shape (C_{2v} symmetry). One of the angles at the metal, involving the terminal phosphine groups of pp$_3$, P(1)—Fe—P(2), is opened to 159.7 (2)°. Such a (pp$_3$)M conformation has been observed for metals of the second and third rows of the transition-element series, but is unprecedented for Fe. The carboxylate ligand lies in the equatorial plane. The two O atoms are almost symmetrically coordinated to the Fe^{II} ion in a chelating fashion [the Fe—O(1) and Fe—O(2) distances being 2.080 (7) and 2.057 (7) Å, respectively]. As expected, the O-atom donors have a weaker *trans* influence than the phosphine ligands. In fact, both Fe—P bonds *trans* to the O atoms are slightly shorter than those *trans* to a second P-atom donor. To our knowledge no other structure of an octahedral Fe^{II} complex containing a chelating carboxylate ligand has been reported.

References

BIANCHINI, C., MASI, D., MELI, A., PERUZZINI, M., RAMIREZ, J. A., VACCA, A. & ZANOBINI, F. (1989). *Organometallics*, **8**, 2179–2187.

BIANCHINI, C., PERUZZINI, M. & ZANOBINI, F. (1988). *J. Organomet. Chem.* **354**, 19–22.

MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

WALKER, N. & STUART, D. (1983). *Acta Cryst.* A**39**, 158–166.

cis-1,1-Dimethyl-2,6-diphenyl-1-silacyclohexan-4-one

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Abstract. $C_{19}H_{22}OSi$, $M_r = 294.5$, orthorhombic, $P2_12_12_1$, $a = 8.896$ (3), $b = 11.006$ (3), $c = 17.310$ (6) Å, $V = 1695$ (2) Å^3, $Z = 4$, $D_m = 1.150$, $D_x = 1.154$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 1.00$ cm^{-1}, $F(000) = 632$, $T = 298$ K, $R = 0.058$ for 1263 observed reflections. The molecule assumes a somewhat distorted chair conformation to accommodate the longer Si—C bonds and sp^2 C(4) bond angle.

Experimental. Crystals were grown by slow evaporation from ethanol. A colorless plate, 0.15 × 0.30 × 0.25 mm (density determined by flotation in KI solution), was used for data collection on an Enraf–Nonius CAD-4 diffractometer with Mo $K\alpha$ radiation, using ω–2θ scans of width (0.9 + 0.35tanθ)° and speed 1.4 to 16.5° min^{-1}. 24 reflections with $12 \le \theta \le 16$° were used to refine cell constants; systematic absences: $h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; $00l$, $l = 2n + 1$. No absorption correction was applied. Data were collected to $2\theta_{max} = 53$° for $0 \le h$ ≤ 11, $0 \le k \le 13$, $0 \le l \le 21$. Three standard reflections measured after every 3600 s of X-ray exposure showed no deterioration. Of 2007 unique reflections (no redundant reflections measured), 1263 were observed [$F \ge 4\sigma(F)$]. The structure was solved by direct methods with *SHELX76* (Sheldrick, 1976). Refinement was based on F, minimizing $\sum w(F_o - F_c)^2$, where $w = 4F_o^2[\sigma^2(I) + (0.04F_o^2)^2]^{-1}$. H atoms were placed at calculated positions with fixed isotropic thermal parameters, updated after each cycle of refinement but not refined. Non-H atoms were refined with anisotropic thermal parameters. The polarity of the structure was not clearly established, the reported configuration giving only slightly better agreement than the inverted structure. $R = 0.058$, $wR = 0.057$, $S = 2.00$; (Δ/σ)$_{max}$ in the final cycle was less than 1%; the final difference map maxima were ± 0.25 e Å^{-3}. Atomic scattering factors and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV); all calculations were performed with *SHELX76* (Sheldrick, 1976).

A perspective drawing of the molecule with the numbering scheme is given in Fig. 1 (Johnson, 1976). Final positional parameters for the non-H atoms are

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given in Table 1.* Bond lengths, bond angles and conformational angles about the silacyclohexanone ring are given in Table 2. The substituted silacyclohexane ring system assumes a somewhat distorted chair conformation to accommodate the longer Si—C bond lengths and the more open C(3)—C(4)—C(5) bond angle, relative to those of cyclohexane. Calculation of the ring-puckering coordinates (Cremer & Pople, 1975) gives a total puckering amplitude, Q, of 0.62 Å, $\varphi_2 = 56°$† and $\theta = 7°$, while an ideal cyclohexane chair would have $Q = 0.63$ Å, $\varphi_2 =$ a multiple of 60° and $\theta = 0°$. The phenyl rings show some distortion from ideal geometry. In both phenyl rings, the internal ring angles at the points of attachment to the silacyclohexanone ring and the angles para to them are significantly smaller than the other interior ring angles.

