Table 1. *Atomic coordinates and equivalent isotropic displacement parameters* (Å^2 × 10^2), *with e.s.d.'s in parentheses*

$$B_{\text{eq}} = (8\pi^2/3)\sum_{i=1}^{3}\sum_{j=1}^{3} U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Ni(1)	1.0000	$\frac{1}{4}$	$\frac{1}{8}$	1.99 (2)
Cl(1)	0.39099 (6)	0.6410	$\frac{1}{8}$	1.08 (3)
N(1)	1.0682 (2)	0.3161 (2)	0.0366 (2)	2.3 (1)
C(1)	1.1066 (3)	0.2758 (3)	−0.0223 (2)	3.1 (2)
C(2)	1.1502 (3)	0.3180 (4)	−0.0804 (3)	4.1 (3)
C(3)	1.1565 (3)	0.4036 (4)	−0.0780 (3)	4.2 (3)
C(4)	1.1179 (3)	0.4460 (3)	−0.0180 (3)	3.4 (2)
C(5)	1.0747 (3)	0.4009 (3)	0.0377 (2)	2.7 (2)

Table 2. *Bond lengths* (Å) *and angles* (°), *with e.s.d.'s in parentheses*

Ni(1)—Cl(1)	2.433 (1)	C(1)—C(2)	1.373 (6)
Ni(1)—N(1)	2.121 (3)	C(2)—C(3)	1.356 (7)
N(1)—C(1)	1.330 (5)	C(3)—C(4)	1.362 (6)
N(1)—C(5)	1.342 (5)	C(4)—C(5)	1.366 (5)
Cl(1)—Ni(1)—Cl(1*)	180.00	C(1)—N(1)—C(5)	116.9 (3)
Cl(1)—Ni(1)—N(1)	90.63 (9)	N(1)—C(1)—C(2)	122.3 (4)
Cl(1)—Ni(1)—N(1*)	89.37 (9)	C(1)—C(2)—C(3)	119.9 (5)
N(1)—Ni(1)—N(1*)	90.0 (2)	C(2)—C(3)—C(4)	118.6 (4)
Ni(1)—N(1)—C(1)	121.8 (3)	C(3)—C(4)—C(5)	119.0 (4)
Ni(1)—N(1)—C(5)	121.3 (3)	N(1)—C(5)—C(4)	123.2 (4)

* Indicates symmetry related atom.

3.343 (7) Å, well beyond the proximity needed for chemical bonding, and it shows diamagnetic behavior. The Ni—Cl distance, 2.433 (1) Å, in the title compound indicates that a chemical bond does exist and therefore the compound should be paramagnetic. The structural characterization of this compound, as well as the related Co compound, has been previously reported (Porai-Koshits, 1954). The present study determines all the relevant parameters to a higher degree of accuracy. A partial study has also been carried out on the related Fe system showing that it is isostructural (Forster & Dahm, 1972).

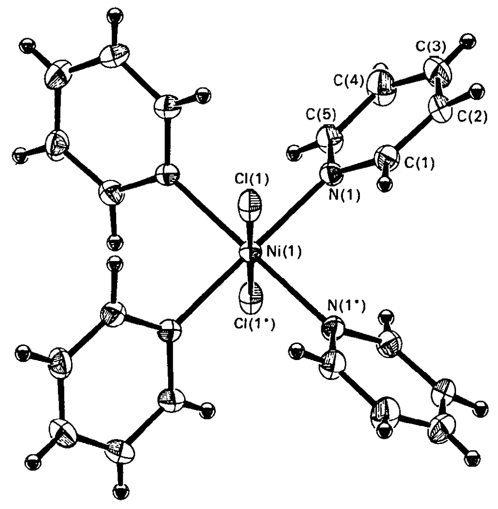

Fig. 1. *ORTEP*II (Johnson, 1976) representation showing the coordination of the central Ni atom and the atomic numbering scheme.

KHW thanks the Robert A. Welch Foundation for financial support of this research and the National Science Foundation for financial assistance in the purchase of the diffractometer.

