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Electronic Structural Effects in the Structure of Trichloro(η^5-ethyltetramethylcyclopentadienyl)titanium(IV), Ti($C_{11}H_{17}$)Cl_3

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Abstract. $M_r = 303{\cdot}5$, monoclinic, $P2_1/m$, $a = 6{\cdot}618\,(1)$, $b = 11{\cdot}400\,(1)$, $c = 9{\cdot}262\,(2)$ Å, $\beta = 95{\cdot}81\,(2)°$, $U = 695{\cdot}1\,(3)$ Å^3, $Z = 2$, $D_x = 1{\cdot}448$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, $\mu = 11{\cdot}6$ cm^{-1}, $F(000) = 312$, $T = 153$ K, $R_w = 0{\cdot}029$ for 1368 reflections with $I/\sigma(I) \geq 3{\cdot}0$. The C_5 ring is slightly dished with Ti—C=2·352 (15) Å (av.); the Ti—Cl distance of 2·243 (10) Å (av.) is significantly shorter than in the parent (η^5-C_5H_5)$TiCl_3$. The reason for this shortening is discussed in terms of the inductive effect of the alkyl groups.

Introduction. It is well known that replacing a cyclopentadienyl group (η^5-C_5H_5) by a peralkylated species (η^5-C_5R_5; R = alkyl) in various metal derivatives significantly affects the chemical reactivity (Pez & Armor, 1981, and references cited by them; Maitlis, 1978). However, little information is available on the precise structural changes which are induced by this replacement. In the case of titanium in particular, structural data are available for (η^5-C_5X_5)$_2$$TiCl_2$ [X = H or Me (Tkachev & Atovmyan, 1972; McKenzie, Sanner & Bercaw, 1975)], where it was observed that steric interactions caused the methyl groups to be distorted out of the C_5 ring. The (C_5Me_5) derivative also showed greater distortion from tetrahedral geometry around the metal atom, with the (C_5Me_5)—Ti—(C_5Me_5) and (C_5Me_5)—Ti—Cl angles being 137·4 and 104° respectively, compared with 129 and 95° in (C_5H_5)$_2$$TiCl_2$. We were interested to assess the effects of alkylation in the presence of only one such group where steric effects would be expected to be minimal. We have therefore prepared the unreported derivative (η^5-C_5Me_4Et)$TiCl_3$, and have determined its crystal structure for comparison with the known structure of (η^5-C_5H_5)$TiCl_3$ (Duff, 1982).

Experimental. (η^5-C_5Me_4Et)$TiCl_3$ was prepared by a similar method to that used for the corresponding (C_5H_5) compound (Gorsich, 1958). Li(C_5Me_4Et) was added to an equimolar quantity of $TiCl_4$ under ether; after 24 h the solvent was removed, and the brown residue washed with cold pentane and extracted with 40 – 60° petroleum ether. Concentration of this extract, followed by cooling to 253 K, yielded red crystals, recrystallized from dichloromethane; Syntex $P2_1$ four-circle diffractometer, max. 2θ 50°, scan range ± 0·9° (2θ) around the $K\alpha_1$ – $K\alpha_2$ angles, scan speed 1 – 29° min^{-1}, depending on the intensity of a 2 s pre-scan; backgrounds measured at each end of the scan for 0·25 of the scan time; crystal held at 153 K with Syntex LT – 1 attachment; 3 standard reflections monitored every 100 reflections, no significant changes; unit-cell dimensions and standard deviations obtained by least-squares fit to 15 high-angle reflections; 1368 observed reflections corrected for absorption with *ABSCOR* (Alcock, 1970), max. and min. transmission factors 0·87 and 0·74; crystal 0·10 × 0·35 × 0·35 mm; systematic absence $0k0$, $k \neq 2n$ indicated space group $P2_1$ or $P2_1/m$, the latter shown to be correct by the successful refinement; h 0–7, k 0–13, l –10–10; Ti, Cl(1), C(1), C(11) and C(12) lie on special position 2(e), with m symmetry; initial structure solution by direct methods (*SHELX*; Sheldrick, 1976) locating Ti, Cl(1) and Cl(2); light atoms found on successive Fourier syntheses; hydrogen atoms visible on later maps, refined with isotropic temperature factors; final refinement on F by least squares; unit weights shown to be satisfactory by a weight analysis; final $R_w = 0{\cdot}029$; $\Delta_{\max}/\sigma = 0{\cdot}23$; computing with *XRAY76* system (Stewart, 1976) on a Burroughs B6700 computer; scattering factors in the analytical form and anomalous dispersion factors were taken from *International Tables for X-ray Crystallography* (1974).‡

Discussion. Final atomic coordinates are given in Table 1, and bond lengths and angles in Table 2.