From the relative magnitudes of the trans vs cis coupling constants which had been determined from the solution ^{1}H NMR data, application of Lambert's relationships (Lambert, 1971) had previously allowed the average torsion angle for Si(1)—C(2)—C(3)—C(4) [or Si(1)—C(6)—C(5)—C(4)] to be estimated as 61° (Soderquist & Hassner, 1983). The average of these angles in the present solid-state structure is 57°, a value which is also obtained in the minimum-energy conformation which results from MMX calculations (PCMODEL, 1989) on this compound. These calculations, while giving a somewhat more symmetrical structure, duplicate many of the features of the solid-state structure, including the conformation of the phenyl rings relative to the silacyclohexanone ring. However, in the solid-state structure, the exocyclic Si—C bonds are significantly shorter than the endocyclic Si—C bonds, and this, in conjunction with a distortion from ideal tetrahedral angles about

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55272 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: GR0200]

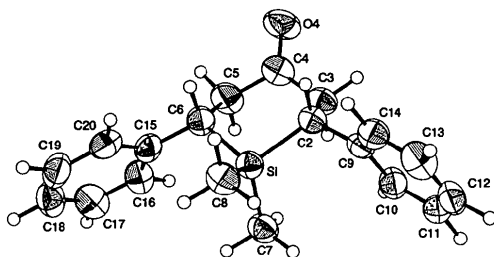† Coordinates input in the order Si—C(2)—C(3)—C(4)—C(5)—C(6).

Fig. 1. Perspective view of the molecule with numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

Table 1. *Positional parameters and equivalent isotropic thermal parameters* (Å^2)

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

	x	y	z	U_{eq}
Si(1)	0.1587 (2)	0.0432 (2)	0.0641 (1)	0.048 (1)
C(2)	0.2517 (6)	0.0468 (5)	0.1636 (3)	0.048 (3)
C(3)	0.1274 (6)	0.0483 (6)	0.2253 (3)	0.057 (3)
C(4)	0.0300 (6)	-0.0611 (6)	0.2221 (3)	0.059 (4)
O(4)	0.0296 (5)	-0.1377 (4)	0.2731 (3)	0.086 (3)
C(5)	-0.0672 (7)	-0.0771 (6)	0.1509 (3)	0.072 (4)
C(6)	0.0211 (6)	-0.0875 (5)	0.0758 (3)	0.056 (4)
C(7)	0.0618 (7)	0.1891 (5)	0.0419 (3)	0.062 (4)
C(8)	0.2992 (6)	0.0058 (5)	-0.0111 (3)	0.062 (4)
C(9)	0.3665 (7)	0.1452 (5)	0.1709 (3)	0.047 (3)
C(10)	0.3306 (7)	0.2658 (6)	0.1862 (3)	0.062 (4)
C(11)	0.4418 (10)	0.3547 (6)	0.1889 (4)	0.074 (5)
C(12)	0.5889 (9)	0.3253 (7)	0.1785 (4)	0.075 (5)
C(13)	0.6255 (7)	0.2068 (8)	0.1622 (3)	0.074 (5)
C(14)	0.5181 (7)	0.1173 (6)	0.1586 (3)	0.057 (4)
C(15)	-0.0735 (7)	-0.1062 (5)	0.0042 (3)	0.057 (4)
C(16)	-0.2107 (7)	-0.0515 (7)	-0.0083 (3)	0.065 (4)
C(17)	-0.2896 (7)	-0.0711 (7)	-0.0765 (4)	0.077 (5)
C(18)	-0.2331 (9)	-0.1432 (7)	-0.1339 (4)	0.077 (5)
C(19)	-0.0981 (10)	-0.1983 (6)	-0.1228 (4)	0.077 (5)
C(20)	-0.0190 (8)	-0.1812 (5)	-0.0546 (4)	0.070 (4)

Table 2. *Bond lengths* (Å), *bond angles* (°) *and selected torsion angles* (°)

