

Table 5. Signals obtained from 200 MHz ^1H NMR spectra of derivatives of bis(4,5-dihydro-3,5,5-trimethylpyrazolium) hexachlorostannate (PYRA) in $(\text{CD}_3)_2\text{SO}$

Carbonyl moiety	Chemical shifts (δ , TMS _{int} = 0)		
	C(4)H ₂	C(3)—CH ₃	H ₃ C—C(5)—CH ₃
Cyclopentanone*	3.36	2.28	1.66
3-Methylcyclopentanone	3.33	2.26	1.62, 1.65
3-R-Methylcyclopentanone	3.32	2.25	1.62, 1.64

* Rathbone, Stephen, Schwersenski & Tyler (1975).

Schalkwyk, Stephen & Hodgson, 1976). The NMR result is consistent with the presence in (I) of the *cis* (C-3'/C-5) isomers only, as shown by crystal analysis (Table 2). Two NMR signals for the *gem*-dimethyl groups at C-5 in (II) are consistent with the different relative effects of the C-3' methyl. The proton integral values for the two sets of *gem*-dimethyl protons are similar, but could allow for a preponderance of the unaffected methyls, as would be the case for the small proportion of the alternative *trans* (C'-3/C-5) isomer which X-ray crystallographic analysis indicates.

The molecular conformations of the cycloalkylidene rings, one in compound (I) and two in compound (II), can be expressed (Table 6) as linear combinations of the standard primitive forms of five-membered puckered rings, such as envelope (*E*) and twist (*T*), with the program *CONFOR* (Evans & Boeyens, 1989). The normalized numerical coefficients *a* and *b* indicate the relative contributions of the primitive forms in order of increasing mode *m* in the linear sum. The phase angles φ_m of the relevant primitive form, *E* or *T*, are expressed as multiples of

Table 6. Conformational analysis of five-membered alkylidene rings using computer program *CONFOR*

Molecule	Puckering parameters		Assignment $a\varphi(E) + b\varphi(T)$	Classic form
	Q_2 (Å)	φ_2 (°)		
(I)	0.297 (7)	277.0 (9)	39 (16) + 61 (15)	Mixed <i>E</i> and <i>T</i>
(II) <i>M</i> ₂	0.062 (20)	129.9 (12)	22 (8) + 78 (7)	Mixed <i>E</i> and <i>T</i>
(II) <i>M</i> ₁	0.400 (12)	100.4 (16)	58 (6) + 42 (5)	Mixed <i>E</i> and <i>T</i>

$\pi/2N$, for an *N*-membered polygon, where *N* = 5. From Table 6 it is clear that all three rings are mixed forms of *E* and *T*, with relative percentages indicated by the *a* and *b* values.

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Geometry of the Iminium Moiety. IV. Structure of 4,5-Dihydro-3,5,5-trimethylpyrazolium Aquapentachlorostannate Monohydrate

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Abstract. Compound PYFA, 4,5-dihydro-3,5,5-trimethylpyrazolium aquapentachlorostannate monohydrate, $[\text{C}_6\text{H}_{13}\text{N}_2]^+[\text{SnCl}_5(\text{H}_2\text{O})]^- \cdot \text{H}_2\text{O}$, $M_r = 469.2$, monoclinic, $P2_1/n$, $a = 10.788$ (1), $b = 18.560$ (1), $c = 8.158$ (1) Å, $\beta = 96.18$ (1)°, $V = 1624.0$ (3) Å³, $Z = 4$, $D_m = 1.92$ (1), $D_x =$

1.919 g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 24.1$ cm⁻¹, $F(000) = 920$, $T = 294$ K, $R = 0.026$ for 2304 observed reflections with $I > 2\sigma(I)$. The modified anion was formed on treatment of a dihydropyrazolium hexachlorostannate (PYRA) with hexafluoroacetone trihydrate. The water present causes replacement of a Cl⁻ ion from the hexachlorostannate anion by an H₂O molecule, one base

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moiety only being associated with the resulting monovalent complex anion. Five hydrogen bonds exist in the structure. To determine the effect of a different dipolar aprotic solvent mixed with water, PYRA was treated with DMSO–H₂O (4:1 *v/v*). The product was SnCl₄(C₂H₆OS)₂, two DMSO molecules displacing two Cl[−] ions from the Sn complex, which was then no longer associated with the dihydropyrazolium ion. The same compound was obtained by a different route [Kisenyi, Willey & Drew (1985). *Acta Cryst.* C41, 700–702].