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Acta Cryst. (1992). C**48**, 1837–1839

Structure of the μ-Azido-dichloro(η^5-methylcyclopentadienyl)titanium(IV) Dimer

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(*Received* 15 *October* 1991; *accepted* 20 *February* 1992)

Abstract. Di-μ-azido-N:N-bis[dichloro(η^5-methylcyclopentadienyl)titanium(IV)], $[\text{TiCl}_2(\text{N}_3)(\text{C}_6\text{H}_7)]_2$, $M_r = 479.90$, monoclinic, $P2_1/c$, $a = 7.101$ (2), $b =$ 13.920 (3), $c = 19.050$ (4) Å, $\beta = 98.47$ (2)°, $V =$ 1863 (5) Å^3, $Z = 4$, $D_x = 1.71$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 14.4$ cm^{-1}, $F(000) = 960$, $T =$

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294 (1) K, $R = 0.048$ for 2018 unique reflections with $F_o^2 > 3.0\sigma(F_o^2)$. The solid-state structure of the title compound consists of two $(CH_3C_5H_4)TiCl_2(N_3)$ units that form a dimer through azido bridges; both azido ligands are 1,1-μ-*N*-bonded to each Ti atom. The coordination sphere around Ti is distorted square pyramidal with two N and two Cl atoms describing the base and C* (center of the cyclopentadienyl ring) at the apex of the polyhedron with C*—Ti—*L* angles (*L* = Cl or N) of 110.6–114.4°. Some rotational disorder in the cyclopentadienyl rings causes large thermal ellipsoids and a wide range of C—C bond distances in the rings.

Experimental. $[(CH_3C_5H_4)TiCl_2(N_3)]_2$ was synthesized from the reaction of NaN_3 and $(CH_3C_5H_4)TiCl_3$ in THF (tetrahydrofuran), and red single crystals were obtained on cooling saturated THF solutions to 243 K. Choukroun, Gervais & Dilworth (1979) describe the preparation of $(C_5H_5)TiCl_2(N_3)$ using $(CH_3)_3SiN_3$. A chunky crystal, 0.30 × 0.40 × 0.40 mm, was mounted in a glass capillary on an Enraf–Nonius CAD-4 diffractometer and data were collected using graphite-monochromated Mo $K\alpha$ radiation and ω–2θ-scan technique to maximum $2\theta = 52.0°$ and for $0 \le h \le 8$, $0 \le k \le 17$, $-23 \le l \le 23$. Cell dimensions were obtained from least-squares refinement on 25 reflections ($9 < \theta < 15°$). Lorentz and polarization corrections were applied. Three standard reflections indicated a total gain in intensity of 0.5%; an anisotropic decay correction was applied (from 0.946 to 1.045 on *I*). An empirical absorption correction (from 0.925 to 0.999 on *I*) was made. Reflection averaging gave $R_{\text{int}} = 0.015$ based on *I*. A total of 4139 reflections were measured, of which 3824 were unique and 2018 had $F_o^2 > 3.0\sigma(F_o^2)$. The structure was solved by direct methods (*MULTAN*80; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and difference Fourier syntheses. Refinement was by full-matrix least squares minimizing $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$. H atoms were calculated at idealized positions and included in the refinement as riding atoms with fixed thermal parameters. Non-H atoms were refined with anisotropic thermal parameters. Refinement of 217 parameters converged to $R = 0.048$, $wR = 0.067$, $S = 2.01$; final $(\Delta/\sigma)_{\max} \le 0.01$; high peak in final difference map 0.48 (8), low peak −0.19 (8) e Å^{-3}. Scattering factors for neutral atoms and the values for f' and f'' were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2, pp. 71–102; Table 2.3.1, pp. 149–150). Computations were performed with *MolEN* (Fair, 1990); Fig. 1, showing the atom-numbering scheme, was produced with *ORTEP*II (Johnson, 1976). Table 1 gives the final atomic coordinates, and selected bond lengths and angles are listed in Table 2.*

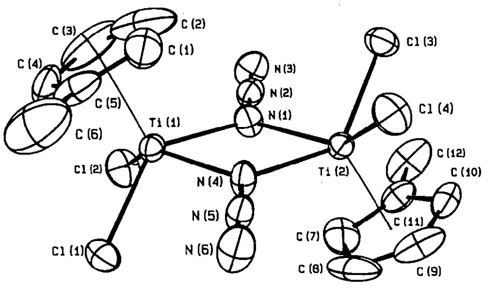

Fig. 1. Molecular structure and numbering scheme of $[(CH_3C_5H_4)TiCl_2(N_3)]_2$ with 30% probability ellipsoids.