Si(1)—C(2)	1.910 (5)	Si(1)—C(6)	1.900 (6)
Si(1)—C(7)	1.863 (6)	Si(1)—C(8)	1.852 (6)
C(2)—C(3)	1.539 (7)	C(2)—C(9)	1.494 (8)
C(3)—C(4)	1.485 (9)	C(4)—O(4)	1.220 (8)
C(4)—C(5)	1.516 (8)	C(6)—C(15)	1.513 (8)
C(5)—C(6)	1.524 (8)	C(9)—C(10)	1.391 (8)
C(9)—C(14)	1.399 (9)	C(10)—C(11)	1.392 (10)
C(11)—C(12)	1.360 (12)	C(13)—C(14)	1.373 (10)
C(12)—C(13)	1.374 (11)	C(15)—C(16)	1.378 (9)
C(15)—C(20)	1.397 (9)	C(16)—C(17)	1.390 (9)
C(17)—C(18)	1.368 (10)	C(19)—C(20)	1.388 (10)
C(18)—C(19)	1.358 (11)		
C(2)—Si(1)—C(6)	101.5 (2)	C(2)—Si(1)—C(7)	111.6 (2)
C(2)—Si(1)—C(8)	110.3 (2)	C(6)—Si(1)—C(7)	112.1 (3)
C(6)—Si(1)—C(8)	110.0 (3)	C(7)—Si(1)—C(8)	111.0 (3)
Si(1)—C(2)—C(3)	108.4 (3)	Si(1)—C(2)—C(9)	112.8 (4)
C(3)—C(2)—C(9)	115.2 (5)	C(2)—C(3)—C(4)	112.6 (5)
C(3)—C(4)—O(4)	122.3 (5)	C(3)—C(4)—C(5)	117.2 (5)
O(4)—C(4)—C(5)	120.4 (6)	C(4)—C(5)—C(6)	114.1 (5)
Si(1)—C(6)—C(5)	111.5 (4)	Si(1)—C(6)—C(15)	111.9 (4)
C(5)—C(6)—C(15)	115.0 (5)	C(2)—C(9)—C(10)	123.4 (5)
C(2)—C(9)—C(14)	119.2 (5)	C(10)—C(9)—C(14)	117.4 (5)
C(9)—C(10)—C(11)	120.9 (6)	C(10)—C(11)—C(12)	120.8 (6)
C(11)—C(12)—C(13)	118.7 (7)	C(12)—C(13)—C(14)	121.7 (6)
C(9)—C(14)—C(13)	120.5 (6)	C(6)—C(15)—C(16)	124.2 (5)
C(6)—C(15)—C(20)	118.9 (6)	C(16)—C(15)—C(20)	116.8 (6)
C(15)—C(16)—C(17)	120.9 (6)	C(16)—C(17)—C(18)	121.4 (6)
C(17)—C(18)—C(19)	118.8 (7)	C(18)—C(19)—C(20)	120.5 (7)
C(15)—C(20)—C(19)	121.6 (6)		
Si(1)—C(2)—C(3)—C(4)	61.0 (5)	Si(1)—C(6)—C(5)—C(4)	-52.4 (6)
C(2)—Si(1)—C(6)—C(5)	47.2 (4)	C(2)—C(3)—C(4)—C(5)	-66.1 (7)
C(3)—C(2)—Si(1)—C(6)	-50.5 (4)	C(3)—C(4)—C(5)—C(6)	60.9 (7)
C(2)—C(3)—C(4)—O(4)	112.0 (6)	C(2)—Si(1)—C(6)—C(15)	177.6 (4)
C(3)—C(2)—Si(1)—C(7)	69.1 (4)	C(3)—C(2)—Si(1)—C(8)	-167.0 (4)
C(4)—C(3)—C(2)—C(9)	-171.6 (5)	C(4)—C(5)—C(6)—C(15)	178.8 (5)
O(4)—C(4)—C(5)—C(6)	-117.2 (6)	C(5)—C(6)—Si(1)—C(7)	-72.1 (4)
C(5)—C(6)—Si(1)—C(8)	163.9 (4)	C(6)—Si(1)—C(2)—C(9)	-179.2 (4)

the Si atom, suggests some rehybridization of the Si atom, possibly to minimize ring strain. These features, along with the observed distortions in the phenyl rings, apparently involve effects which are beyond the sophistication of the MMX parameters and are not reproduced in the calculated structure. Additional studies on less-substituted derivatives are

necessary to establish the general conformational trends for the silacyclohexane ring.