Introduction. In part I of this series concerning the geometry of the iminium moiety (Nassimbeni, Stephen & Van Schalkwyk, 1991*a*), the condensation of bis(4,5-dihydro-3,5,5-trimethylpyrazolium) hexachlorostannate monohydrate (PYRA) with acetone, yielding a substance containing the ternary iminium ion, bis(4,5-dihydro-3,5,5-trimethyl-1-isopropylidene-pyrazolium) hexachlorostannate (PYCS) (Pugh, 1954), was described. As part of the investigation of the reaction of ketones with secondary amines using [SnCl₆]^{2−} as counter ion and studying the geometry of the iminium ions produced, simulation of the above reaction by replacing acetone with hexafluoroacetone (b.p. 247 K) was contemplated. This acetone analogue was acquired in the form of the trihydrate, (CF₃)₂CO.3H₂O, which is liquid at room temperature.

Experimental. As a first attempt towards obtaining the expected bis(4,5-dihydro-3,5,5-trimethyl-1-hexafluoroisopropylidene-pyrazolium) hexachlorostannate (C₁₈H₂₂F₁₂N₄SnCl₆), 0.35 g (0.61 mmol) of PYRA were dissolved in the minimum amount of dry ethanol at room temperature and added to 0.5 mL (3.6 mmol) hexafluoroacetone trihydrate. The prismatic white crystals obtained were characterized as unchanged PYRA. 0.5 g (0.87 mmol) PYRA was then dissolved in 0.5 mL (3.6 mmol) of hexafluoroacetone trihydrate at room temperature. Stable prismatic crystals (PYFA), m.p. 439 K, formed within a few hours on cooling. Crystal-density measurement was obtained by flotation in a mixture of bromobenzene and bromoform, and the use of a Paar DMA 35 density meter. Preliminary X-ray photographic measurements on a suitable crystal for space-group assignment and standard intensity data collection at 294 K on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo K α radiation were completed. A least-squares analysis of 24 reflections in the range 16 < θ < 17° was used to determine accurate cell parameters. Scans in the range 1 < θ < 25° were performed in the ω –2 θ mode with varying speeds and a maximum recording time of 30 s. Intensities of three standard

reflections were monitored every 100 reflections and automatic re-centring was carried out. Intensities were corrected for Lorentz and polarization factors as well as for absorption (North, Phillips & Mathews, 1968). Table 1 contains additional intensity measurement and refinement data. The structure was solved by direct methods and refined by full-matrix least squares, based on *F*, using the *SHELX76* (Sheldrick, 1976) program system. Final refinements on all non-H atoms were carried out anisotropically and H atoms in the dihydropyrazolium moiety were constrained to ride at 1.0 Å from the parent atom, linked with common isotropic temperature factors. The H atoms in the water molecules were found in a difference electron density map and subjected to constrained refinement, with O–H = 1.0 Å. Atomic scattering curves used for non-H atoms were obtained from Cromer & Mann (1968) and for H atoms from Stewart, Davidson & Simpson (1965). The final fractional atomic coordinates of PYFA are listed in Table 2.*

Discussion. The structure of the final product was different from that which was expected, the F-containing analogue of PYCS. F atoms were not found in the product PYFA. Excess H₂O, in the form of the trihydrate, and the presence of the dipolar aprotic solvent (the ketone), had caused one Cl[−] ion in the anion to be replaced by an H₂O molecule, and accounted for the presence of an uncoordinated water molecule. [SnCl₅(H₂O)][−] being monovalent, a molecule of the base is displaced from its association with the complex anion. Hence the cation consists of a single dihydropyrazolium ion, as in PYCL, 4,5-dihydro-3,5,5-trimethylpyrazolium chloride, C₆H₁₃N₂⁺.Cl[−] (Nassimbeni, Stephen & Van Schalkwyk, 1991*a*), and without the anticipated iminium moiety. Perspective views of PYFA and its packing diagram are shown in Fig. 1. Microanalysis carried out at two separate laboratories yielded satisfactory results, showing in particular the absence of F and a ratio for N:Cl of 2:5 (found: C 16.6, H 3.9, N 6.5, Cl 39.5%; calculated for C₆H₁₇N₂O₂SnCl₅: C 16.2, H 3.8, N 6.3, Cl 39.8%). Corroboration of the presence of an intact 4,5-dihydro-3,5,5-pyrazolium ion in a solution of PYFA in dimethyl sulfoxide-*d*₆ was provided by ¹H NMR spectroscopy, three characteristic singlets, for the *gem*-dimethyl (6*p*) on C-5, for the C-4 methylene (2*p*), and for methyl (3*p*) on C-3, being observed (Rathbone & Stephen, 1971).

