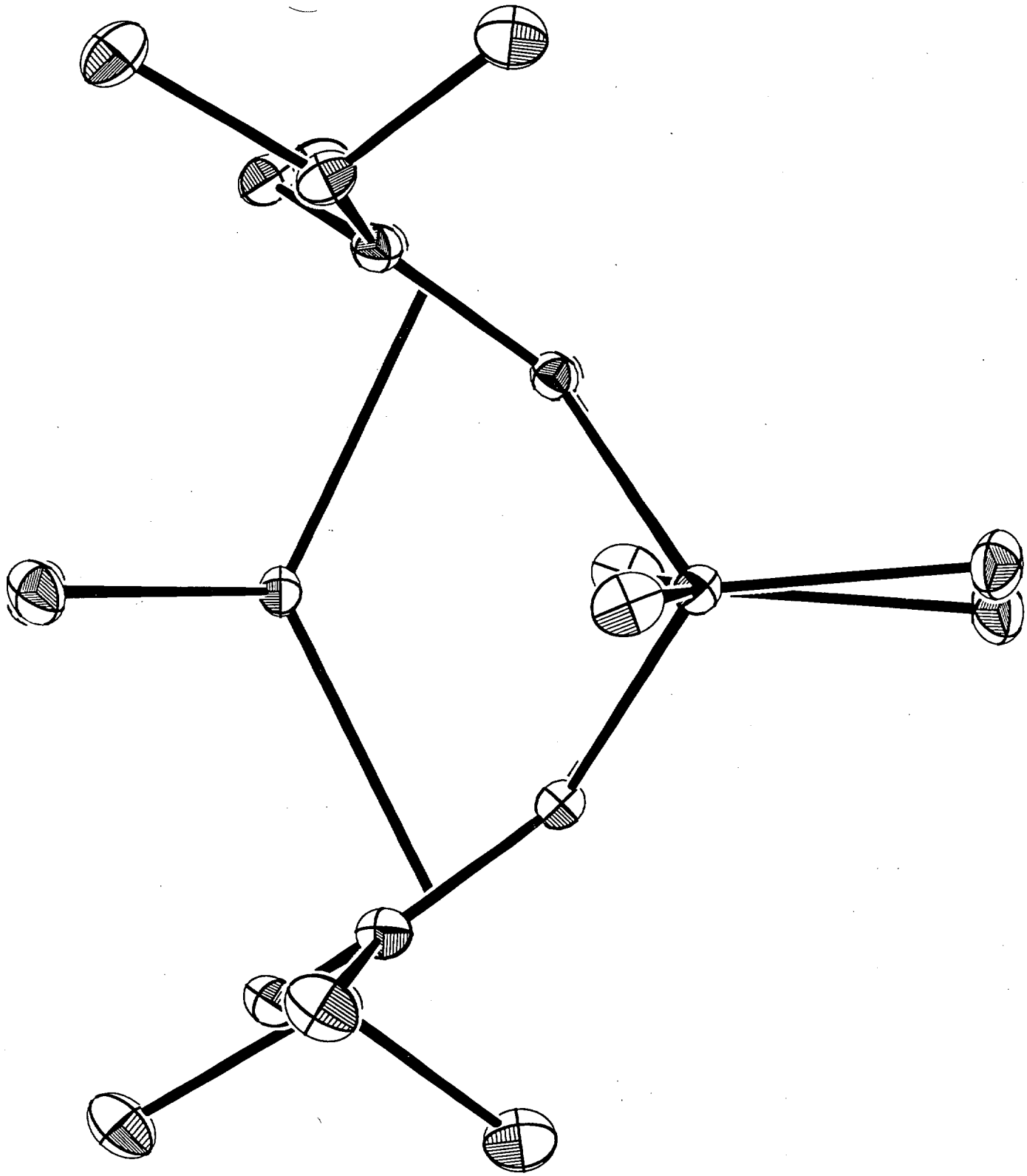
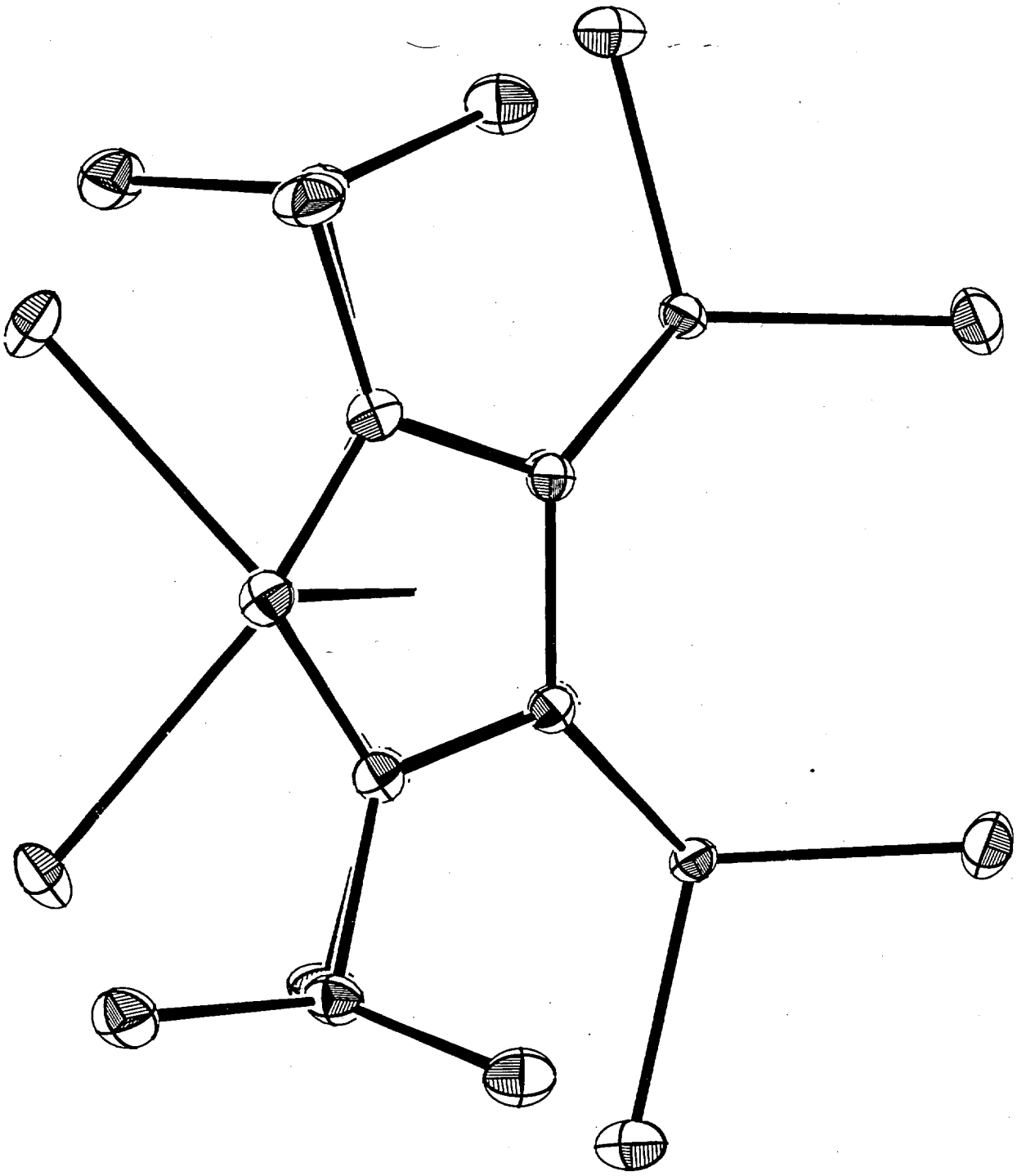
ORGANOMETALLICS
Organometallics, 1998, 17(25), 5528-5533, DOI:10.1021/om980505m