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

$B_{\text{eq}} = (8\pi^2/3) \times$ trace of the orthogonalized **U** tensor. C(1*) is the centroid of the C(1)—C(5) ring, C(2*) is the centroid of the C(7)—C(11) ring.

	x	*y*	*z*	B_{eq}
Ti(1)	0.6932 (1)	0.46992 (7)	0.65993 (5)	3.54 (2)
Ti(2)	0.8047 (1)	0.49655 (7)	0.84539 (5)	3.22 (2)
Cl(1)	0.4690 (2)	0.5788 (1)	0.61374 (9)	5.82 (4)
Cl(2)	0.4877 (3)	0.3453 (1)	0.6268 (1)	6.65 (5)
Cl(3)	1.0251 (2)	0.3852 (1)	0.89107 (9)	5.26 (4)
Cl(4)	1.0204 (2)	0.6180 (1)	0.87363 (9)	5.51 (4)
N(1)	0.7478 (6)	0.3984 (3)	0.7592 (2)	4.5 (1)
N(2)	0.7569 (6)	0.3108 (4)	0.7646 (2)	4.5 (1)
N(3)	0.7644 (8)	0.2295 (4)	0.7693 (3)	6.2 (1)
N(4)	0.7412 (6)	0.5688 (3)	0.7473 (2)	4.3 (1)
N(5)	0.7364 (6)	0.6561 (3)	0.7405 (2)	4.4 (1)
N(6)	0.7319 (8)	0.7364 (4)	0.7347 (3)	6.1 (1)
C(1)	1.0075 (9)	0.5098 (7)	0.6517 (4)	8.0 (2)
C(2)	0.996 (1)	0.4135 (6)	0.6503 (5)	12.8 (3)
C(3)	0.891 (1)	0.3857 (7)	0.5961 (5)	12.1 (3)
C(4)	0.824 (1)	0.4623 (6)	0.5557 (3)	7.5 (2)
C(5)	0.9020 (9)	0.5455 (5)	0.5910 (3)	6.6 (2)
C(6)	0.879 (1)	0.6425 (7)	0.5608 (5)	13.3 (3)
C(7)	0.4910 (8)	0.4597 (6)	0.8585 (4)	7.4 (2)
C(8)	0.5144 (9)	0.5618 (6)	0.8612 (4)	9.1 (2)
C(9)	0.637 (1)	0.5834 (5)	0.9187 (4)	7.7 (2)
C(10)	0.6928 (8)	0.5026 (5)	0.9541 (3)	5.1 (1)
C(11)	0.6028 (8)	0.4239 (4)	0.9189 (3)	5.0 (1)
C(12)	0.621 (1)	0.3229 (5)	0.9426 (4)	9.3 (2)
C(1*)	0.9241	0.4634	0.6090	
C(2*)	0.5876	0.5063	0.9023	

Related literature. For reviews on transition-metal chemistry, which include titanium–azido complexes, see Poli (1991) and Vrieze & van Koten (1987). Structural studies on Ti–azido compounds show the azido as a 1,1-μ-bridging ligand $\{[(C_6H_5)_4As]_2[TiCl_4(N_3)]_2$ (Müller, Dyck & Dehnicke, 1980); $[TiCl_3(N_3)]_x$ (Wellern & Müller, 1976)} or as a terminal ligand $\{[(C_5H_5)_2Ti(N_3)_2]$ (de Gil, de Burguera, Rivera & Maxfield, 1977); $[(C_6H_5)_4As]_2[TiCl_4(N_3)_2]$ (Dyck, Dehnicke, Weller & Müller, 1980)}.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond distances and angles, torsion angles and a selection of least-squares planes, as well as a packing diagram, have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55220 (32 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR0406]

Table 2. *Selected distances* (Å) *and angles* (°)

C(1*) is the centroid of the C(1)—C(5) ring, C(2*) is the centroid of the C(7)—C(11) ring.

