Table II. Final Fractional Coordinates ($\times 10^4$) with Estimated Standard Deviations for C₁₅H₁₉BrSi

atom	x	y	z
Br	-7364 (1)	-699.5 (0.6)	-4340.3 (0.4)
Si	-6491 (3)	1162 (2)	-3223 (1)
C(1)	-6691 (9)	-495 (5)	-3362 (3)
C(2)	-8035 (10)	-1105 (6)	-2915 (4)
C(3)	-8486 (10)	1895 (6)	-3500 (4)
C(4)	-6199 (8)	1448 (5)	-2274 (3)
C(5)	-4696 (8)	1129 (5)	-1893 (3)
C(6)	-3231 (8)	562 (6)	-2185 (3)
C(7)	-1822 (9)	269 (6)	-1814 (4)
C(8)	-1750 (10)	525 (6)	-1101 (4)
C(9)	-3099 (9)	1074 (6)	-808 (3)
C(10)	-4603 (9)	1387 (6)	-1178 (3)
C(11)	-5990 (10)	1987 (6)	-869 (3)
C(12)	-7400 (11)	2274 (6)	-1232 (3)
C(13)	-7489 (10)	2010 (5)	-1935 (3)
C(14)	-4642 (9)	1758 (6)	-3731 (3)
C(15)	-4382 (9)	2996 (6)	-3758 (3)
C(16)	-3111 (9)	3483 (6)	-4159 (3)
C(17)	-2044 (8)	2795 (6)	-4547 (3)
C(18)	-2255 (9)	1591 (6)	-4533 (3)
C(19)	-3514 (9)	1083 (5)	-4140 (3)

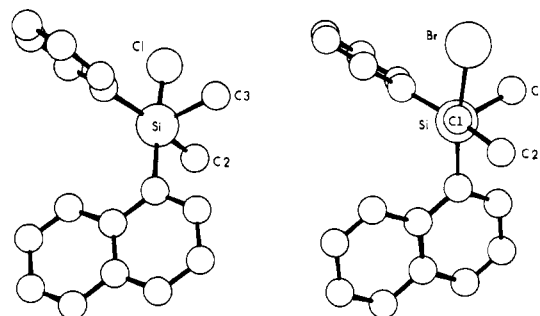


Figure 2. Conformations of 1a and 2 looking down the Si-C(halogen) bond. 1a has the opposite absolute configuration from 2; hence 2 was shown with the carbon in front of Si in order to emphasize the conformational similarities.

termination of the stereochemistry at carbon. We, therefore, resorted to an X-ray diffraction analysis of the pure single diastereomers of 1a and 2.

The structure determined for 2 is shown in Figure 1, and heavy-atom coordinates are in Table II. The molecule exists in the crystal in the conformation in which the two methyl groups are gauche, with the torsion angle C(2)-C(1)-Si-C(3) of -66.6° . The aromatic ring systems are essentially eclipsed with other bonds; pertinent torsion angles being C(1)-Si-C(14)-C(19) = -2.1° and C(3)-Si-C(4)-C(13) = 6.3° . This conformation is also found in the isomorphous (but enantiomeric) chloro analogue¹³ in which

(10) Chloromethyltrimethylsilane has been shown to react with nucleophiles: Ambash, S.; Chin, S. K.; Peterson, P. E.; Queen, J. *Synthesis* 1980, 318.

(11) For a review of reactions of this type see: O'Brien, D. H.; Hairston, T. *J. Organomet. Chem. Rev. A* 1971, 7, 95.

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Table III. Bond Distances (Å) in $C_{19}H_{19}BrSi$

Si-C(1)	1.904 (6)	C(8)-C(9)	1.338 (10)
Si-C(3)	1.828 (7)	C(9)-C(10)	1.410 (9)
Si-C(4)	1.895 (7)	C(10)-C(11)	1.402 (10)
Si-C(14)	1.861 (6)	C(11)-C(12)	1.337 (10)
C(1)-Br	1.992 (6)	C(12)-C(13)	1.406 (9)
C(1)-C(2)	1.519 (9)	C(14)-C(15)	1.418 (9)
C(4)-C(5)	1.422 (8)	C(15)-C(16)	1.370 (9)
C(4)-C(13)	1.358 (8)	C(16)-C(17)	1.361 (9)
C(5)-C(6)	1.418 (8)	C(17)-C(18)	1.375 (9)
C(5)-C(10)	1.427 (8)	C(18)-C(19)	1.363 (9)
C(6)-C(7)	1.346 (8)	C(19)-C(14)	1.406 (9)
C(7)-C(8)	1.423 (10)		

the indicated torsion angles are 65.2°, 3.2°, and -5.7°, respectively. The conformational similarities are emphasized in the views down the C(1)-Si bond of the chloro and bromo analogues shown in Figure 2.