SHM2 $[(SiMe_2)_2(3\text{-}^iPr, 5\text{-}Me\text{-}Cp)_2]TiCl_2$

Solution and Refinement:

A hemisphere of data was collected with 1.0° ω-scans. No decay correction was needed. Individual backgrounds were replaced with a background function of 2θ derived from the backgrounds of reflections with $I < 3\sigma(I)$. Lorentz and polarization factors were applied and the multiples were merged in point group 2/m. CRYM programs were used for data processing.

The structure was solved with SHELXS-86. The titanium atom is on a crystallographic 2-fold axis parallel to the b-axis which relates the two halves of the molecule by $-x, y, 1/2-z$. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were refined isotropically. Refinement was full-matrix least-squares using CRYM programs.

Weights w are calculated as $1/\sigma^2(F_o^2)$; variances ($\sigma^2(F_o^2)$) were derived from counting statistics plus an additional term, $(0.014I)^2$; variances of the merged data were obtained by propagation of error plus another additional term, $(0.014\bar{I})^2$.

Definitions:

$$R = \frac{\Sigma|F_o - F_c|}{\Sigma F_o} \text{ for } F_o > 0; \quad R_w = \left\{ \frac{\Sigma w(F_o^2 - F_c^2)^2}{\Sigma w(F_o^2)^2} \right\}^{\frac{1}{2}}$$

$$S = \left\{ \frac{\Sigma w(F_o^2 - F_c^2)^2}{n - p} \right\}^{\frac{1}{2}}$$

where n = number of data,

p = number of parameters refined.

Comment:

Excellent quality crystal. The crystals were noticably dichroic, changing in color from red to orange. No attempt was made to correlate the color with the unit cell orientation.

References

The CRYM Crystallographic Computing System

Duchamp, D. J. (1964). Am. Crystallogr. Assoc. Meet., Bozeman, Montana, Paper B14, p. 29-30.

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Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467-473.

ORTEP

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA.

XP/PC

Siemens Analytical X-ray Instruments, Inc. (1989). Madison, WI, USA.

Figure Legends.

Figure 1. An ORTEP drawing of the molecule with 50% probability ellipsoids showing the numbering scheme. Hydrogen atoms are not shown.

Figure 2. An unlabelled ORTEP drawing of the molecule with 50% probability ellipsoids. Hydrogen atoms are not shown.

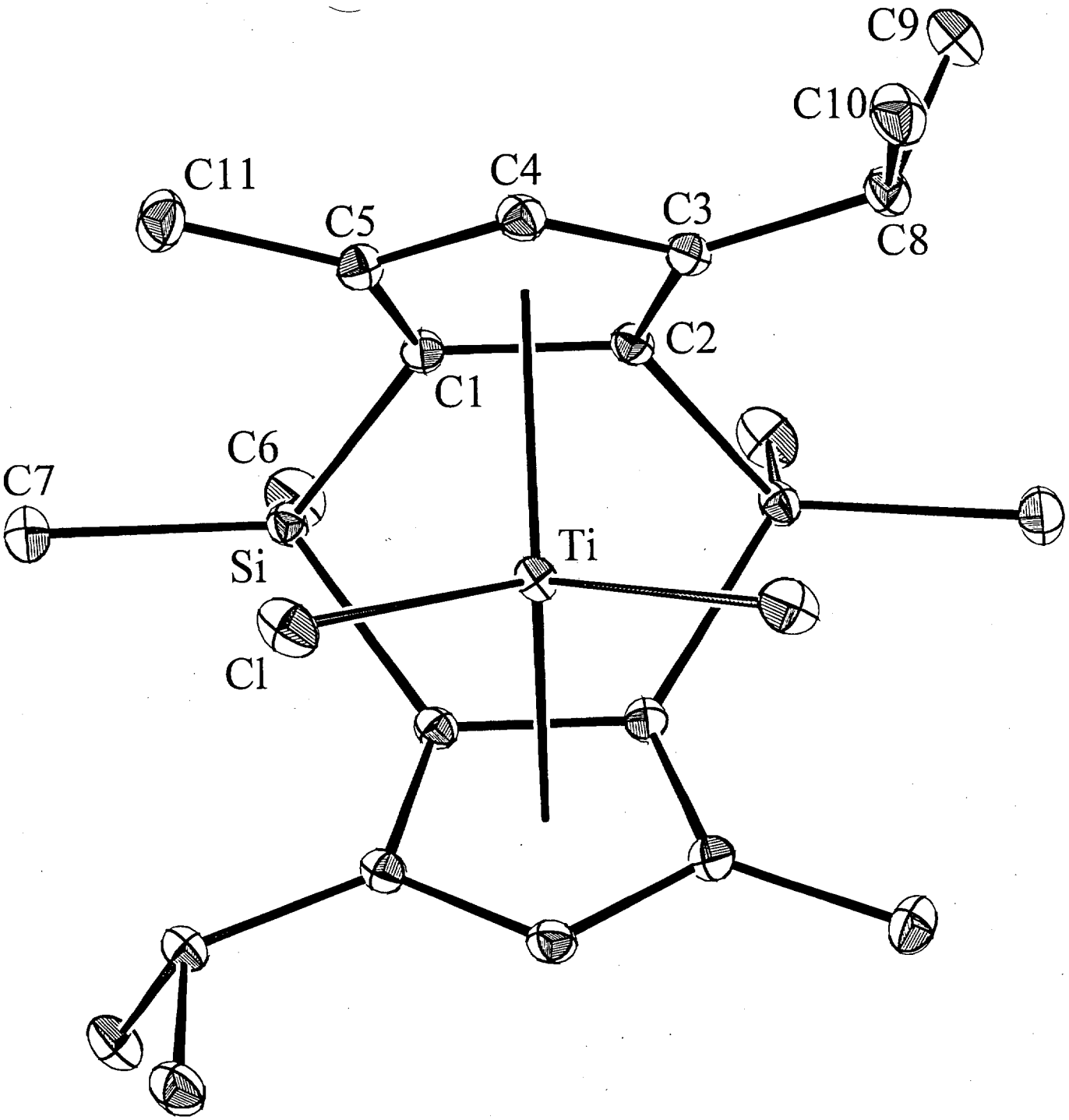
Figure 3. An unlabelled ORTEP drawing of the molecule with 50% probability ellipsoids. Hydrogen atoms are shown at one-tenth scale.