* Lists of structure factors, anisotropic thermal parameters, torsion angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55433 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: GE0302]

Table 1. *Experimental data and structure-refinement parameters*

Crystal dimensions (mm)	0.20 × 0.25 × 0.28
Range of indices <i>h</i>	−12→12
<i>k</i>	0→22
<i>l</i>	0→9
Transmission factor minimum/maximum (%)	93.8/99.8
Standard reflections (<i>hkl</i>)	3,11,1, 2,10,4, 525
Minimum, maximum θ (°)	1.0, 25.0
Stability (%)	1.2
Scan width parameter y^*	0.90
Aperture width parameter x^\dagger	1.12
No. of reflections measured	3182
No. of unique reflections, R_{int}	2624, 0.015
No. of observed reflections [$I > 2\sigma(I)$]	2304
No. of variables	172
Minimum, maximum $\Delta\rho$ (e Å ^{−3})	−0.43, 0.44
Final Δ/σ	< 0.25
<i>R</i>	0.026
<i>wR</i>	0.030
<i>S</i>	0.58
Weighting scheme, w	$[\sigma^2(F) + gF^2]^{-1}$
<i>g</i>	0.0013

* Scan width, $\Delta\omega = (y + 0.35\tan\theta)^\circ$.† Aperture width = $(x + 1.05\tan\theta)$ mm.Table 2. *Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters (Å² × 10³)*

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Sn(1)	2195 (1)	1035 (1)	2451 (1)	35 (1)
Cl(1)	570 (1)	1226 (1)	4236 (1)	44 (1)
Cl(2)	3518 (1)	635 (1)	465 (2)	57 (1)
Cl(3)	772 (1)	1525 (1)	206 (1)	59 (1)
Cl(4)	3424 (1)	464 (1)	4646 (2)	69 (1)
Cl(5)	3186 (1)	2169 (1)	2895 (2)	59 (1)
O(1)	1245 (3)	20 (2)	1929 (5)	57 (1)
O(2)	1209 (3)	148 (2)	7537 (4)	49 (1)
N(1)	8101 (3)	1263 (2)	1324 (4)	41 (1)
N(2)	7594 (3)	1072 (2)	−335 (4)	39 (1)
C(3)	6570 (4)	1404 (2)	−670 (5)	39 (1)
C(4)	6197 (3)	1882 (2)	644 (5)	43 (1)
C(5)	7207 (3)	1781 (2)	2094 (5)	43 (1)
C(6)	5820 (5)	1314 (3)	−2282 (6)	58 (2)
C(7)	7913 (5)	2468 (3)	2549 (7)	68 (2)
C(8)	6736 (6)	1397 (4)	3542 (8)	91 (3)

Bond lengths and angles for the $[\text{SnCl}_5(\text{H}_2\text{O})]^-$ and dihydropyrazolium moieties are shown in Table 3. A survey using the Cambridge Structural Database (1991) (CSD) revealed the X-ray crystal structures of only two compounds containing the $[\text{SnCl}_5(\text{H}_2\text{O})]^-$ ion, *viz.* (i) with a highly complex Mo- and Sn- containing cation (Einstein & Field, 1975) and (ii) with another Mo complex as cation (Ginzburg, Aleksandrov, Struchkov, Setkina & Kursanov, 1980). Another compound (iii) contains the $[\text{SnCl}_5(\text{thf})]^-$ ion, the counter ion being *trans*- $[\text{TiCl}_2(\text{thf})_4]^+$; the O atom of a thf moiety is bonded to the Sn atom in the complex anion (Janas, Sobota & Lis, 1988). The range of the Sn—Cl bond lengths for PYFA is 2.361 (2)–2.436 (1) Å and for (i), (ii) and (iii) is 2.376 (3)–2.399 (3) Å. The bond length of Sn—O(1) for PYFA is 2.166 (4) Å and the range for (i), (ii) and (iii) is 2.235 (7)–2.269 (8) Å. Bond angles about the Sn atom vary from 83.6 (1) to 97.0 (1)°, and for (i), (ii) and (iii) from 82.4 (1) to 95.8 (1)°. The

bond lengths and bond angles of the dihydropyrazolium ring agree well with those recently published in the iminium moiety series (Nassimbeni, Stephen & Van Schalkwyk, 1991*a,b*).

