Journal of Organometallic Chemistry, 247 (1983) 1–6
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

DIAZASILAMETALLACYCLES: CRYSTAL AND MOLECULAR STRUCTURE OF $\overline{Ti(NBu^tSiMe_2NBu^t)}Cl_2$

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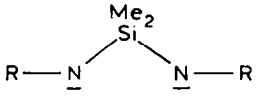
(Received September 24th, 1982; in revised form December 13th, 1982)

Summary

The crystal and molecular structure of $\overline{Ti(NBu^tSiMe_2NBu^t)}Cl_2$ has been determined by X-ray diffraction studies. Crystal data: tetragonal, space group $P4_12_12$, a 9.197(5), c 20.838(8) Å, d_{calcd} 1.20 g cm^{-3} for $Z = 4$ and $V = 1762.6$ Å^3. Final R factor based on 944 reflections (654 observed) was 0.038 ($R_w = 0.039$). The complex consists of mononuclear units with the titanium atoms in a distorted tetrahedral environment.

Introduction

There is currently much interest in four-membered carbocyclic metallocycles of the *d*-block transition metals since they are thought to be important intermediates in catalytic reactions such as olefin metathesis and cyclooligomerizations of alkenes and alkynes [1]. However, four-membered metallocycles formed from diamide dianions of type I and transition metals are relatively rare.



(I)

So far complexes containing I as part of a four-membered metallocycle include those of tin(II) [2] and titanium(IV) [3] for which structural data from X-ray diffraction studies are available for $(\overline{SnNBu^tSiMe_2NBu^t})_2$ [4] and for $\overline{Ti(NBu^tSiMe_2NBu^t)}_2$ [5].

The interaction of the dianion II derived from $(HNBu^t)_2SiMe_2$ with $TiCl_4$ yields the titanacyclobutane $\overline{Ti(NBu^tSiMe_2NBu^t)}Cl_2$ (1) [3]. We have determined the X-ray crystal structure of II in order to gain further structural information on these ususal titanium(IV) heterocycles.

0022-328X/83/$03.00

Experimental

$Ti(NBu^tSiMe_2NBu^t)Cl_2$ was prepared according to the literature method [3]. Crystals were grown from concentrated hexane solutions at −30°C and an appropriate single crystal was sealed under nitrogen in a thin-walled glass capillary. Final lattice parameters as determined from 15 high-angle reflections ($2\theta > 40°$) carefully centered on an Enraf–Nonius CAD-4 are given in Table 1. Intensity data were recorded on the diffractometer in the usual manner [6]. All reflections in one independent octant out to $2\theta = 50°$ were measured; 654 reflections were considered observed ($I \geq 3\sigma(I)$). The intensities were corrected for Lorentz and polarization effects but, not for absorption.

The space group was determined to be $P4_32_12$ or its enantiomorh $P4_12_12$ based on the systematic absences of $00l$; $l = 4n$ and $h00$; $h = 2n$. Using the MULTAN74 system of programs and choosing $P4_32_12$ as the space group, the titanium and silicon atoms were found to reside on the two-fold rotation axis. Difference Fourier maps phased on these positions revealed the location of the remaining non-hydrogen atoms. Refinement with isotropic temperature factors led to a reliability index of $R = \Sigma||F_0| - |F_c||/|F_0| = 0.087$. Conversion to anisotropic thermal parameters and further refinement led to $R = 0.051$. The hydrogen atoms of the methyl group were placed at calculated positions 1.00 Å from the bonded carbon atoms. The hydrogen atoms were given fixed isotropic thermal parameters of 6.33 Å^2. The methyl groups were refined as rigid bodies using the SHELX [7] system. Further cycles of refinement led to final values of $R = 0.040$ and $R_w = [\Sigma w(|F_0 - F_c|)^2/\Sigma(F_0)^2]^{1/2} = 0.041$. Transformation of the atomic coordinates to the enantiomorphic space group

TABLE 1

CRYSTAL DATA AND SUMMARY OF INTENSITY DATA COLLECTION AND STRUCTURAL REFINEMENT

Molecular weight	319.24
Space group	$P4_12_12$
Cell constants	
a (Å)	9.197(5)
c (Å)	20.838(8)
Cell volume (Å^3)	1762.6
Molecules/unit cell	4
ρ_{calcd} (g cm^{-3})	1.20
μ_{calcd} (cm^{-1})	8.51
Radiation	Mo-K_α 0.71069 Å
Maximum crystal dimensions (nm)	0.15 × 0.21 × 0.55
Scan width (°deg)	0.8 + 0.2 tan(θ)
Standard reflections	(200), (020), (004)
Decay of standards	±2%
Reflections measured	944
$2\theta_{max}$ (deg)	50
Reflections observed	654
Number of variables	74
GOF	1.03
R	0.038
R_w	0.039

$P4_12_12$ and further cycles of refinement led to final values of $R = 0.038$ and $R_w = 0.039$. Based on this, $P4_12_12$ was chosen as the correct space group. The largest parameter shifts in the final cycle of refinement were less than 0.01 of their estimated standard deviations.

