Structure of a Scandium–(Silicon-Bridged Cp, Cp*) Complex

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Abstract. ({η^5-3-[2-(Di-*tert*-butylphosphino)ethyl]-cyclopentadienyl}(dimethyl)(η^5-tetramethylcyclo-pentadienyl)silane)bis(trimethylsilyl)methylscandium, $C_{33}H_{62}PScSi_3$, $M_r = 595.04$, monoclinic, $P2_1/n$, $a = 14.449$ (3), $b = 12.807$ (5), $c = 20.848$ (5) Å, $\beta = 99.52$ (2)°, $V = 3804.8$ (18) Å^3, $Z = 4$, $D_x = 1.04$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 3.18$ cm^{-1}, $F(000) = 1352$, $T = 296$ K, final $R = 0.108$ for 3100 reflections with $F_o^2 > 0$, 0.054 for 1766 reflections with $F_o^2 > 3\sigma(F_o^2)$. The Sc—C(1) bond [2.253 (8) Å] is insignificantly shorter than the 2.271 (7) Å found in a similar compound; the geometry about C(1) is nearly trigonal, with angles 118.5 (5), 116.0 (5) and 119.4 (6)°.

Introduction. Organoscandium derivatives may serve as model catalysts for the oligomerization or polymerization of olefins. Since these are well defined, single-component catalyst systems, an investigation of their reactions with α-olefins provides a rare opportunity to probe the mechanisms of chain propagation and chain termination in Ziegler–Natta polymerization. The tertiary phosphine adducts [(η^5-$C_5Me_4)_2SiMe_2$]ScH(PMe$_3$) (Piers & Bercaw, 1990; Piers, Shapiro, Bunel & Bercaw, 1990) and {[(η^5-C_5-Me$_4$)SiMe$_2$(η^1-NCMe$_3$)](PMe$_3$)Sc}$_2$(μ-H)$_2$ (Shapiro, Bunel, Schaefer & Bercaw, 1990) are effective catalysts; however, the role of the phosphine in stabilizing their structures and/or inhibiting olefin insertion is not yet clear. The title compound, with a tertiary phosphine ligand linked to a cyclopentadienyl group, was prepared to examine the reactivity of a scandium alkyl with a high effective [PR$_3$] concentration. {(η^5-$C_5Me_4)SiMe_2[\eta^5$-$C_5H_3CH_2CH_2P(CMe_3)_2]$}ScCH(Si-Me$_3$)$_2$ was synthesized by reaction of ScCl$_3$(THF)$_3$ (THF = tetrahydrofuran) with Li$_2${(C_5Me_4)-SiMe$_2$[$C_5H_3CH_2CH_2P(CMe_3)_2$]} in toluene solution, followed by treatment of the isolated {(η^5-$C_5Me_4)SiMe_2[\eta^5$-$C_5H_3CH_2CH_2P(CMe_3)_2]$}Sc-($\mu$-Cl)$_2$Li(THF) with LiCH(SiMe$_3$)$_2$ in toluene. The dilithio salt of the ligand, Li$_2${(C_5Me_4)SiMe$_2$[C_5H_3-CH$_2$CH$_2$P(CMe$_3$)$_2$]}, was prepared by reaction of

Li[$C_5H_3CH_2CH_2P(CMe_3)_2$)] with Me$_2$ClSi(C_5Me_4) in THF solution, followed by deprotonation with two equivalents of *n*-butyllithium in petroleum ether. Suitable crystals of the title compound were obtained by recrystallization from petroleum ether.