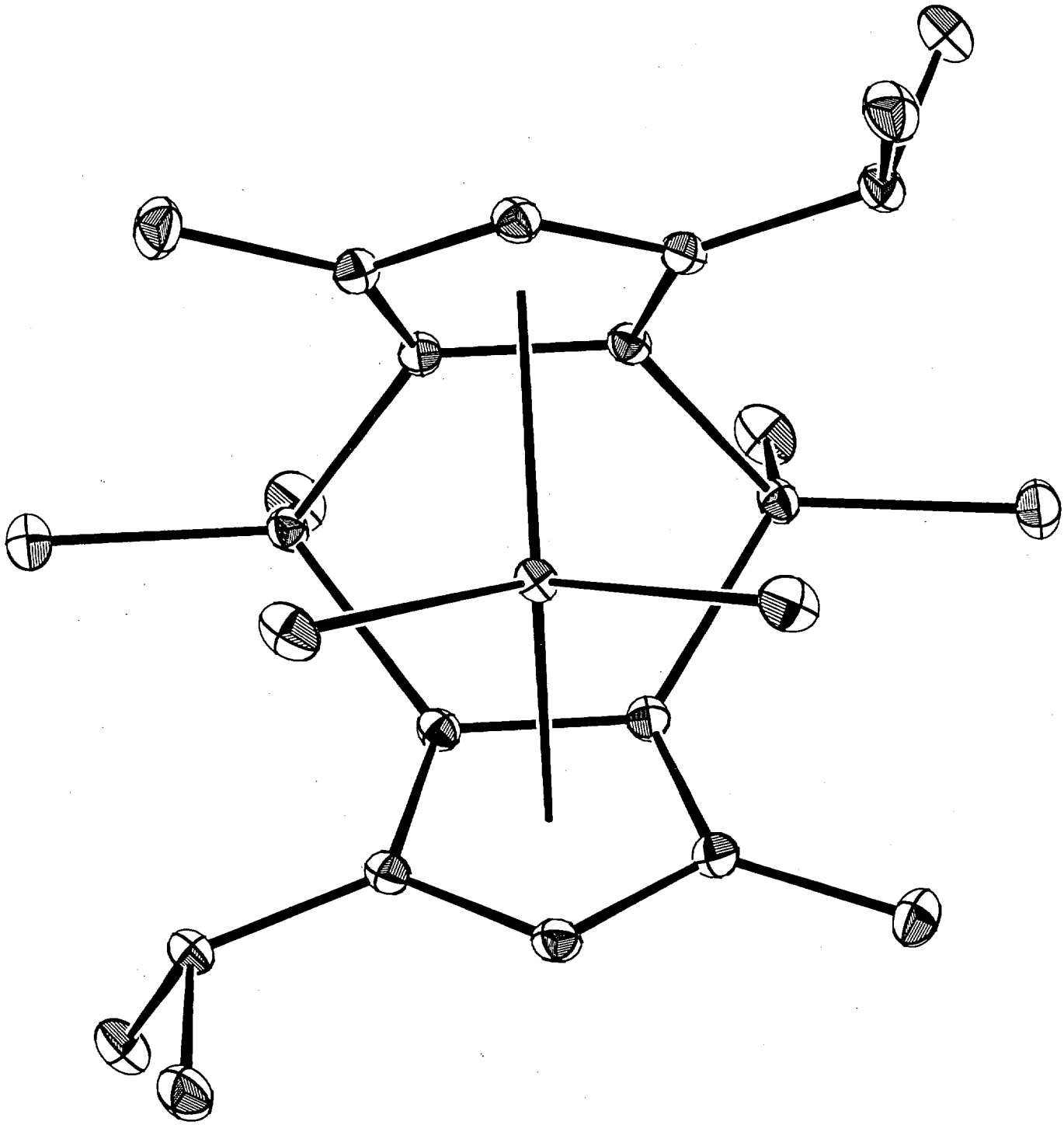
Figure 4. A color TELP drawing of the molecule with 50% probability ellipsoids. Hydrogen atoms are shown at arbitrary scale.