Fig. 1 shows a general view of the molecule, which adopts a conformation with Cl(1) and the ethyl group

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‡ Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39062 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Atomic coordinates* ($\times 10^5$; *for* H $\times 10^4$) *and thermal parameters* (Å$^2 \times 10^3$) *with e.s.d.'s in parentheses*

$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

	x	y	z	U_{eq}/U_{iso}
Ti	9677 (2)	25000	30259 (1)	221
Cl(1)	21392 (2)	25000	53968 (2)	338
Cl(2)	25487 (2)	9660 (1)	21340 (1)	388
C(1)	−19123 (9)	25000	13577 (6)	257
C(2)	−20492 (6)	35062 (4)	22436 (4)	239
C(3)	−22230 (6)	31207 (3)	36776 (4)	225
C(11)	−18201 (11)	25000	−2603 (7)	380
C(12)	−39692 (13)	25000	−10421 (9)	463
C(21)	−21813 (8)	47537 (4)	17383 (6)	366
C(31)	−25031 (8)	38881 (5)	49535 (5)	336
H(111)	−1016 (8)	1843 (5)	−558 (5)	490 (16)
H(121)	−4713 (9)	1825 (5)	−752 (6)	556 (17)
H(123)	−3973 (16)	2500	−2007 (11)	827 (33)
H(211)	−1484 (10)	5295 (6)	2412 (7)	663 (19)
H(212)	−1588 (9)	4827 (5)	876 (6)	531 (17)
H(213)	−3490 (11)	5001 (6)	1590 (7)	733 (21)
H(311)	−1996 (9)	4630 (5)	4853 (5)	521 (17)
H(312)	−1841 (9)	3558 (5)	5805 (6)	582 (18)
H(313)	−3884 (10)	3947 (5)	5091 (6)	627 (18)

Table 2. *Bond lengths* (Å) *and angles* (°)

Ti–Cl(1)	2·2536 (5)	Cl(1)–Ti–Cl(2)	103·42 (1)
Ti–Cl(2)	2·2383 (2)	Cl(2)–Ti–Cl(2′)	102·75 (1)
Ti–C(1)	2·3289 (7)		
Ti–C(2)	2·3525 (5)		
Ti–C(3)	2·3626 (5)		
C(1)–C(2)	1·4185 (6)	C(2)–C(1)–C(1′)	107·92 (5)
C(2)–C(3)	1·4147 (6)	C(2)–C(1)–C(11)	125·94 (3)
C(3)–C(3′)	1·4152 (6)	C(1)–C(11)–C(12)	109·98 (6)
C(1)–C(11)	1·5060 (9)	C(1)–C(2)–C(3)	107·94 (4)
C(11)–C(12)	1·5293 (11)	C(1)–C(2)–C(21)	126·34 (4)
C(2)–C(21)	1·4970 (7)	C(3)–C(2)–C(21)	125·51 (4)
C(3)–C(31)	1·4968 (7)	C(2)–C(3)–C(3′)	108·10 (4)
C(11)–H(11)	0·975 (5)	C(2)–C(3)–C(31)	126·01 (4)
		C(3′)–C(3)–C(31)	125·77 (4)
		H(11)–C(11)–H(11′)	100·4 (5)

C(methyl)–H 0·931 (average, range 0·893–0·966, individual σ 0·005).

Primed atoms are related to unprimed ones by $x, \frac{1}{2} - y, z$.

Table 3. *Comparative distances* (Å)

E.s.d.'s quoted are the larger of the experimental e.s.d.'s and the spread between averaged values.

Compound	(C_5H_5)-$TiCl_3$	(C_5Me_4Et)-$TiCl_3$	$(C_5H_5)_2$-$TiCl_3$	$(C_5Me_5)_2$-$TiCl_2$
Reference	(*a*)	This work	(*b*)	(*c*)
Ti–Cl (av.)	2·303 (3)	2·243 (10)	2·36 (1)	2·349 (3)
Ti–C(av.)	2·29 (2)	2·352 (15)	2·43 (4)	2·442 (20)
Ti–ring plane	2·00	2·020 (1)	2·11	2·13
C–C (av.)	1·32 (2)	1·416 (2)	1·44 (4)	1·409 (10)

References: (*a*) Duff (1982); (*b*) Tkachev & Atovmyan (1972); (*c*) McKenzie *et al.* (1975).

opposite each other. One significant structural feature is that the ring is 'dished', with the alkyl carbon atoms out of the ring plane in the direction away from the metal atom by 0·060 (1) to 0·130 (1) Å (Fig. 2). The major bond distances for this and three related molecules are collected in Table 3. They show significant differences, though these are not easy to interpret, and the problems are compounded by the varying accuracy of the studies. In particular, the very short C–C distance in (C_5H_5)-$TiCl_3$ (a room-temperature investigation) may be attributed to thermal vibration and libration leading to an *apparent* shortening. This will also affect the Ti–C distance, but not the Ti–ring-plane distance, and it will be much less important in $(C_5H_5)_2TiCl_2$, because of steric interaction between the ring hydrogens.