Experimental. Crystal: a flat trapezoidal blade 0.64 mm long, 0.37 and 0.22 mm high and 0.10 mm thick; CAD-4 diffractometer, ω scans; 25 reflections with $30 < 2\theta < 35°$ used for unit-cell dimensions; no absorption correction ($\mu = 3.2$ cm^{-1}, $\mu r_{max} = 0.12$); $(\sin\theta/\lambda)_{max} = 0.48$ Å^{-1}; h from -13 to 13, k from -12 to 12, l from 0 to 19; three standard reflections ($\overline{2}1\overline{5}$, $\overline{3}26$ and 430) collected every 10000 s showed a minor linear decay which was corrected for; 8377 reflections collected, 3544 independent, goodness of fit 0.96 for merging 3370 reflections, $R_{int} = 0.058$ for merging 1848 unique reflections with exactly two observations with $F_o^2 > 0$; all 3544 independent reflections used in the solution and refinement of the structure; Sc-atom coordinates found from Patterson map, remaining atoms located in successive structure factor–Fourier calculations; least-squares refinement using F_o^2; H atoms placed at calculated positions or, for methyl groups, at idealized positions based on difference maps calculated in the expected planes; hydrogen parameters were not refined but were adjusted once; coordinates and anisotropic displacement parameters for all non-H atoms plus a scale factor refined; $R = 0.108$ for 3100 reflections with $F_o^2 > 0$ and $R = 0.054$ for 1766 reflections with $F_o^2 > 3\sigma(F_o^2)$, wR (on F_o^2) = 0.006, goodness of fit (S) = 1.34 for 3544 reflections and 343 parameters; $w = 1/\sigma^2(F_o^2)$; variances [$\sigma^2(F_o^2)$] derived from counting statistics plus an additional term, $(0.014I)^2$; variances of the merged data by propagation of error plus another additional term, $(0.0141\bar{I})^2$; ratio of max. shift to e.s.d. in final least-squares cycle 0.05; max. height 0.6 and min. height -0.6 e Å^{-3} in final difference Fourier map, most noise in vicinity of C25, P and C30; atomic scattering factors and dispersion corrections taken from Cromer & Waber (1974); programs used were those of the *CRYRM* crystallographic computing system (Duchamp, 1964)

Table 1. *Final refined parameters for the scandium– (silicon-bridged* Cp, Cp*) *complex* (x, y, z *and* $U_{eq} \times 10^4$)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}(Å²)
Sc	2273 (1)	2119 (1)	503 (1)	469 (4)
C1	2917 (4)	730 (5)	1073 (3)	477 (20)
Si2	3670 (1)	961 (2)	1868 (1)	635 (7)
C2	4649 (5)	8 (7)	2035 (4)	1199 (35)
C3	4239 (5)	2269 (6)	1895 (4)	1003 (28)
C4	3042 (5)	924 (6)	2585 (4)	959 (29)
Si3	2269 (2)	-501 (2)	931 (1)	594 (6)
C5	1251 (5)	-322 (6)	255 (4)	1036 (32)
C6	1755 (5)	-1036 (6)	1620 (4)	993 (30)
C7	2979 (5)	-1596 (5)	679 (4)	998 (31)
Si1	1469 (2)	4188 (2)	-333 (1)	719 (7)
C8	2371 (5)	3193 (6)	-453 (3)	429 (23)
C9	2161 (5)	2160 (7)	-694 (3)	512 (25)
C10	2944 (6)	1542 (6)	-503 (4)	539 (24)
C11	3642 (5)	2131 (8)	-135 (3)	511 (25)
C12	3299 (6)	3152 (6)	-93 (3)	536 (25)
C13	1287 (6)	1786 (6)	-1114 (4)	815 (27)
C14	3099 (6)	423 (6)	-725 (4)	960 (30)
C15	4644 (5)	1770 (7)	113 (4)	1017 (32)
C16	3870 (5)	4056 (7)	214 (4)	941 (29)
C17	1916 (7)	5551 (6)	-222 (5)	1397 (46)
C18	418 (6)	4217 (7)	-962 (4)	1246 (35)
C19	1204 (6)	3626 (6)	432 (4)	630 (28)
C20	663 (5)	2749 (7)	529 (4)	603 (25)
C21	923 (5)	2354 (5)	1164 (4)	457 (22)
C22	1672 (6)	2940 (7)	1465 (4)	647 (25)
C23	1853 (6)	3719 (5)	1037 (5)	664 (31)
C24	383 (5)	1570 (6)	1465 (4)	711 (24)
C25	-261 (5)	2063 (6)	1900 (4)	757 (24)
P	-1090 (2)	1193 (2)	2193 (1)	606 (6)
C26	-2107 (5)	2090 (6)	2225 (4)	567 (23)
C27	-1884 (5)	3143 (6)	2549 (4)	898 (28)
C28	-2838 (5)	1552 (6)	2554 (4)	1074 (33)
C29	-2541 (6)	2289 (6)	1512 (4)	1161 (35)
C30	-482 (5)	857 (6)	3035 (3)	576 (25)
C31	-1039 (6)	43 (7)	3326 (4)	1229 (35)
C32	-318 (6)	1730 (7)	3531 (4)	1141 (35)
C33	463 (6)	400 (8)	2981 (4)	1380 (40)