Related literature. Subsequent syntheses of less-substituted systems, also prepared *via* a cyclic hydroboration sequence, have been reported (Soderquist, Shiau & Lemesh, 1984; Soderquist & Negron, 1989).

References

CREMER, D. & POPLE, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
JOHNSON, C. K. (1976). *ORTEPII.* Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
LAMBERT, J. B. (1971). *Acc. Chem. Res.* **4**, 87–94.
PCMODEL (1989). *Molecular Modeling Software.* Serena Software, Bloomington, IN 47402-3076, USA.
SHELDRICK, G. M. (1976). *SHELX76.* Program for crystal structure determination. Univ. of Cambridge, England.
SODERQUIST, J. A. & HASSNER, A. (1983). *J. Org. Chem.* **48**, 1801–1810.
SODERQUIST, J. A. & NEGRON, A. (1989). *J. Org. Chem.* **54**, 2462–2464.
SODERQUIST, J. A., SHIAU, F.-Y. & LEMESH, R. A. (1984). *J. Org. Chem.* **49**, 2565–2569.

Structure of 4-Amino-5-phenyl-4*H*-1,2,4-triazole-3-thione

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Abstract. $C_8H_8N_4S$, $M_r = 192.24$, triclinic, $P\bar{1}$, $a = 6.1917(8)$, $b = 7.1417(6)$, $c = 9.9643(8)$ Å, $\alpha = 81.822(7)$, $\beta = 84.638(8)$, $\gamma = 78.682(9)°$, $V = 426.67(8)$ Å^3, $Z = 2$, $D_x = 1.496$ g cm^{-3}, λ(Mo $K\alpha$) $= 0.71073$ Å, $\mu = 3.17$ cm^{-1}, $F(000) = 200$, $T = 298$ K, $R = 0.033$ for 1250 reflections [$I \geq 3\sigma(I)$]. The molecule exists in the tautomeric thione form. The dihedral angle between the triazolyl and phenyl rings is 1(2)°; the S and exocyclic amino N atoms deviate from the least-squares plane of the triazolyl ring by 0.0409(7) and 0.002(2) Å, respectively.

Experimental. The compound was prepared in a multi-step synthesis from benzhydrazide, carbon disulfide and hydrazine (Reid & Heindel, 1976) and crystals were obtained on crystallization from ethanol. The cubic crystal measuring $0.22 \times 0.22 \times 0.22$ mm was mounted on an Enraf–Nonius CAD-4 diffractometer fitted with Mo $K\alpha$ radiation. Unit-cell constants were fixed from the 25 most intense reflections in the $13 \leq \theta \leq 15°$ thin shell. The 1652 unique data which were collected by using the $\theta/2\theta$-scan technique to $2\theta_{max} = 50$ consisted of 1250 reflections with $I \geq 3\sigma(I)$ (collection range: h 0–7, k -8–8, l -11–11). Three reflections ($10\bar{6}$, $2\bar{3}2$ and $3\bar{2}2$), monitored hourly, showed negligible variations in intensity. The data set was corrected for absorption by using ψ-scan data (minimum/maximum transmission factors 0.9788/0.9997, average 0.9885). The

structure was solved by a combination of direct and heavy-atom methods. The H atoms were located from a difference Fourier map, and were refined with a thermal factor $B = 5$ Å^2. The non-H atoms were refined anisotropically; 142 variables were refined. The weighting scheme $w = [\sigma(F)^2 + (0.02F)^2 + 1]^{-1}$ was used. Full-matrix least-squares refinement based on F converged at $R = 0.033$, $wR = 0.039$; $S = 0.564$; $(\Delta/\sigma) \leq 0.01$ for all atoms. The largest $\Delta\rho$ was 0.14 (2) e Å^{-3}. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2B and 2.3.1). All computations were performed using the *MolEN* structure determination package (Fair, 1990) on a DEC MicroVAX minicomputer. The atomic coordinates are listed in Table 1;* bond dimensions are gathered in Table 2. Fig. 1 shows the atomic labelling scheme.

Related literature. Katritzky, Bird, Boulton, Cheeseman, Lagowski, Lwowski, McKillop, Potts & Rees (1985) have reviewed the literature on heterocyclic chemistry. Their review contains references to