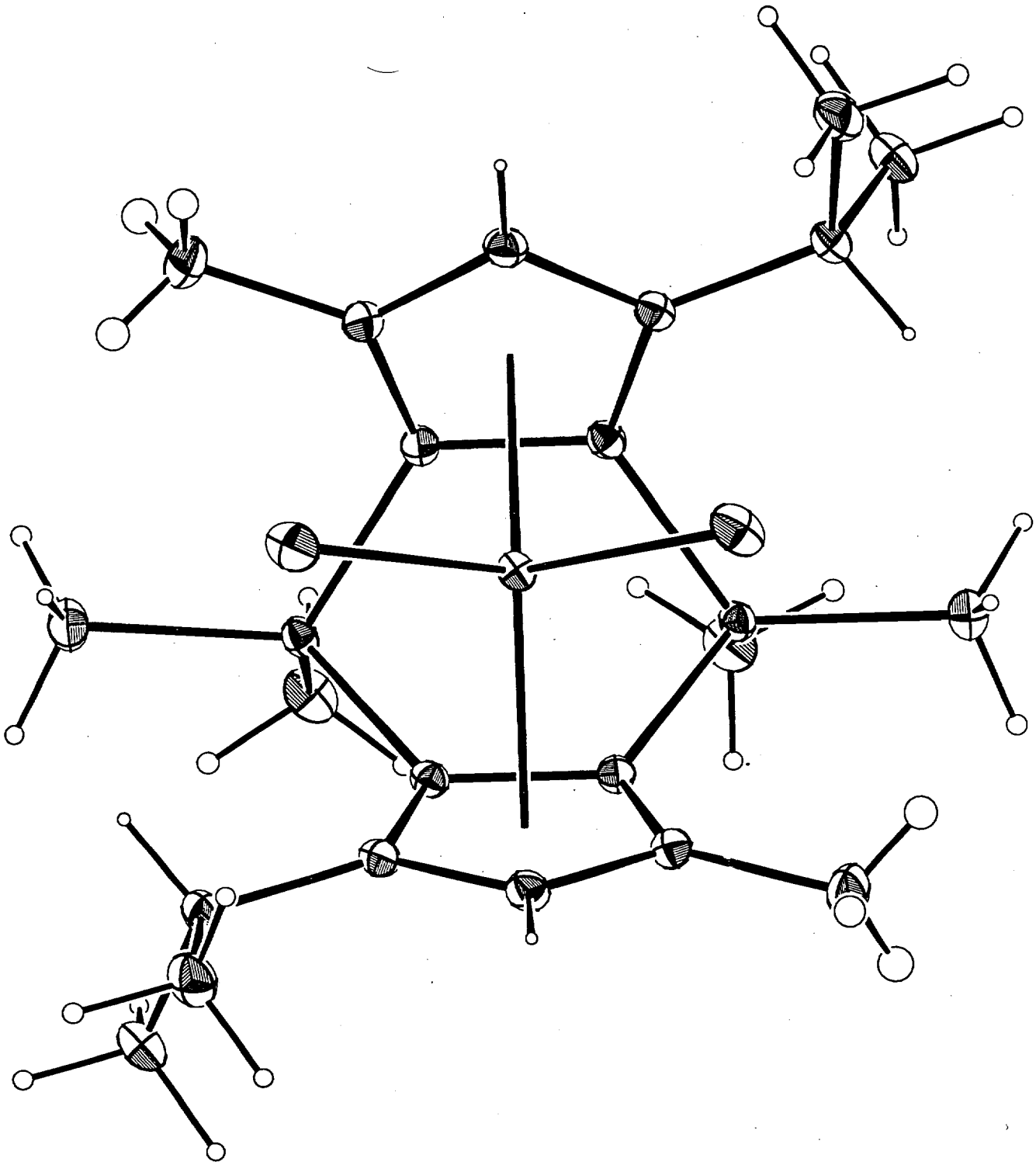
Figure 5. An ORTEP drawing of the unit cell contents viewed down the *a*-axis. Hydrogen atoms have been omitted.

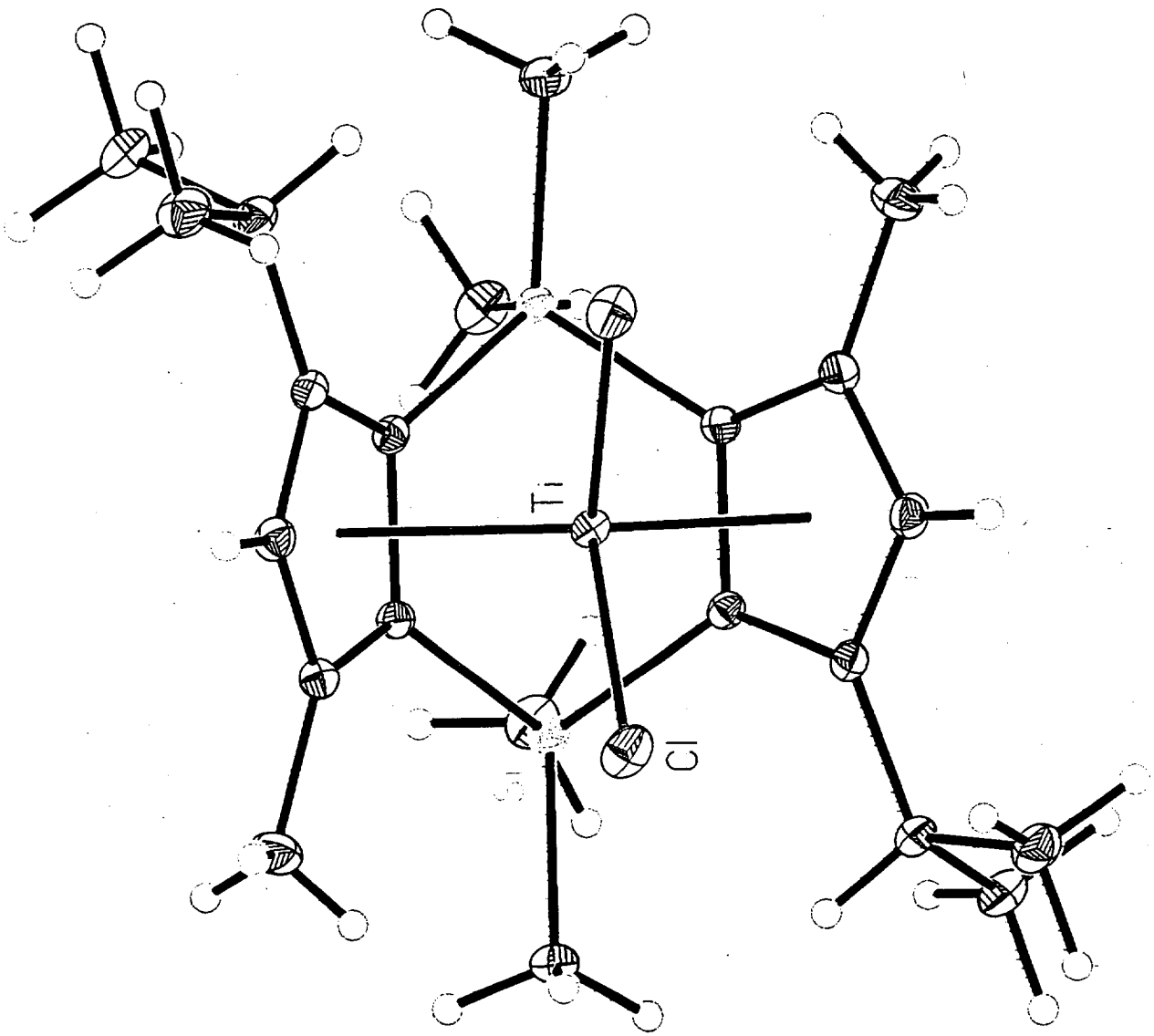
Figure 6. An ORTEP drawing of the unit cell contents viewed down the *a*-axis. Hydrogen atoms have been omitted.