Table 2. *Selected distances* (Å) *and angles* (°) *for the scandium–(silicon-bridged* Cp, Cp*) *complex*

Sc—C1	2.253 (6)	Si3—C6	1.853 (8)
Sc—Cp*	2.200	Si3—C7	1.865 (8)
Sc—Cp	2.203	Si1—C8	1.867 (7)
C1—Si2	1.848 (6)	Si1—C17	1.863 (9)
C1—Si3	1.833 (6)	Si1—C18	1.836 (9)
Si2—C2	1.857 (8)	Si1—C19	1.847 (9)
Si2—C3	1.864 (8)	C25—P	1.815 (7)
Si2—C4	1.875 (8)	P—C26	1.875 (7)
Si3—C5	1.875 (8)	P—C30	1.880 (8)
Cp*—Sc—Cp	128.1	C7—Si3—C6	104.5 (3)
Sc—C1—Si2	118.5 (3)	C17—Si1—C8	114.9 (4)
Sc—C1—Si3	116.0 (3)	C18—Si1—C8	115.6 (4)
Cp*—Sc—C1	113.4	C19—Si1—C8	95.7 (4)
Cp—Sc—C1	118.1	C18—Si1—C17	107.4 (4)
Si3—C1—Si2	119.4 (3)	C19—Si1—C17	112.0 (4)
C2—Si2—C1	112.4 (3)	C19—Si1—C18	111.1 (4)
C3—Si2—C1	111.3 (3)	C9—C8—Si1	124.5 (5)
C4—Si2—C1	114.9 (3)	C12—C8—Si1	124.8 (6)
C3—Si2—C2	105.4 (4)	P—C25—C24	116.3 (5)
C4—Si2—C2	106.7 (4)	C26—P—C25	101.6 (3)
C4—Si2—C3	105.5 (3)	C30—P—C25	102.9 (3)
C5—Si3—C1	109.4 (3)	C30—P—C26	110.7 (3)
C6—Si3—C1	116.9 (3)	C27—C26—P	116.8 (5)
C7—Si3—C1	113.7 (3)	C28—C26—P	110.3 (5)
C6—Si3—C5	105.2 (3)	C29—C26—P	105.3 (5)
C7—Si3—C5	106.2 (3)		

and *ORTEP* (Johnson, 1971). The H atoms on methyl carbon atom C13 appeared to be disordered in two sets approximately 60° apart and were so modelled, with population 0.5 for each set.

Table 1* lists the atomic parameters and Table 2 lists selected bond distances and angles. The atom-numbering scheme is shown in Fig. 1 and Fig. 2 shows the packing of the molecules.

Discussion. Bond distances and angles in this compound are normal except around C1. The Si—C(H₃) bond distances average 1.861 (13) Å and the P—C(H₃) distances average 1.877 [3] (12) Å, compared to 1.857 and 1.855 Å expected (Allen,
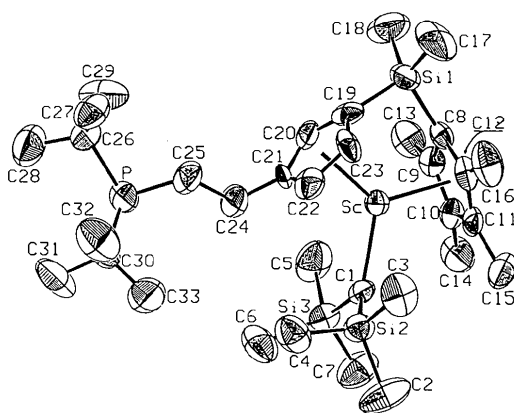
Fig. 1. An *ORTEP* (Johnson, 1971) drawing of the molecule with 50% probability ellipsoids, showing the numbering system; H atoms are not shown.
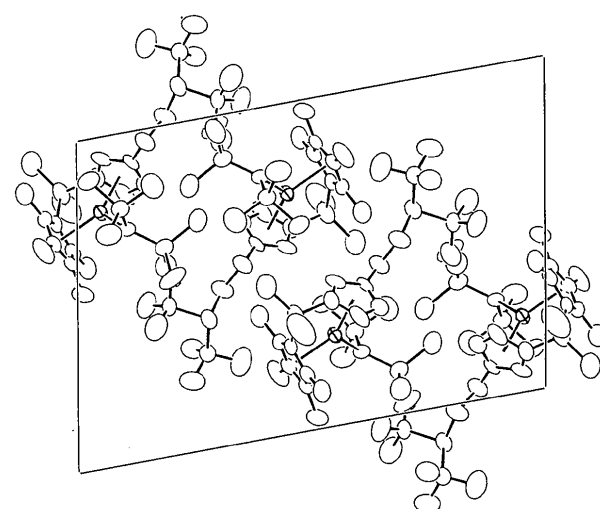