To our knowledge, five other crystal structures containing the α -naphthylphenylmethylsilyl group have been determined. These include the aforementioned 1-chloroethyl derivative, the hydride,¹⁴ the fluoride,¹⁴ the benzyl *p*-bromobenzoate,¹⁵ and a Pt complex¹⁶ in which α -naphthylphenylmethylsilyl serves as a ligand. The distances and angles (Tables III and IV) within the silyl moiety of the present determination fall within the limits defined by the earlier studies. The Si-C(3)(methyl) distance of 1.861 (6) Å compares with the range 1.845-1.906 Å, the SiC(4)(naphthyl) distance of 1.895 (7) Å with the range 1.863-1.905 Å, and the Si-C(14)(phenyl) distance of 1.828 (7) Å with the range 1.827-1.863 Å. The Si-C(1)(bromoethyl) distance of 1.904 (6) Å is identical with that found in the chloroethyl compound, 1.900 (3) Å.

The phenyl group is strictly planar, with a maximum deviation from the best plane of 0.002 (6) Å. The Si atom, however, lies slightly (0.118 (2) Å) out of this plane. Similar deviations, in the range 0.074-0.15 Å, are observed in all of the previously studied derivatives. The mean bond distance within the phenyl group is 1.382 Å, and interior angles are in the range 115.5 (6)-122.0 (6) Å.

The α -naphthyl group exhibits the pattern of bond lengths expected from resonance contributors¹⁷ and observed for naphthalene¹⁸ ranging from 1.337 (10) Å (C(11)-C(12)) to 1.427 (8) Å (C(5)-C(10)). The deviations from planarity of the α -naphthyl group are less pronounced than in previously studied analogues; the maximum deviation is only 0.016 (6) Å (C(10)), and the average deviation is 0.008 (5) Å. The Si atom lies in the plane (deviation 0.005 (2) Å). No unusually short intermolecular contacts are noted.

Experimental Section

All reactions were carried out in standard apparatus, flame-dried prior to use. Solvents were dried and distilled prior to use. ¹H, ¹³C, and ²⁹Si NMR analyses were carried out on a JEOLCO FX90Q spectrometer in CCl₄ or CDCl₃ solutions with internal Me₄Si standard. *n*-Butyllithium and *sec*-butyllithium were purchased from Foote Mineral Co. and titrated prior to use. (*R*)-(+)-Silane **3** (mp 63-64 °C; [α]_D²⁵ 33.16° (c 12.45, cyclohexane) and (*S*)-(-)-chlorosilane **9** (oil; [α]_D²⁵ -5.9° (c 2.9, cyclohexane) were prepared according to Sommer et al.⁴ Tri-*n*-butyltin was prepared

by the method of Van Der Kerk.¹⁹

(*S*)-(+)-(Dichloromethyl)-1-naphthylphenylmethylsilane (**4**). A 1-L flask equipped with condenser and magnetic stirring was charged with 40 g (0.161 mol) of (*R*)-(+)-**3**, 0.4 g of 18-crown-6, 89.5 g (0.483 mol) of sodium trichloroacetate, and 700 mL of toluene. The reaction mixture was refluxed for 6 h, cooled, filtered through Celite, washed with water, and dried over Na₂SO₄. The solvent was removed at reduced pressure and the dark liquid residue, which showed a clean ¹H NMR spectrum, flash chromatographed eluting with hexane to give 44.8 g (84%) of **4**: [α]_D²⁵ +23.8° (c 2.08, pentane) (lit.⁵ [α]_D²⁵ +22.6° (c 2.0, pentane)); ¹H NMR δ 8.02-6.90 (12 H, m), 5.8, (1 H, s), 0.93 (3 H, s); ¹³C NMR δ 136.8, 135.9, 135.3, 131.3, 130.4, 129.8, 129.3, 128.0, 126.2, 125.7, 125.1, 61.8, -5.1; ²⁹Si NMR δ -4.4.