A final difference Fourier showed no feature greater than 0.4 e/Å^3. The standard deviation of an observation of unit weight was 1.03. Unit weights were used at all stages; no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The function $w(|F_o| - |F_c|)^2$ was minimized. The SHELX [7] system was used for all calculations. Neutral atom scattering factors stored within the SHELX program were used for Si, N, C and H; those for Ti were taken from ref. 8.

Discussion

In order to gain further structural information concerning the nature of the unusual $(NBu^t)_2SiMe_2^{2-}$ ligand we have determined the structure of $\overline{Ti(NBu^tSiMe_2\text{-}NBu^t)}Cl_2$ (II) by X-ray diffraction. Details of crystal data collection and structural refinement are shown in Table 1, bond distances and angles are presented in Table 2, and the atomic positional and thermal parameters are listed in Tables 3 and 4, respectively. Tables of structure factors are deposited elsewhere [10].

The molecular structure of II consists of monomeric units in which the atoms of the TiNSiN metallocycle are coplanar. This plane is orthogonal to that which contains the two chloride ligands thus giving the titanium atom a distorted tetrahedral environment. A view of II is shown in Fig. 1, which also shows the atom numbering scheme used.

The bonding parameters for II are similar to those found for the spirocyclic complex $\overline{Ti(NBu^tSiMe_2NBu^t)}_2$. However, significant differences are observed in the

TABLE 2

BOND DISTANCES AND ANGLES FOR $\overline{Ti(NBu^tSiMe_2NBu^t)}Cl_2$

Atoms	Distance	Atoms	Distance
Ti–Cl(1)	2.250(2)	Ti–Si	2.604(3)
Ti–N(1)	1.829(5)	Si–N(1)	1.766(5)
Si–C(5)	1.845(6)	N(1)–C(1)	1.476(7)
C(1)–C(2)	1.49(1)	C(1)–C(3)	1.44(1)
C(1)–C(4)	1.51(1)		

Atoms	Angle	Atoms	Angle
Cl(1)–Ti–Cl(1)	96.89(8)	Cl(1)–Ti–Si	124.50(7)
Cl(1)–Ti–N(1)	115.0(2)	C(5)–Si–C(5)	97.3(3)
Ti–Si–C(5)	124.1(3)	N(1)–Si–C(5)	113.3(3)
Ti–N(1)–Si	92.8(2)	Ti–N(1)–C(1)	136.1(5)
Si–N(1)–C(1)	131.1(4)	N(1)–C(1)–C(2)	108.4(6)
N(1)–C(1)–C(3)	112.4(7)	C(2)–C(1)–C(3)	113.8(8)
N(1)–C(1)–C(4)	110.1(6)	C(2)–C(1)–C(4)	105.8(8)
C(3)–C(1)–C(4)	106.1(9)		

TABLE 3

ATOMIC POSITIONAL PARAMETERS FOR $\overline{Ti(NBu^tSiMe_2NBu^t)}Cl_2$

Atom	x/a	y/b	z/c	U(eqv)
Ti	0.5287(1)	0.5287(1)	0.0000	0.052
Si	0.3285(2)	0.3285(2)	0.0000	0.055
Cl(1)	0.4972(3)	0.7562(2)	0.0373(1)	0.094
N(1)	0.4661(5)	0.3844(5)	0.0537(2)	0.054
C(1)	0.5086(9)	0.3282(8)	0.1173(3)	0.073
C(2)	0.644(1)	0.405(1)	0.1382(4)	0.206
C(3)	0.392(1)	0.336(2)	0.1632(4)	0.237
C(4)	0.549(2)	0.169(1)	0.1125(5)	0.234
C(5)	0.3555(9)	0.1427(7)	−0.0311(3)	0.085
H(1)	0.689(1)	0.367(1)	0.1786(4)	(iso)
H(2)	0.722(1)	0.444(1)	0.1095(4)	(iso)
H(3)	0.574(1)	0.485(1)	0.1490(4)	(iso)
H(4)	0.406(1)	0.284(2)	0.2058(4)	(iso)
H(5)	0.362(1)	0.441(2)	0.1750(4)	(iso)
H(6)	0.293(1)	0.289(2)	0.1421(4)	(iso)
H(7)	0.628(2)	0.216(1)	0.0868(5)	(iso)
H(8)	0.592(2)	0.120(1)	0.1508(5)	(iso)
H(9)	0.498(2)	0.096(1)	0.0854(5)	(iso)
H(10)	0.3254(9)	0.0664(7)	0.0068(3)	(iso)
H(11)	0.2915(9)	0.1209(7)	−0.0701(3)	(iso)
H(12)	0.4592(9)	0.1221(7)	−0.0444(3)	(iso)