A strong hydrogen-bonding scheme, five bonds in all, exists in PYFA (Fig. 1*b*), interlinking some of the ions, the pyrazolium ring and water of crystallization. The coordinated water molecule is linked to the water of crystallization *via* a hydrogen bond, O(1)—H···O(2), with O···O distance 2.746 (5) Å, and to N(2) *via* a hydrogen bond O(1)—H···N(2) with O···N distance 2.778 (5) Å. The water in turn is linked to Cl(2), the O(2)—H···Cl(2) bond having an O···Cl distance of 3.383 (3) Å. Finally, N(1) is linked through two H atoms, the bonds being N(1)—H···O(2) and N(1)—H···Cl(3) with distances N···O and N···Cl of 2.851 (5) and 3.152 (4) Å respectively. Hydrogen-bond angles range from 146.3 (3) to 172.4 (4)°.

On the grounds that the function of $(\text{CF}_3)_2\text{CO}$ was to provide a dipolar aprotic medium for the interaction of water with hexachlorostannate, PYRA was dissolved in DMSO-containing water (20%) and

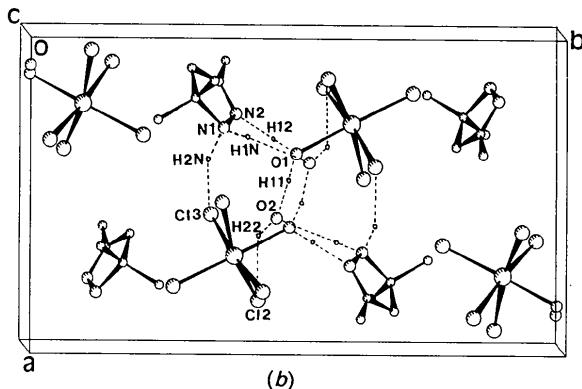
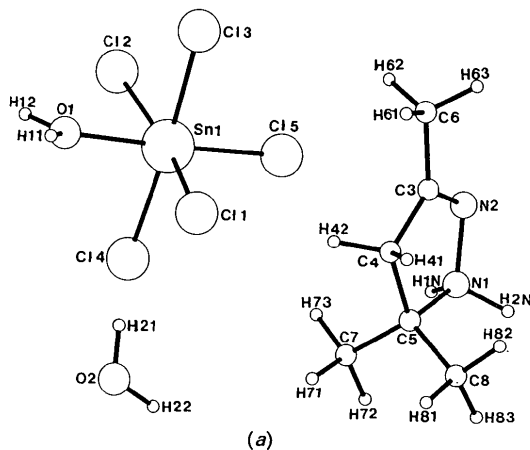


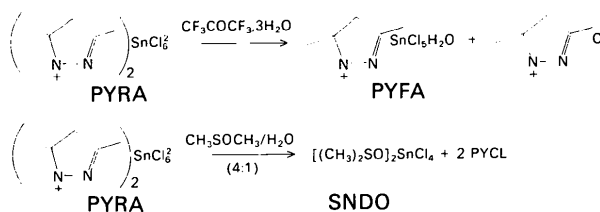
Fig. 1. Diagrams showing (a) perspective view of PYFA with atomic nomenclature and (b) packing of PYFA viewed along [001] with the hydrogen-bonding scheme.

Table 3. Bond distances (Å) and bond angles (°)