(*S*)-(+)-(Chloromethyl)-1-naphthylphenylmethylsilane (**6**). A standard apparatus was charged with 2 g (6 mmol) of **4**, 0.3 g of AIBN, and 10 mL of dry hexane. To this was added 3.2 mL (12 mmol) of tri-*n*-butyltin hydride. The reaction mixture was stirred for 24 h, the solvent removed, and the tri-*n*-butyltin chloride distilled at reduced pressure. The residue was subjected to moderate-pressure liquid chromatography (MPLC) eluting with hexane to give 0.72 g (50%) of **6**: mp 57-57.5 °C; [α]_D²⁵ +6.98° (c 2.17, hexane); ¹H NMR δ 7.85-6.97 (12 H, m), 3.25 (2 H, s), 0.80 (3 H, s); ¹³C NMR δ 136.9, 135.3, 135.0, 134.5, 133.5, 131.8, 130.9, 129.9, 128.1, 125.9, 125.5, 125.1, 29.7, -4.0. Anal. Calcd for C₁₉H₁₇ClSi: C, 72.82; H, 5.77. Found: C, 72.62; H, 5.85.

(*S*)-(+)-(α,α -Dichloroethyl)-1-naphthylphenylmethylsilane (**5**). Following the procedure of Rosario and Larson,⁷ a 250-mL standard flask was charged with 1.7 g (19 mmol) of diisopropylamine and 50 mL of THF. When the mixture was cooled to 0 °C, 15.8 mL of a 1.2 M *n*-butyllithium in hexane solution was added, the mixture was then cooled to -78 °C, and 6 g (18 mmol) of **4** in 20 mL of THF was added followed by stirring for 1.5 h, after which time 7.6 g (54 mmol) of iodomethane was added and the reaction stirred at -78 °C or 1 h and allowed to reach room temperature. Hydrolysis was achieved by the addition of 20 mL of 1.5 N HCl, the layers were separated, the aqueous layer was extracted with ether (2 \times 15 mL), and the combined organic layers were dried over MgSO₄. After solvent removal the residue was chromatographed on silica gel eluting with hexane to give 4.6 g (75%) of **5**: mp 63-64 °C; [α]_D²⁵ +8.4° (c 4.05, cyclohexane); ¹H NMR δ 8.5-7.1 (12 H, m), 2.2 (3 H, s), 0.96 (3 H, s); ¹³C NMR δ 136.9, 135.3, 133.7, 131.3, 130.1, 129.4, 129.1, 128.7, 127.9, 125.7, 125.4, 124.8, 80.6, 34.9, -3.4. Anal. Calcd for C₁₉H₁₈Cl₂Si: C, 66.08; H, 5.25. Found: C, 66.12; H, 5.27.

(*S*)-Si(*S*)-(+)-(α -Chloroethyl)-1-naphthylphenylmethylsilane (**1a**). A standard apparatus was charged with 4 g (11.6 mmol) of **5**, 10 mL of dry benzene, and 0.1 g of AIBN. To this was added 3.5 g (12 mmol) of tri-*n*-butyltin hydride, and the reaction mixture was stirred for 24 h. After workup and distillation of tri-*n*-butyltin chloride at reduced pressure, the residue was chromatographed on silica gel eluting with hexane to give 2.78 g (77%) of **1** as a mixture of diastereomers: ¹H NMR δ 7.94-7.18 (12 H, m), 4.20 and 4.13 (1 H, q, *J* = 8 Hz), 1.62 and 1.45 (3 H, d, *J* = 8 Hz), 0.85 and 0.82 (3 H, s); ¹³C NMR δ 135.7, 135.5, 135.1, 135.0, 130.8, 129.7, 129.1, 128.5, 128.4, 128.0, 125.9, 125.8, 125.4, 125.1, 43.68, 43.85, 20.77, -4.96; ²⁹Si NMR -5.95, -6.20. Dissolution of 0.06 g of the mixture in a minimal amount of hot hexane followed by slow cooling to room temperature gave 0.02 g of (*S*)-Si(*S*)-(+)-**1**: mp 96.5-97 °C; [α]_D²⁵ +23.8° (c 2.53, cyclohexane); ¹H NMR δ 7.86-7.20 (12 H, m), 4.19 (1 H, q, *J* = 8 Hz), 1.46 (3 H, d, *J* = 8 Hz), 0.82 (3 H, s); ¹³C NMR 137.2, 135.7, 135.3, 135.1, 133.8, 132.4, 130.9, 129.7, 129.2, 128.4, 128.0, 125.9, 125.6, 125.1, 43.9, 20.8, -4.9; ²⁹Si NMR δ -5.95. Anal. Calcd for C₁₉H₁₉ClSi: C, 73.40; H, 6.16. Found: C, 73.25; H, 6.21.