TABLE 4

THERMAL PARAMETERS FOR $\overline{Ti(NBu^tSiMe_2NBu^t)}Cl_2$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ti	0.0491(6)	0.0491(6)	0.0591(8)	−0.0034(8)	−0.0003(6)	0.0003(6)
Si	0.052(1)	0.052(1)	0.062(1)	−0.004(1)	−0.002(1)	0.002(1)
Cl(1)	0.105(2)	0.063(1)	0.116(2)	−0.000(1)	0.008(1)	−0.023(1)
N(1)	0.057(3)	0.057(3)	0.051(3)	0.001(3)	−0.005(3)	0.008(2)
C(1)	0.070(5)	0.087(5)	0.063(4)	0.003(5)	−0.013(4)	0.017(4)
C(2)	0.19(1)	0.30(2)	0.130(9)	−0.09(1)	−0.103(9)	0.10(1)
C(3)	0.14(1)	0.51(3)	0.064(6)	0.05(1)	0.006(7)	0.05(1)
C(4)	0.46(3)	0.112(8)	0.13(1)	0.09(1)	−0.11(1)	0.039(7)
C(5)	0.108(6)	0.056(4)	0.093(5)	−0.011(5)	−0.006(5)	−0.002(4)
H(1)	6.3					
H(2)	6.3					
H(3)	6.3					
H(4)	6.3					
H(5)	6.3					
H(6)	6.3					
H(7)	6.3					
H(8)	6.3					
H(9)	6.3					
H(10)	6.3					
H(11)	6.3					
H(12)	6.3					

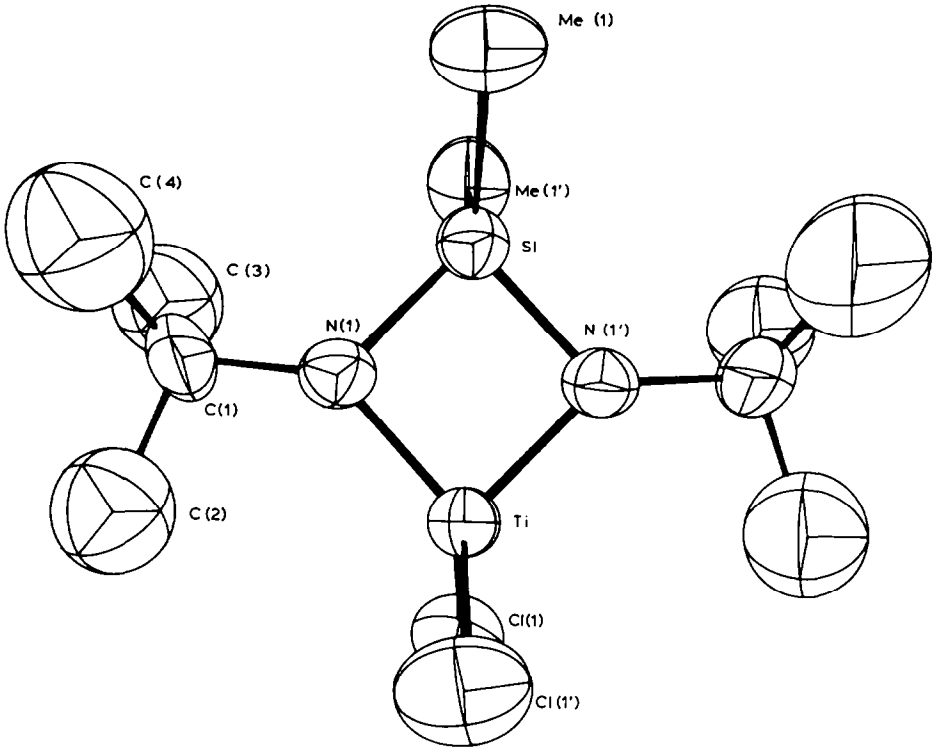


Fig. 1. View of $\overline{Ti(NBu^tSiMe_2NBu^t)}Cl_2$ (II).

Ti–N lengths found in II, which are significantly shorter than those found for $Ti(NBu^t)_2SiMe_2)_2$ (1.829(5) vs, 1.890(4) Å). The effect could be due to increased $N_{p\pi} \rightarrow Ti_{d\pi}$ bonding [9] caused by the presence of two chlorides instead of another $(NBu^t)_2SiMe_2^{2-}$ ligand. The latter is no doubt not as electronegative as two Cl^- groups. A decrease N–Si interaction in accord with this effect is reflected by an increased N–Si bond length in II (1.766(5) vs. 1.742(10) Å).

Acknowledgement

We thank the Robert A. Welch Foundation (RAJ), the National Science Foundation (JLA) and the University Research Institute of the University of Texas (RAJ) for financial support.

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