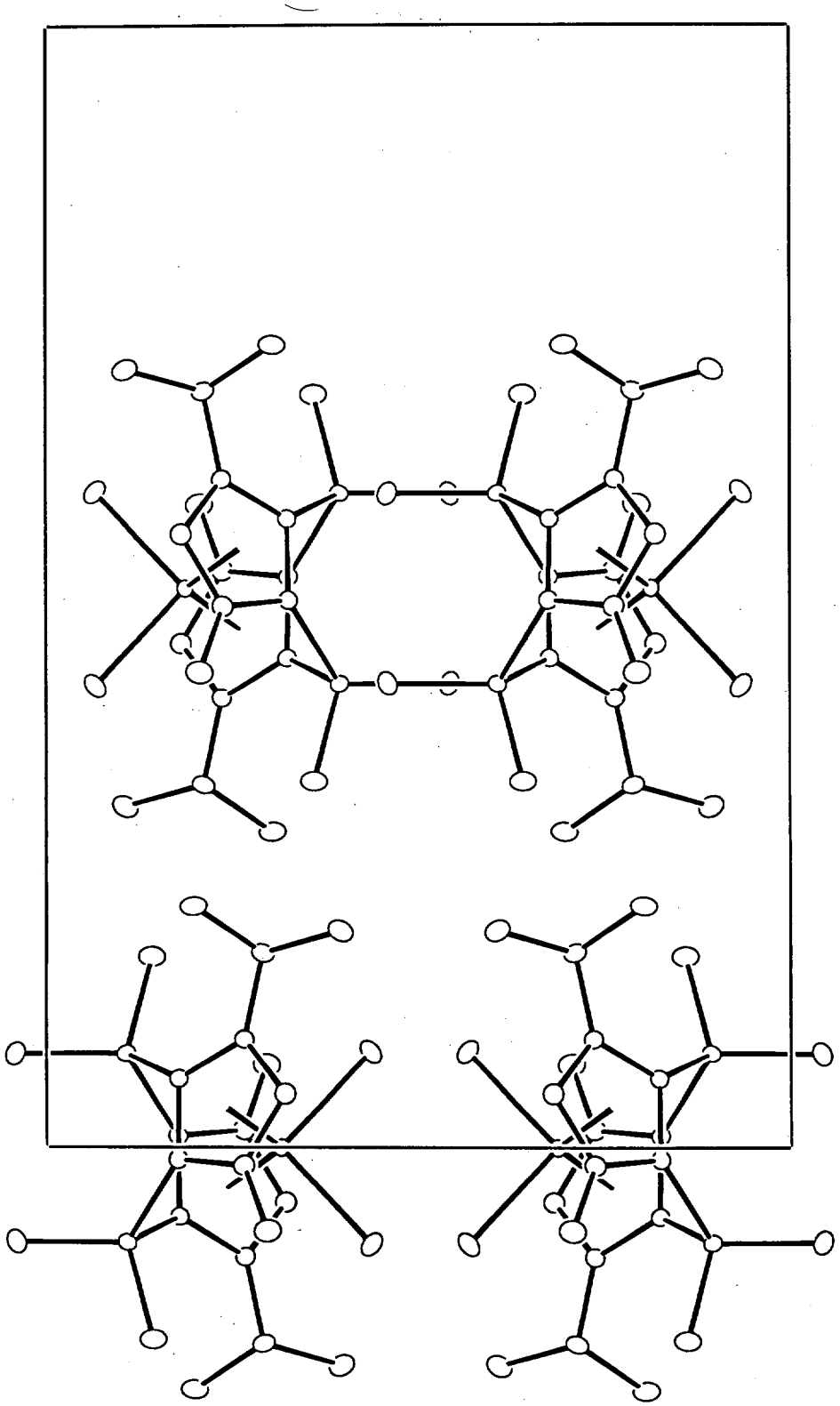
Figure 7. An ORTEP drawing of the unit cell contents viewed down the *a*-axis. Hydrogen atoms have been omitted.