(*R*)-(-)-(Bromochloromethyl)-1-naphthylphenylmethylsilane (**10**). Following the general procedure of Rambaud and Villieras,⁸ 30 mmol of LDA in THF was prepared in the usual fashion and cooled to -90 °C (ether/N₂(l)) and 4.1 g (32 mmol) of bromochloromethane added followed by stirring for 1.5 h. To the reaction mixture was then added 4.6 g (16 mmol) of **9** in 10 mL of THF. This was stirred at -90 °C for 1.5 h and allowed to reach room temperature. The reaction mixture was hydrolyzed

(13) The full structural details for **1a** will appear elsewhere. Ferguson, G.; Parvez, M.; Pavkovic, S. F. *J. Crystallogr. Spectrosc. Res.*, submitted for publication.

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Table IV. Bond Angles (deg) in C₁₉H₁₅BrSi

C(1)-Si-C(3)	109.8 (3)	C(5)-C(4)-C(13)	117.6 (6)	C(10)-C(11)-C(12)	120.5 (6)
C(1)-Si-C(4)	108.5 (3)	C(4)-C(5)-C(6)	123.5 (6)	C(11)-C(12)-C(13)	120.6 (7)
C(1)-Si-C(14)	110.1 (3)	C(4)-C(5)-C(10)	120.0 (6)	C(12)-C(13)-C(4)	122.4 (8)
C(3)-Si-C(4)	108.1 (3)	C(6)-C(5)-C(10)	116.5 (6)	Si-C(14)-C(15)	119.1 (5)
C(3)-Si-C(14)	108.7 (3)	C(5)-C(6)-C(7)	122.4 (6)	Si-C(14)-C(19)	125.3 (5)
C(4)-Si-C(14)	111.6 (3)	C(6)-C(7)-C(8)	120.5 (7)	C(15)-C(14)-C(19)	115.5 (6)
Si-C(1)-Br	105.8 (3)	C(7)-C(8)-C(9)	118.8 (7)	C(14)-C(15)-C(16)	121.4 (6)
Si-C(1)-C(2)	115.0 (5)	C(8)-C(9)-C(10)	122.3 (6)	C(15)-C(16)-C(17)	121.2 (6)
Br-C(1)-C(2)	108.7 (4)	C(9)-C(10)-C(5)	119.4 (7)	C(16)-C(17)-C(18)	119.1 (6)
Si-C(4)-C(5)	124.4 (5)	C(9)-C(10)-C(11)	121.7 (7)	C(17)-C(18)-C(19)	120.9 (6)
Si-C(4)-C(13)	118.0 (5)	C(5)-C(10)-C(11)	118.9 (7)	C(18)-C(19)-C(14)	122.0 (6)

(1.5 N HCl), extracted with hexane (2 × 20 ml), dried (MgSO₄), and concentrated at reduced pressure. Flash chromatography with hexane gave 4.2 g (70%) of 10 as a 1:1 mixture of diastereomers: mp 60–61 °C; [α]_D²⁵ -15.9 (c 3.02, cyclohexane); ¹H NMR δ 7.94–7.25 (12 H, m), 5.94 and 5.91 (1 H, two s), 0.97 (3 H, s); ¹³C NMR δ 136.8, 135.9, 135.3, 133.0, 131.3, 130.3, 129.3, 128.0, 126.1, 125.7, 125.1, 48.8, 48.7, -4.6; ²⁹Si NMR δ -4.50, -4.53. Anal. Calcd for C₁₉H₁₅BrClSi: C, 57.51; H, 4.29. Found: C, 57.41; H, 4.32.

This diastereomeric mixture defied separation attempts by crystallization from a variety of solvent systems: MPLC, HPLC, and TLC.