Sn(1)—Cl(1)	2.422 (1)	N(1)—C(5)	1.539 (5)
Sn(1)—Cl(2)	2.390 (2)	N(2)—C(3)	1.267 (5)
Sn(1)—Cl(3)	2.436 (1)	C(3)—C(4)	1.479 (6)
Sn(1)—Cl(4)	2.361 (2)	C(3)—C(6)	1.476 (6)
Sn(1)—Cl(5)	2.371 (2)	C(4)—C(5)	1.531 (5)
Sn(1)—O(1)	2.165 (4)	C(5)—C(7)	1.511 (7)
N(1)—N(2)	1.449 (5)	C(5)—C(8)	1.511 (8)
Cl(5)—Sn(1)—O(1)	177.2 (1)	N(2)—N(1)—C(5)	110.3 (3)
Cl(4)—Sn(1)—O(1)	88.5 (1)	N(1)—N(2)—C(3)	108.2 (3)
Cl(4)—Sn(1)—Cl(5)	94.3 (1)	N(2)—C(3)—C(6)	121.1 (4)
Cl(3)—Sn(1)—O(1)	86.1 (1)	N(2)—C(3)—C(4)	115.8 (4)
Cl(3)—Sn(1)—Cl(5)	91.2 (1)	C(4)—C(3)—C(6)	123.2 (4)
Cl(3)—Sn(1)—Cl(4)	174.1 (1)	C(3)—C(4)—C(5)	105.1 (3)
Cl(2)—Sn(1)—O(1)	84.3 (1)	N(1)—C(5)—C(4)	100.6 (3)
Cl(2)—Sn(1)—Cl(5)	95.0 (1)	C(4)—C(5)—C(8)	113.0 (4)
Cl(2)—Sn(1)—Cl(4)	92.7 (1)	C(4)—C(5)—C(7)	112.6 (4)
Cl(2)—Sn(1)—Cl(3)	88.9 (1)	N(1)—C(5)—C(8)	107.7 (4)
Cl(1)—Sn(1)—O(1)	83.6 (1)	N(1)—C(5)—C(7)	107.8 (3)
Cl(1)—Sn(1)—Cl(5)	97.0 (1)	C(7)—C(5)—C(8)	114.0 (4)
Cl(1)—Sn(1)—Cl(4)	89.6 (1)		
Cl(1)—Sn(1)—Cl(3)	87.7 (1)		
Cl(1)—Sn(1)—Cl(2)	167.6 (1)		

allowed to stand. The object was to investigate whether in a similar manner the hexachlorostannate ion would undergo nucleophilic displacement by water. Within a matter of days, prismatic crystals grew which had m.p. 450 K (decomposition), micro-analysis showing the substance to be devoid of N. X-ray crystal analysis, using similar procedures to those described for PYFA, proved the compound to be tetrachlorobis(dimethyl sulfoxide)tin(IV), $[\text{SnCl}_4(\text{C}_2\text{H}_6\text{OS})_2]$, [SNDO (see Fig. 2); cell dimensions $a = 7.379$ (1), $b = 14.433$ (1), $c = 13.383$ (1) Å and $\beta = 91.43$ (1)°, space group $P2_1/n$, final $R = 0.033$]. The crystal structure of the same compound, obtained on attempted recrystallization from DMSO of the reaction product of SnCl_4 and N,N' -diethylmalonamide, was published by Kisenyi, Willey & Drew (1985) ($R = 0.065$; no absorption correction applied). The molecules of dimethyl sulfoxide are bonded through O in *cis* positions relative to the Sn atom, the same product being obtained by replacement of two Cl^- ions from $[\text{SnCl}_6]^{2-}$ or by displacement of a 1,3-dicarbonyl moiety from its presumed complex with the neutral SnCl_4 . The standard deviations of bond lengths and bond angles of the structure determined by Kisenyi, Willey & Drew (1985) are, on average, twice those found here, but an analysis of these differences indicates that publication of a complete set of coordinates and other structural parameters for SNDO is not warranted. The ^1H NMR spectrum of SNDO in dimethyl sulfoxide- d_6 consisted of a singlet at δ 2.53, the same chemical shift value as was given by added dimethyl sulfoxide. The scheme below illustrates the displacement reaction within the anion of PYRA leading to PYFA, and the capture of dimethyl sulfoxide by the Sn-containing moiety with concomitant elimination of the dihydropyrazolium ion; PYCL

(Nassimbeni, Stephen & Van Schalkwyk, 1991a) is presumably formed as a by-product in each case. No attempt was made to isolate PYCL.



These examples of displacement of Cl atoms by O atoms led to a CSD search for the existence of examples of the SnCl_4O_2 moiety within crystalline structures. Eight were found. Coordination between Sn and organic moieties *via* O atoms gives rise to the following structures, two in the *cis* positions: (i) $\text{SnCl}_4\cdot 2\text{OPPh}_3$ (Tursina, Aslanov, Medvedev & Yatsenko, 1985) and (ii) $\text{SnCl}_4\cdot(4\text{-}p\text{'BuC}_6\text{H}_4\text{CHO})_2$ (Denmark, Henke & Weber, 1987); and three in the *trans* positions: (iii) $\text{SnCl}_4\cdot 2\text{Me}_2\text{N}_2\text{PO}$ (Aslanov, Ionov, Attiya, Permin & Petrosyan, 1977), (iv) $\text{SnCl}_4\cdot 4\text{C}_6\text{H}_{11}\text{OH}$, with binding through O atoms of two of the cyclohexanol molecules (Fournet & Theobald, 1981) and (v) $\text{SnCl}_4\cdot 2\text{C}_{11}\text{H}_{12}\text{O}_2$, with binding through the carbonyl O atoms of ethyl cinnamate moieties (Lewis, Oxman & Huffman, 1984). Coordination between Sn and crown ether complexes *via* H_2O gives rise to organic moieties located in the *cis* positions: (vi) $\text{SnCl}_4\cdot 18\text{-crown-6}\cdot 4\text{H}_2\text{O}$ (Valle, Cassol & Russo, 1984) and (vii) $\text{SnCl}_4\cdot 18\text{-crown-6}\cdot 4\text{H}_2\text{O}\cdot \text{CHCl}_3$ (Cusack, Patel, Smith, Allen & Nowell, 1984); and in the *trans* positions: (viii) $\text{SnCl}_4\cdot 15\text{-crown-5}\cdot 2\text{H}_2\text{O}$ (Hough, Nicholson & Vasudevan, 1986).