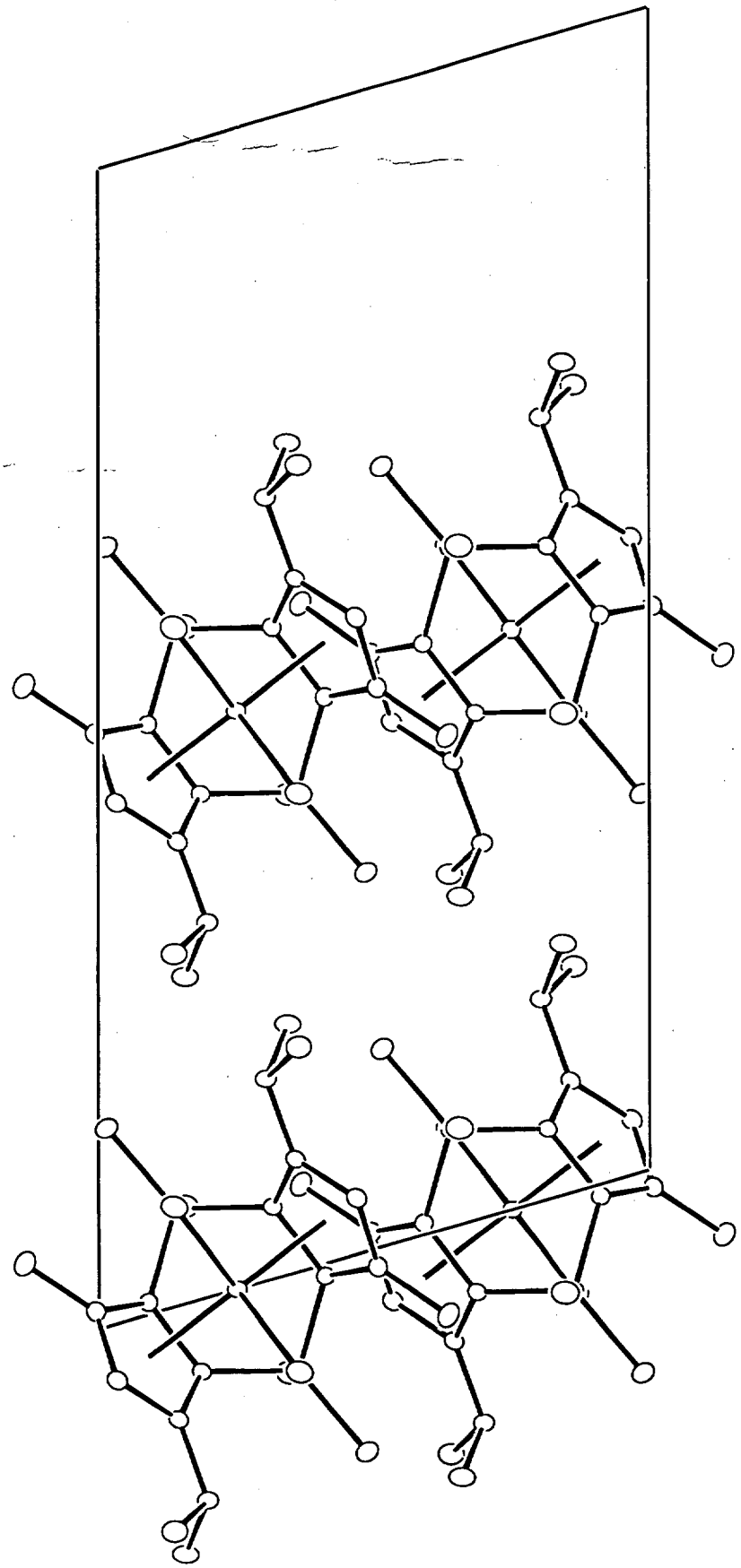












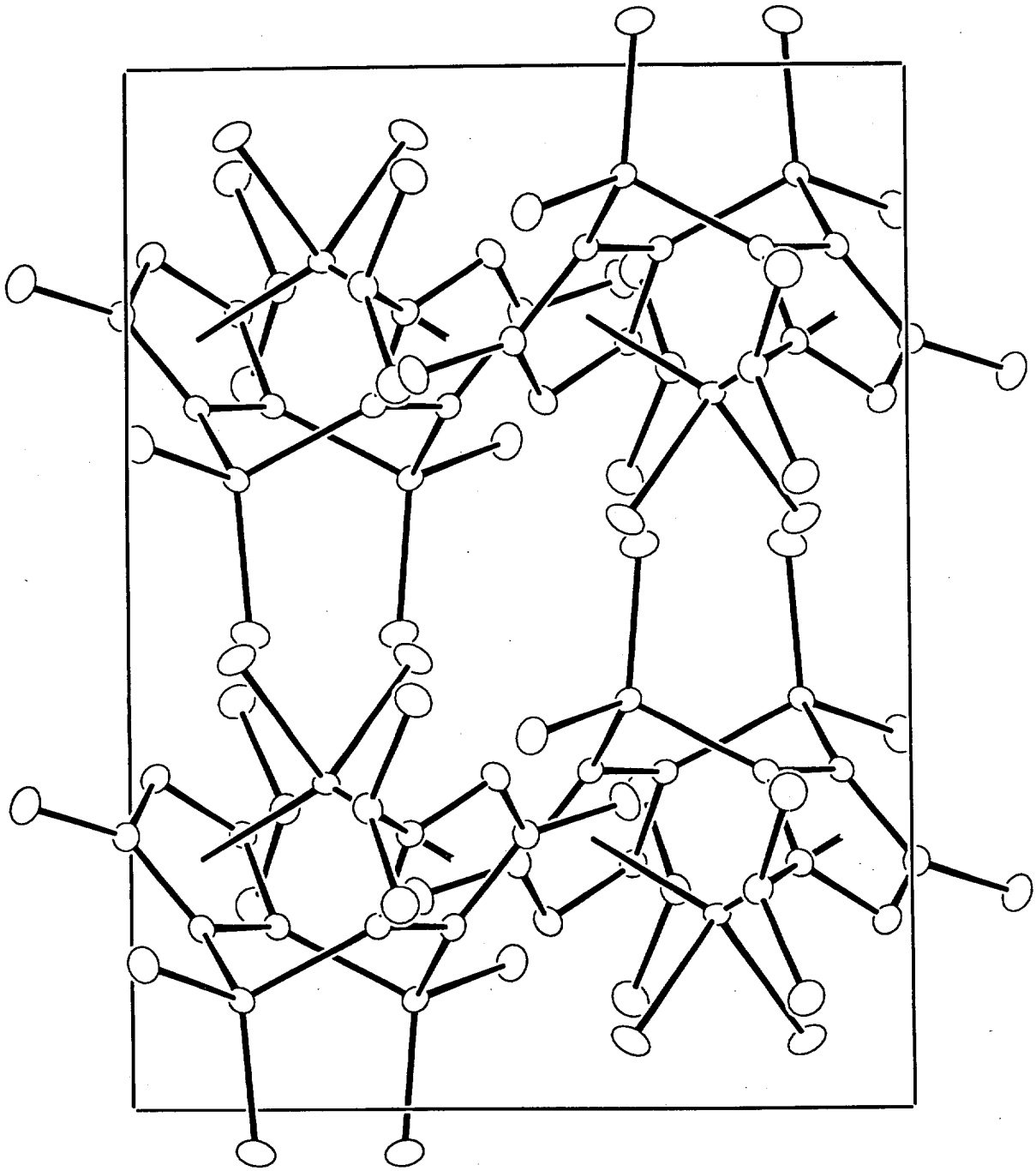


Table 1. Crystal and Intensity Collection Data for SHM2 $[(SiMe_2)_2(3\text{-}^iPr,5\text{-}Me\text{-}Cp)_2]TiCl_2$

Formula: $C_{22}H_{34}Cl_2Si_2Ti$	Formula weight: 473.47
Crystal color: Orange-red dichroic	Habit: Block
Crystal size: 0.44 × 0.46 × 0.48 mm	$\rho_{calc} = 1.352$ g cm^{-3}
Crystal System: Monoclinic	Space group: $C2/c$ (#15)
$a = 19.756(6)$Å	
$b = 12.555(2)$Å	$\beta = 106.28(3)°$
$c = 9.767(2)$Å	
V = 2325.4(9)Å^3	$Z = 4$
Lattice parameters: 25 reflections,	$22° \leq \theta \leq 25°$
$\mu = 7.07$ cm^{-1} ($\mu r_{max} = 0.28$)	Transmission coeff. (ψ-scan)= 0.98 − 1.03
CAD-4 diffractometer	ω scan
MoKα, $\lambda = 0.7107$Å	Graphite monochromator
2θ range: 2°–60°	$-27 \leq h \leq 0, -17 \leq k \leq 17, -13 \leq l \leq 13$
T = 85K	$F_{000} = 1000$
Number of reflections measured: 7777	Number of independent reflections: 3393
Number with $F_o^2 > 0$: 3320	Number with $F_o^2 > 3\sigma(F_o^2)$: 3088
Standard reflections: 3 every 1.25 hrs	Variation: Within counting statistics
GOF_{merge} : 1.22 for 3257 multiples	R_{merge} : 0.014 for 2961 duplicates
Number used in refinement: 3393	Criterion: All reflections used