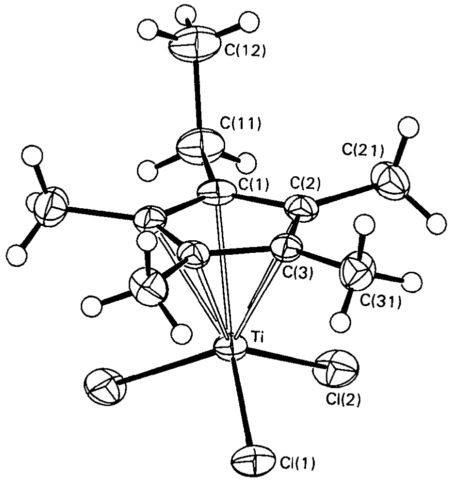

Fig. 1. Oblique view of the molecule, showing the principal atomic numbering.

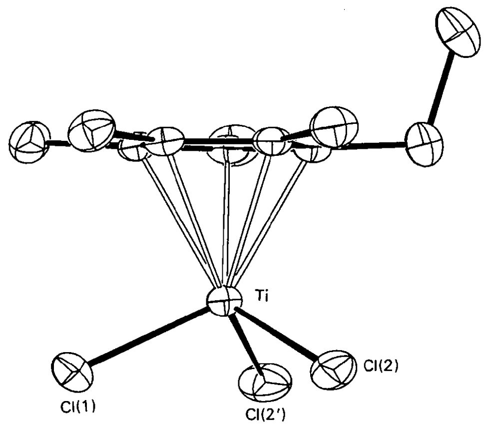

Fig. 2. Side-on view of the molecule, illustrating the deviations of the alkyl groups from the C_5 plane.

The most important effect of alkylation is the decreased Ti—Cl distance. This can be rationalized in terms of the inductive electron donation by the alkyl groups and is in accord with the suggestions of enhanced electron-releasing ability of a peralkylated C_5R_5 group based on chemical reactivity. This can be seen as increasing electron density in orbitals which are of bonding character for the Ti—Cl bonds. The strengthening of these bonds corresponds to the enhanced chemical stability for $(C_5R_5)TiX_3$ compounds. For $(C_5H_5)_2TiCl_2$, the effects are much smaller and the steric interference between the alkylated rings is probably more important (McKenzie *et al.*, 1975).

The crystal contains no significantly short intermolecular distances, and the packing is dominated by CH_3–CH_3 and CH_3–Cl contacts.

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Octacarbonyl-bis(μ-{iodo[tetracarbonyl(triphenylphosphine)rhenio]stannio(IV)})-dirhenium, $[Re_2(CO)_8\{Sn(I)Re(CO)_4[P(C_6H_5)_3]\}_2]$

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Abstract. $M_r = 2208{\cdot}7$, monoclinic, $P2_1/c$, $a = 9{\cdot}096\,(7)$, $b = 29{\cdot}271\,(9)$, $c = 11{\cdot}291\,(7)$ Å, $\beta = 93{\cdot}73\,(5)°$, $U = 3000$ Å^3, $Z = 2$, $D_x = 2{\cdot}445$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 10{\cdot}5$ mm^{-1}, $F(000) = 2012$, $T = 294\,(1)$ K. Final $R = 0{\cdot}034$ for 2978 observed reflections. The central fragment of the molecule consists of a planar Re_2Sn_2 rhombus with an Re—Re bond [r(Re—Re) = 3·176 (1) Å] across the metal ring. The iodine and $Re(C_{18}H_{15}P)(CO)_4$ ligand pairs bonded to Sn are in the *trans* position with respect to the ring plane.

Introduction. In the course of our investigation on the influence of different metal atoms on the geometry of four-membered metal rings in clusters of the type $[Mn_2(CO)_8\{\mu\text{-}M(X)Mn(CO)_5\}_2]$ (M = Ge, X = Br, I; M = Sn, X = Br, Cl) (Preut & Haupt, 1980) we have prepared the compound $[Re_2(CO)_8\{\mu\text{-}Sn(I)\text{-}Re(C_{18}H_{15}P)(CO)_4\}_2]$ and determined the crystal structure. The result of the structure analysis is furthermore used for our study of a relationship between packing forces and the geometry of the molecules in such crystals.

Experimental. The yellow crystals were prepared by a reaction of SnI_2 with $[Re_2(C_{18}H_{15}P)_2(CO)_8]$ in xylene at 443 K during a reaction time of four weeks in a bomb tube.

$\omega/2\theta$ scan, scan speed of 0·74–3·33° min^{-1} in θ, Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$, crystal size 0·3 × 0·3 × 0·4 mm, lattice parameters from least-squares fit with 24 reflections in the range $10{\cdot}6 \le \theta \le 13{\cdot}9°$; three standard reflections, recorded every 4 h: only random deviations; 4589 reflections measured, $2 \le \theta \le 23°$, h 0→9, k 0→32, l −12→12; after averaging: 2978 observed reflections with $F_o > 3\sigma(F_o)$, Lorentz–polarization correction, absorption correction *via* ψ-scans; systematic absences: ($h0l$) $l = 2n+1$ and ($0k0$) $k = 2n+1$, space group $P2_1/c$; structure solution with

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