Ti(1)—Cl(1)	2.279 (2)	Ti(2)—Cl(3)	2.282 (2)
Ti(1)—Cl(2)	2.295 (2)	Ti(2)—Cl(4)	2.292 (2)
Ti(1)—N(1)	2.121 (4)	Ti(2)—N(1)	2.128 (4)
Ti(1)—N(4)	2.148 (4)	Ti(2)—N(4)	2.112 (4)
Ti(1)—C(1)	2.327 (7)	Ti(2)—C(7)	2.336 (6)
Ti(1)—C(2)	2.321 (8)	Ti(2)—C(8)	2.313 (7)
Ti(1)—C(3)	2.308 (9)	Ti(2)—C(9)	2.308 (8)
Ti(1)—C(4)	2.317 (7)	Ti(2)—C(10)	2.327 (6)
Ti(1)—C(5)	2.367 (7)	Ti(2)—C(11)	2.373 (6)
Ti(1)—C(1*)	2.026	Ti(2)—C(2*)	2.014
N(1)—N(2)	1.225 (7)	N(4)—N(5)	1.222 (7)
N(2)—N(3)	1.136 (7)	N(5)—N(6)	1.123 (7)
Ti(1)···Ti(2)	3.524 (1)	N(1)···N(4)	2.383 (7)
Cl(1)—Ti(1)—Cl(2)	90.96 (7)	Cl(3)—Ti(2)—Cl(4)	90.83 (6)
Cl(1)—Ti(1)—N(1)	133.0 (1)	Cl(4)—Ti(2)—N(1)	134.3 (1)
Cl(1)—Ti(1)—N(4)	84.0 (1)	Cl(4)—Ti(2)—N(4)	84.5 (1)
Cl(2)—Ti(1)—N(4)	136.0 (1)	Cl(3)—Ti(2)—N(4)	134.9 (1)
Cl(2)—Ti(1)—N(1)	85.2 (1)	Cl(3)—Ti(2)—N(1)	84.3 (1)
Cl(1)—Ti(1)—C(1*)	114.4	Cl(3)—Ti(2)—C(2*)	112.1
Cl(2)—Ti(1)—C(1*)	111.2	Cl(4)—Ti(2)—C(2*)	111.2
N(1)—Ti(1)—C(1*)	110.6	N(1)—Ti(2)—C(2*)	112.7
N(4)—Ti(1)—C(1*)	110.6	N(4)—Ti(2)—C(2*)	111.3
Average	111.7	Average	111.8
N(1)—Ti(1)—N(4)	67.9 (2)	N(1)—Ti(2)—N(4)	68.3 (2)
Ti(1)—N(1)—N(2)	122.9 (3)	Ti(2)—N(1)—N(2)	124.9 (3)
Ti(1)—N(4)—N(5)	123.8 (3)	Ti(2)—N(4)—N(5)	124.5 (3)
Ti(1)—N(1)—Ti(2)	112.0 (2)	Ti(1)—N(4)—Ti(2)	111.7 (2)
N(1)—N(2)—N(3)	179.3 (5)	N(4)—N(5)—N(6)	179.6 (5)
N(1)···N(4)—N(5)	179.3 (3)	N(4)···N(1)—N(2)	177.9 (4)
N(4)—Ti(2)—N(1)—Ti(1)	2.0 (2)	Cl(4)—Ti(2)—N(1)—Ti(1)	−55.9 (3)
Cl(1)—Ti(1)—N(1)—Ti(2)	−59.6 (3)	C(1*)—Ti(1)—N(1)—Ti(2)	102.7 (2)
Cl(2)—Ti(1)—N(1)—Ti(2)	−146.5 (2)	C(2*)—Ti(2)—N(1)—Ti(1)	107.0 (2)
Cl(3)—Ti(2)—N(1)—Ti(1)	−141.5 (2)		

We thank the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work, and the College of Art and Sciences for support of the X-ray crystallographic facilities.

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Acta Cryst. (1992). C**48**, 1839–1841

Structure of Triphenyltin Chloride–Triphenylphosphine Oxide (1/1) Complex

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(*Received* 21 *October* 1991; *accepted* 27 *January* 1992)

Abstract. Chloro(triphenyl)(triphenylphosphine oxide)tin, $[SnCl\{(C_6H_5)_3PO\}(C_6H_5)_3]$, $M_r = 663.76$, monoclinic, $P2_1/c$, $a = 10.671$ (1), $b = 11.777$ (2), $c = 25.494$ (1) Å, $\beta = 98.148$ (5)°, $V = 3171.5$ (7) Å^3, $Z = 4$, $D_x = 1.390$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 9.67$ cm^{-1}, $F(000) = 1344$, $T = 298$ K, $R = 0.033$ for 3327 $[I \geq 3\sigma(I)]$ reflections. Triphenyltin chloride forms a molecular complex with triphenylphosphine oxide in which Sn—Cl = 2.470 (2) and Sn—O = 2.391 (4) Å. The geometry of Sn is a *trans*-C_3SnClO trigonal bipyramid.

Experimental. Triphenyltin chloride and triphenylphosphine were dissolved in equimolar amounts in chloroform; slow evaporation of the solvent furnished clear crystals of the complex. A crystal measuring approximately 0.14 × 0.22 × 0.25 mm was used in the structure analysis. Measurements were performed on an Enraf–Nonius diffractometer. Accurate unit-cell parameters were obtained from the 25 most intense reflections in the $13 \leq 2\theta \leq 15°$ thin shell. Intensity data were gathered to a Bragg angle of 50° ($0 \leq h \leq 12$, $0 \leq k \leq 14$, $-30 \leq l \leq 30$) by

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