(R)-(-)-(α-Bromo-α-chloroethyl)-1-naphthylphenylmethylsilane (11). In a procedure analogous to the preparation of 5, 2 g of 10 was added to a solution of 5.4 mmol of LDA at -78 °C, this stirred for 1.5 h, and 2.3 g (16 mmol) of iodomethane added. Workup and column chromatography gave 1.74 g (82%) of 11: mp 84.5–85 °C; [α]_D²⁵ -3.48° (c 3.08, cyclohexane); ¹H NMR δ 8.5–7.1 (12 H, m), 2.4 (3 H, s), 0.98 (3 H, s); ¹³C NMR δ 136.9, 135.5, 133.7, 131.3, 130.0, 129.4, 129.1, 128.7, 128.6, 128.0, 125.7, 125.4, 124.8, 70.7, 70.6, 36.3, -2.9; ²⁹Si NMR δ -3.2, -3.4. Anal. Calcd for C₁₉H₁₅BrClSi: C, 58.50, H, 4.65. Found: C, 58.74; H, 4.82.

This diastereomeric mixture defied all separation attempts.

(R)-(-)-(Dibromomethyl)-1-naphthylphenylmethylsilane (12). In a procedure analogous to the preparation of 10, 7.6 g (44 mmol) of dibromomethane was added to 42 mmol of LDA at -90 °C followed by stirring at that temperature for 1.5 h, after which time 6 g (21 mmol) of 9 in THF was added. The reaction was stirred at -90 °C for 1.5 h and allowed to warm to room temperature. Workup, solvent removal, and flash chromatography with hexane gave 8 g (90%) of 12 as a colorless oil. Crystallization from hexane gave white crystals of 12: mp 69–70 °C; [α]_D²⁵ -15.4° (c 2.6, pentane) (lit.⁵ [α]_D²⁵ +14.3 (c 5.5, pentane for the S enantiomer)); ¹H NMR δ 8.3–7.1 (12 H, m), 5.85 (1 H, s), 0.98 (3 H, s); ¹³C NMR δ 136.6, 135.7, 135.2, 133.3, 133.0, 131.0, 130.1, 129.1, 128.5, 127.8, 127.7, 126.0, 125.5, 124.9, 33.5, -4.2; ²⁹Si NMR δ -4.4. Anal. Calcd by C₁₉H₁₅Br₂Si: C, 51.45; H, 3.84. Found: C, 51.55, H, 3.89.

(R)-(-)-(α,α-Dibromoethyl)-1-naphthylphenylmethylsilane (13). In a procedure analogous to that for the preparation of 11, 2.1 g (5 mmol) of 12 was added to 5 mmol of LDA in THF at -78 °C and the reaction mixture stirred at that temperature for 1.5 h before the addition of 2.1 g (15 mmol) of iodomethane. Further stirring for 1.5 h at -78 °C and allowing to warm to room temperature followed by workup, solvent removal, and column chromatography with hexane gave 1.9 g (88%) of 13: mp 60–61 °C; [α]_D²⁵ -6.24° (c 6.04, cyclohexane); ¹H NMR δ 8.5–6.99 (12 H, m), 2.65 (3 H, s), 1.0 (3 H, s); ¹³C NMR δ 137.1, 135.5, 133.9, 133.7, 131.2, 130.0, 129.6, 129.2, 128.7, 128.0, 125.6, 125.4, 124.7, 58.5, 37.5, -2.5. Anal. Calcd by C₁₉H₁₅Br₂Si: C, 52.60; H, 4.18. Found: C, 52.62, H, 4.22.

(R)-Si(R)-(-)-(α-Bromoethyl)-1-naphthylphenylmethylsilane (2). Tin Hydride Reduction. In a procedure analogous to the preparation of 1, 0.3 g (0.7 mmol) of 13 in 5 mL of benzene was stirred with 0.2 g (0.75 mmol) of tri-*n*-butyltin hydride and 0.05 g of AIBN. After workup, flash chromatography with hexane gave 0.21 g (84%) of 2 as a 1:1 diastereomeric mixture: ¹H NMR δ 7.94–7.17 (12 H, m), 4.14 and 4.10 (1 H, q, J = 8 Hz), 1.79 and 1.64 (3 H, d, J = 8 Hz), 0.88 and 0.86 (3 H, s); ¹³C NMR δ 137.0, 136.6, 135.4, 135.1, 135.0, 133.6, 130.8, 129.7, 129.1, 128.2, 128.0, 125.9, 125.8, 125.5, 125.1, 34.5, 34.4, 21.4, -4.3; ²⁹Si NMR δ -5.9, -6.2.