Fig. 2. An *ORTEP* (Johnson, 1971) projection down the *b* axis, showing four molecules (H atoms omitted), with 50% probability ellipsoids and the unit cell outlined.

Kennard, Watson, Brammer, Orpen & Taylor, 1987). C—C distances in the Cp ring average 1.41 (3) Å and in the Cp* ring 1.41 (2) Å and C—C(H₃) distances are 1.515 (14) Å, all within normal ranges. The bonding about scandium is the same as seen in similar compounds (Shapiro, Bercaw, Marsh & Schaefer, 1989; Bunel, Bercaw & Schaefer, 1987): Sc—Cp is 2.20 Å and Sc—Cp* the same. The Sc—C distances to the ring C atoms show the 'tilt' of the rings with respect to the vector, Sc—Cp center, caused by the Si(CH₃)₂ bridge, with Sc—C8 = 2.444 (7), and Sc—C10 and Sc—C11 2.560 (8) Å; in the Cp ring, Sc—C19 is 2.461 (8), Sc—C21 is 2.585 (8) and Sc—C22 is 2.541 (8) Å. The Sc—C1 distance is 2.253 (8) Å, nearly the same as found in a quite similar compound [2.271 (7) Å; Bunel et al. (1987)]. In that compound the coordination about C1 was nearly planar and electron density was found both above and below the plane, where a bonded H atom would be; consequently, in that structure, we placed half-H atoms in both positions. The present compound shows a slightly more tetrahedral C atom, with no residual electron density on the Sc, Si2, Si3 side of C1, so we have considered C1 as a normal C atom, even though the angles about it involving Sc, Si2 and Si3 are 118, 116 and 119°. In a difference map calculated after final refinement, but with H1 omitted from the structure-factor calculation, the largest peak (0.90 e Å⁻³) was 0.95 Å from C1, with Sc—, Si2— and Si3—C—(peak) angles 99, 89 and

107°. Thus we conclude that, although the heavy-atom geometry about C1 is nearly planar, the coordination in the present compound is best described as distorted tetrahedral, with the H atom clearly positioned on one side.

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Structure of N,N-[Bis(2-pyridylmethyl)-γ-aminobutyrato]copper(II) Bromide Methanol Solvate

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Abstract. [Cu(C₁₆H₁₈N₃O₂)]Br.CH₄O, $M_r = 459.83$, orthorhombic, $P2_12_12_1$, $a = 10.452$ (4), $b = 12.197$ (7), $c = 14.984$ (6) Å, $V = 1910$ (3) Å³, $Z = 4$, $D_m = 1.61$ (1), $D_x = 1.599$ g cm⁻³, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 32.37$ cm⁻¹, $F(000) = 932$, $T = 174$ K, $R = 0.0396$, $wR = 0.0419$, 1146 observed reflections [$I > 3\sigma(I)$]. The title compound is a polymeric species in the solid state, with a unit cell consisting of two segments of one-dimensional chains. The ligand, a derivative of γ-aminobutyric acid in which the amino group is substituted with two 2-pyridylmethyl moieties, coordinates to one copper atom through the three nitrogen atoms and to another copper atom through the two carboxylate oxygen atoms. The copper(II) atom has a pseudo square-pyramidal geometry, distorted by a distant sixth interaction to a carboxylate oxygen atom [Cu—O(2), 2.770 (7) Å].

Introduction. The title compound, hereafter referred to as [Cu{GABA(mpy)₂}]Br, is the first to be structurally characterized with this substituted γ-amino-