Final R(F_o): 0.025 for 3088 reflections with $F_o^2 > 3\sigma(F_o^2)$

Final R(F_o): 0.027 for 3320 reflections with $F_o^2 > 0$

Final weighted R(F_o^2) : 0.067 for 3393 reflections

Final goodness of fit: 2.18 for 191 parameters and 3393 reflections

$(\Delta/\sigma)_{max}$ in final least squares cycle: 0.02

$\Delta\rho_{max}$: 0.47 eÅ^{-3}, $\Delta\rho_{min}$: −0.29 eÅ^{-3} in final difference map

Table 2. Final Heavy Atom Parameters for

SHM2 $[(SiMe_2)_2(3\text{-}^iPr,5\text{-}Me\text{-}Cp)_2]TiCl_2$

x, y, z and U_{eq}

Atom	x	y	z	U_{eq}
Ti	0.0	0.31390(2)	0.25	0.00899(4)
Cl	0.08631(1)	0.43461(2)	0.36296(3)	0.01671(4)
Si	0.08485(1)	0.10644(2)	0.36121(3)	0.00967(4)
C1	0.01035(5)	0.17520(8)	0.41056(11)	0.0099(2)
C2	−0.06197(6)	0.17685(8)	0.31480(11)	0.0096(2)
C3	−0.09764(6)	0.26482(8)	0.35675(11)	0.0105(2)
C4	−0.04880(6)	0.31949(9)	0.46754(12)	0.0121(2)
C5	0.01560(6)	0.26349(9)	0.50570(11)	0.0117(2)
C6	0.08449(6)	−0.04177(9)	0.34500(14)	0.0167(2)
C7	0.17223(6)	0.14095(10)	0.48533(12)	0.0163(2)
C8	−0.17533(6)	0.28953(9)	0.30321(12)	0.0126(2)
C9	−0.21684(6)	0.19666(10)	0.34312(14)	0.0176(2)
C10	−0.19464(6)	0.39424(10)	0.36282(14)	0.0175(2)
C11	0.07453(7)	0.29476(11)	0.63347(13)	0.0175(2)

[a] $U_{eq} = \frac{1}{3}\sum_i \sum_j [U_{ij}(a_i^* a_j^*)(\vec{a}_i \cdot \vec{a}_j)]$

Table 3. Selected Distances and Angles for

SHM2 $[(SiMe_2)_2(3\text{-}^iPr,5\text{-}Me\text{-}Cp)_2]TiCl_2$

	Distance(Å)		Angle(°)
Ti –Cl	2.3168(3)	Cp –Ti –Cp^i	128.1
Ti –Cp	2.120	Cp –Ti –Cl	106.9
Si –C1	1.882(1)	Cp –Ti –Cl^i	106.4
Si –C2^i	1.872(1)	Cl –Ti –Cl^i	98.28(1)
Si –C6	1.867(1)	C1 –Si –C2^i	90.79(5)
Si –C7	1.861(1)	C1 –Si –C6	119.6(1)
C1 –C2	1.472(1)	C1 –Si –C7	112.1(1)
C1 –C5	1.431(2)	C6 –Si –C2^i	113.5(1)
C2 –C3	1.430(2)	C7 –Si –C2^i	115.4(1)
C3 –C4	1.410(2)	C7 –Si –C6	105.6(1)
C3 –C8	1.508(2)	C2 –C1 –Si	122.2(1)
C4 –C5	1.409(2)	C5 –C1 –Si	127.0(1)
C5 –C11	1.501(2)	C5 –C1 –C2	106.4(1)
C8 –C9	1.537(2)	C1 –C2 –Si^i	121.2(1)
C8 –C10	1.529(2)	C3 –C2 –Si^i	128.0(1)
		C3 –C2 –C1	107.3(1)
		C4 –C3 –C2	108.0(1)
		C8 –C3 –C2	126.5(1)
		C8 –C3 –C4	125.2(1)
		C5 –C4 –C3	109.4(1)

Table 3. (Cont.)

			Angle(°)
C4	–C5	–C1	108.6(1)
C11	–C5	–C1	129.8(1)
C11	–C5	–C4	121.4(1)
C9	–C8	–C3	108.6(1)
C10	–C8	–C3	112.5(1)
C10	–C8	–C9	110.3(1)

Symmetry code (i) $-x, y, 1/2 - z$

Table 4. Anisotropic Displacement Parameters for

SHM2 $[(SiMe_2)_2(3\text{-}^iPr, 5\text{-}Me\text{-}Cp)_2]TiCl_2$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ti	0.0086(1)	0.0072(1)	0.0113(1)	0	0.0030(1)	0
Cl	0.0161(1)	0.0137(1)	0.0219(1)	−0.0058(1)	0.0079(1)	−0.0070(1)
Si	0.0082(1)	0.0099(1)	0.0108(1)	0.0010(1)	0.0025(1)	0.0016(1)
C1	0.0095(5)	0.0102(5)	0.0100(4)	−0.0004(3)	0.0026(4)	0.0011(3)
C2	0.0092(5)	0.0096(4)	0.0104(4)	−0.0004(3)	0.0035(4)	0.0007(3)
C3	0.0102(5)	0.0109(5)	0.0111(5)	0.0003(4)	0.0043(4)	0.0007(4)
C4	0.0121(5)	0.0127(5)	0.0124(5)	0.0000(4)	0.0048(4)	−0.0024(4)
C5	0.0115(5)	0.0131(5)	0.0106(5)	−0.0007(4)	0.0034(4)	−0.0004(4)
C6	0.0165(6)	0.0113(5)	0.0231(6)	0.0027(4)	0.0069(5)	0.0028(4)
C7	0.0110(5)	0.0216(6)	0.0148(5)	−0.0003(4)	0.0013(4)	0.0021(4)
C8	0.0095(5)	0.0150(5)	0.0134(5)	0.0020(4)	0.0036(4)	−0.0009(4)
C9	0.0112(5)	0.0217(6)	0.0212(6)	−0.0008(4)	0.0065(4)	0.0001(5)
C10	0.0136(5)	0.0188(6)	0.0204(6)	0.0037(4)	0.0054(4)	−0.0034(4)
C11	0.0145(5)	0.0219(6)	0.0136(5)	−0.0011(5)	−0.0001(4)	−0.0047(4)