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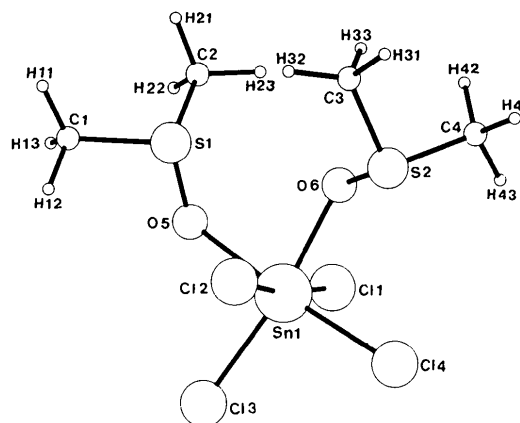


Fig. 2. Perspective view of SNDO with atomic nomenclature.

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Structure of Dichloro(η^5 -cyclopentadienyl)(2-propenyl- η^5 -cyclopentadienyl)titanium(IV)

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Abstract. $[\text{TiCl}_2(\text{C}_5\text{H}_5)(\text{C}_8\text{H}_9)]$, $M_r = 289.06$, monoclinic, $P2_1/c$, $a = 8.276$ (1), $b = 12.032$ (2), $c = 12.987$ (2) Å, $\beta = 97.11$ (1)°, $V = 1283.3$ (7) Å³, $Z = 4$, $D_m = 1.45$ (5), $D_x = 1.496$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 1.05$ mm⁻¹, $F(000) = 592$, $T = 298$ K, final $R = 0.0422$ and $wR = 0.0504$ for 1710 observed reflections with $I > 2.5\sigma(I)$. The cyclopentadienyl ring is symmetrically bonded to Ti [range of Ti—C distances 2.364 (7)–2.384 (8) Å] but the 2-propenylcyclopentadienyl ring is asymmetrically bonded [Ti—C 2.345 (4)–2.478 (4) Å]. There is rotational disorder in the cyclopentadienyl ring with a 60:40 occupancy ratio.

Introduction. Alkenylcyclopentadienylmetal complexes are of interest as precursors to organometallic polymers, but there have been few structural studies of such complexes (Ogasa *et al.*, 1991). The title complex is of interest since it can act as a precursor to titanium carbide by pyrolysis of its vinyl polymer.

Experimental. The title compound was synthesized by reaction of 2-propenylcyclopentadienyllithium (22.6 mmol) with $[\text{TiCl}_3(\eta^5\text{-C}_5\text{H}_5)]$ (22.6 mmol) in tetrahydrofuran (20 mL) at 193 K under a dry nitrogen atmosphere, then warmed to room temperature and allowed to react for 4 h. It was purified by chromatography on silica gel with benzene eluent and isolated in 60% yield. A suitable single crystal was obtained from tetrahydrofuran solution by slow cooling to 238 K. Then density was determined by flotation in aqueous ZnCl_2 solution; a dark red crystal (0.33 × 0.33 × 0.16 mm) was mounted on a glass fibre.

Measurements were made using an Enraf–Nonius CAD-4F diffractometer. Unit-cell dimensions were obtained from 20 high-angle reflections ($25.4 < 2\theta < 35.4^\circ$). Intensity data were collected with graphite-monochromated Mo $K\alpha$ radiation at 298 K in the θ – 2θ mode, with variable scan speed (1.37–2.75° min⁻¹) and scan width of $(0.9 + 0.35\tan\theta)^\circ$ with additional 25% extensions at both ends for backgrounds and a maximum time per datum of

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