A mixture of the diastereomers (0.75 g) was dissolved in a minimum of hot hexane and refrigerated for 5 days to give an initial crop of crystals which after two recrystallizations gave 0.11 g of the *R,R* diastereomer: mp 71–72 °C; [α]_D²⁵ -15.45° (c 3.65 cyclohexane); ¹H NMR δ 7.9–7.14 (12 H, m), 4.14 (1 H, q, J = 8 Hz), 1.63 (3 H, d, J = 8 Hz), 0.85 (3 H, s); ¹³C NMR δ 136.9, 135.6, 135.0, 133.5, 132.1, 130.8, 129.7, 129.1, 128.2, 127.9, 125.9, 125.5, 125.1, 34.4, 21.4, -4.3; ²⁹Si NMR δ -5.9. Anal. Calcd for C₁₉H₁₅BrSi: C, 64.23; H, 5.39. Found: C, 64.04; H, 5.42.

(-)-(α-Bromoethyl)-1-naphthylphenylmethylsilane (2). Metal-Bromine Exchange. Protonation of 13. In a procedure based on that of Brook et al.,²⁰ a 50-mL flask was charged with 0.5 g (1.1 mmol) of 13 and 5 mL of THF. This mixture was cooled to -100 °C (ether-N₂(l)) and treated with 1.3 mL (1.1 mmol) of a 0.8 M *sec*-butyllithium solution in hexane and stirred for 5 min at -100 °C, after which 0.1 g of HBr was added and the reaction mixture allowed to reach room temperature. After workup and solvent removal MPLC with hexane gave 0.14 g (36%) of 2 as a 1:1 diastereomeric mixture.

(+)-(α-Chloroethyl)-1-naphthylphenylmethylsilane (1) from 11. Analogous to the procedure above, 0.31 g (0.8 mmol) of 11 was treated with 1 mL of a 0.8 M *sec*-butyllithium-hexane solution at -100 °C and then with 1.5 N HCl. After workup the crude material showed a 1:1 diastereomeric mixture of 1 (NMR analysis) and an unidentified compound in small amount.

(-)-(α-Chloroethyl)-1-naphthylphenylmethylsilane (1b) from 10. Treatment of 0.9 g (2.4 mmol) of 10 with 3 mL of a 0.8 M *sec*-butyllithium-hexane solution (2.4 mmol) at -100 °C for 5 min followed by the addition of 1.0 g (7.2 mmol) of iodomethane gave after workup, solvent removal and MPLC with hexane 0.5 g (68%) of 1 as a 1:1 mixture of diastereomers by NMR analysis. Crystallization from hexane gave 1b, whose ¹H, ¹³C and ²⁹Si NMR spectra and IR spectrum were identical with those of 1a. This material showed [α]_D²⁵ -18.2.

X-ray Experimental Data. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer equipped with a Mo Kα tube (λ = 0.71073 Å) and a graphite monochromator, using a crystal of dimensions 0.12 × 0.35 × 0.40 mm at 27 °C. The crystal was sealed in a thin-walled glass capillary for protection from humidity. Crystal data: SiC₁₉H₁₅Br; *M*_r = 355.4, orthorhombic space group *P*2₁2₁2₁; *a* = 7.696 (4) Å, *b* = 11.332 (2) Å, *c* = 19.523 (3) Å; *Z* = 4; *d*_{calcd} = 1.386 g cm⁻³; μ(Mo Kα) = 24.50 cm⁻¹. Data were measured by the ω-2θ scan technique at rates varying from 0.38 to 5.0 deg min⁻¹ in order to measure all significant reflections with *I* ≈ 50σ(*I*). Scan rates were determined in a 5.0 deg min⁻¹ prescan, and reflections failing to have *I* > σ(*I*) during the prescan were not subjected to a slow scan. A maximum of 240 s was spent on a single measurement. One octant of data was measured to θ = 25°, and a Friedel-related octant was measured to θ = 20°.

Data reduction included corrections for background, Lorentz, polarization, crystal decay (19% of intensities), and absorption. The absorption corrections were based upon ψ scans of reflections near χ = 90°, and the minimum relative transmission coefficient was 70.80%. Of 2372 unique data measured, 1404 had *I* > 3σ(*I*) and were used in the refinement.