The form of the displacement factor is:

$$\exp -2\pi^2(U_{11}h^2a^{*^2} + U_{22}k^2b^{*^2} + U_{33}\ell^2c^{*^2} + 2U_{12}hka^*b^* + 2U_{13}h\ell a^*c^* + 2U_{23}k\ell b^*c^*)$$

Table 5. Final Refined Hydrogen Parameters for

SHM2 $[(SiMe_2)_2(3\text{-}^iPr,5\text{-}Me\text{-}Cp)_2]TiCl_2$

x, y, z and U_{iso}

Atom	x	y	z	U_{iso}
H4	−0.0577(7)	0.3823(10)	0.512(1)	0.009(3)
H6a	0.1336(9)	−0.0665(13)	0.359(2)	0.032(5)
H6b	0.0678(8)	−0.0738(12)	0.417(2)	0.024(4)
H6c	0.0596(9)	−0.0642(12)	0.254(2)	0.030(4)
H7a	0.2096(8)	0.1091(12)	0.447(2)	0.023(4)
H7b	0.1795(8)	0.2120(12)	0.503(2)	0.017(4)
H7c	0.1740(9)	0.1028(12)	0.576(2)	0.028(4)
H8	−0.1898(7)	0.2941(10)	0.202(2)	0.011(3)
H9a	−0.2082(8)	0.1297(12)	0.302(2)	0.022(4)
H9b	−0.2062(8)	0.1886(11)	0.451(2)	0.021(4)
H9c	−0.2682(9)	0.2091(12)	0.306(2)	0.027(4)
H10a	−0.1707(8)	0.4522(13)	0.336(2)	0.025(4)
H10b	−0.2462(9)	0.4080(13)	0.325(2)	0.029(4)
H10c	−0.1842(8)	0.3933(12)	0.466(2)	0.024(4)
H11a	0.0825(14)	0.2477(21)	0.697(3)	0.083(8)
H11b	0.1146(14)	0.3085(18)	0.622(3)	0.071(8)
H11c	0.0689(11)	0.3641(19)	0.660(2)	0.063(7)

Table 6. Complete Distances and Angles for

SHM2 $[(SiMe_2)_2(3\text{-}^iPr,5\text{-}Me\text{-}Cp)_2]TiCl_2$

	Distance(Å)		Distance(Å)
Ti –Cl	2.3168(3)	C6 –H6b	0.946(16)
Ti –Cp	2.120	C6 –H6c	0.931(17)
Ti –C1	2.314(1)	C7 –H7a	1.001(16)
Ti –C2	2.301(1)	C7 –H7b	0.911(15)
Ti –C3	2.513(1)	C7 –H7c	1.000(17)
Ti –C4	2.569(1)	C8 –C9	1.537(2)
Ti –C5	2.510(1)	C8 –C10	1.529(2)
Si –C1	1.882(1)	C8 –H8	0.953(14)
Si –$C2^i$	1.872(1)	C9 –H9a	0.966(15)
Si –C6	1.867(1)	C9 –H9b	1.024(16)
Si –C7	1.861(1)	C9 –H9c	0.990(17)
C1 –C2	1.472(1)	C10 –H10a	0.943(16)
C1 –C5	1.431(2)	C10 –H10b	0.996(17)
C2 –C3	1.430(2)	C10 –H10c	0.967(16)
C3 –C4	1.410(2)	C11 –H11a	0.84(3)
C3 –C8	1.508(2)	C11 –H11b	0.85(3)
C4 –C5	1.409(2)	C11 –H11c	0.92(2)
C4 –H4	0.943(14)		
C5 –C11	1.501(2)		
C6 –H6a	0.991(18)		

Table 6. (Cont.)

	Angle(°)		Angle(°)
Cp –Ti –Cp^{i}	128.1	H4 –C4 –C3	126.0(8)
Cp –Ti –Cl	106.9	H4 –C4 –C5	124.5(8)
Cp –Ti –Cl^{i}	106.4	C4 –C5 –C1	108.6(1)
Cl –Ti –Cl^{i}	98.28(1)	C11 –C5 –C1	129.8(1)
C1 –Si –C2^{i}	90.79(5)	C11 –C5 –C4	121.4(1)
C1 –Si –C6	119.6(1)	H6a –C6 –Si	108.7(10)
C1 –Si –C7	112.1(1)	H6b –C6 –Si	110.7(10)
C6 –Si –C2^{i}	113.5(1)	H6c –C6 –Si	111.7(10)
C7 –Si –C2^{i}	115.4(1)	H6b –C6 –H6a	107.2(14)
C7 –Si –C6	105.6(1)	H6c –C6 –H6a	105.8(15)
C2 –C1 –Si	122.2(1)	H6c –C6 –H6b	112.4(14)
C5 –C1 –Si	127.0(1)	H7a –C7 –Si	108.1(9)
C5 –C1 –C2	106.4(1)	H7b –C7 –Si	114.7(10)
C1 –C2 –Si^{i}	121.2(1)	H7c –C7 –Si	105.2(10)
C3 –C2 –Si^{i}	128.0(1)	H7b –C7 –H7a	111.5(13)
C3 –C2 –C1	107.3(1)	H7c –C7 –H7a	107.2(13)
C4 –C3 –C2	108.0(1)	H7c –C7 –H7b	109.8(14)
C8 –C3 –C2	126.5(1)	C9 –C8 –C3	108.6(1)
C8 –C3 –C4	125.2(1)	C10 –C8 –C3	112.5(1)
C5 –C4 –C3	109.4(1)	H8 –C8 –C3	110.6(9)

Table 6. (Cont.)

			Angle(°)				Angle(°)
C10	–C8	–C9	110.3(1)	H11c	–C11	–H11b	92.0(22)
H8	–C8	–C9	106.5(9)				
H8	–C8	–C10	108.1(9)				
H9a	–C9	–C8	112.8(9)				
H9b	–C9	–C8	111.6(9)				
H9c	–C9	–C8	110.5(10)				
H9b	–C9	–H9a	109.3(13)				
H9c	–C9	–H9a	105.4(13)				
H9c	–C9	–H9b	106.9(13)				
H10a	–C10	–C8	111.1(10)				
H10b	–C10	–C8	110.1(10)				
H10c	–C10	–C8	112.4(10)				
H10b	–C10	–H10a	107.6(14)				
H10c	–C10	–H10a	108.5(14)				
H10c	–C10	–H10b	106.9(14)				
H11a	–C11	–C5	111.9(18)				
H11b	–C11	–C5	118.7(17)				
H11c	–C11	–C5	110.8(14)				
H11b	–C11	–H11a	104.6(25)				
H11c	–C11	–H11a	117.8(23)				

Symmetry code (i) $-x, y, 1/2 - z$