The structure was solved by heavy-atom methods, completed by Fourier methods, and refined by full-matrix least squares on the basis of *F*, with weights *w* = σ⁻²(*F*_o), using the Enraf-Nonius SDP programs.²¹ Observational variances were estimated from

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counting statistics and included a term $(0.025)^2$, where S is the scan count. Non-hydrogen atoms were refined anisotropically; hydrogen atoms were located in difference maps and included as fixed contributions with isotropic $B = 6.0 \text{ \AA}^2$.

Both enantiomorphs were refined independently, and the correct choice is unambiguous. The refinement of the S,S isomer yielded $R = 0.061$, $R_w = 0.075$, and $\text{GOF} = 2.267$ and had 33 reflections for which $\Delta F > 5\sigma(F_o)$. The R,R isomer yielded $R = 0.039$, $R_w = 0.044$, and $\text{GOF} = 1.334$ and had only one such reflection. The improvement in R_w is approximately seven times that necessary to distinguish the correct enantiomer with 99.5% probability of the Hamilton R factor ratio test,²² and thus the R,R absolute configuration is shown to be correct. The maximum residual in a final difference map was 0.56 e \AA^{-3} , associated with the Br position.

Acknowledgment. We wish to thank the NSF for partial support for the purchase of a JEOL FX90Q (UPR)

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and an Enraf-Nonius CAD4 diffractometer (LSU). G.L.L. and S.S. wish to thank the NIH-MBRS program (Grant 8102-10) for financial support and Lucy Torres and Hiram Carrasquillo for repeat preparations of certain starting materials. S. F. Pavkovic and G. Ferguson are thanked for X-ray data on compound **1a** prior to publication.

Registry No. (S)-Si(R)-1, 85067-20-5; (R)-Si(S)-1, 85067-21-6; **1a**, 85082-06-0; **1b**, 85067-10-3; (R)-Si(R)-(-)-2, 85067-12-5; (R)-Si(S)-2, 85067-11-4; (R)-(+)-3, 1025-08-7; (S)-(+)-4, 22368-85-0; (S)-(+)-5, 85067-13-6; (S)-(+)-6, 85067-14-7; 7, 16116-99-7; (S)-8, 32147-43-6; (S)-(-)-9, 960-82-7; (R)-Si(R)-10, 85067-15-8; (R)-Si(S)-10, 85067-18-1; (R)-Si(R)-11, 85067-16-9; (R)-Si(S)-11, 85067-19-2; (R)-(-)-12, 85114-69-8; (R)-(-)-13, 85067-17-0; $\text{Cl}_3\text{C-CO}_2\text{Na}$, 650-51-1; bromochloromethane, 74-97-5; dibromomethane, 74-95-3.

Supplementary Material Available: Complete listings of atomic coordinates and anisotropic thermal parameters, hydrogen atom coordinates, and observed and calculated structure factors (13 pages). Order information is given on any current masthead page.

Conformational Preferences in Transition-Metal Carbenes

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Received November 2, 1982

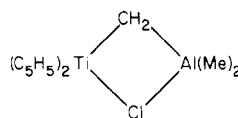
The equilibrium structures and conformational preferences of titanium and zirconium methyldiene complexes have been examined by using ab initio molecular orbital theory. All systems considered prefer planar arrangements. For highly electron-deficient methyldienes, perpendicular forms are 10–20 kcal mol⁻¹ higher in energy; this difference increases with increasing saturation of the metal center. While these barriers to rotation in main-group olefin analogues (which are generally much larger) may be related to π -bond strengths, it is shown that such a relationship is not appropriate for bonds involving transition metals.

Introduction

Transition-metal carbene complexes are known to participate in, or have been implicated in, numerous organometallic reactions.² Tantalum, chromium, molybdenum, and tungsten carbenes have been extensively characterized, as have compounds incorporating double bonds between carbon and many of the later transition metals.³ Transition metal to carbon triple bonds have also been observed.⁴ This situation is in direct contrast to that

for compounds incorporating multiple bonds to heavy main-group elements, few of which are stable. In addition to their potential utility as catalytic agents then, these species are of interest in understanding the chemistry of their main-group analogues.

At present, there is no example of an isolable metal carbene involving a group 4 metal (titanium, zirconium, or hafnium). Adducts with Lewis acids are known, e.g., the Tebbe reagent⁵



These exhibit behavior consistent with that expected for free carbenes, for example, catalysis of olefin metathesis and methylenation. Little is known about the structures and stabilities of the free species.⁶

(1) (a) Chevron Fellow. (b) National Science Foundation Predoctoral Fellow.

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