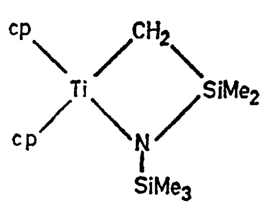
4,4-Bis-(π-cyclopentadienyl)-2,2-dimethyl-1-trimethylsilylaza-2-sila-4-titanacyclobutane: a Novel Organometallic Heterocycle

By CHARLES R. BENNETT and DONALD C. BRADLEY*
(*Department of Chemistry, Queen Mary College, Mile End Road, London* E1 4NS)

Summary Titanocene dichloride reacted with lithium bis(trimethylsilyl)amide to give the title compound (I).

THE mixed ligand complexes Ti(cp)$_x$(NR$_2$)$_y$ (cp = π-cyclopentadienyl) of titanium(III) and (IV) have been the subject of continuing studies[1,2] which have revealed some intriguing problems. Thus the dimethylamido-bridged dimers [(cp)$_2$-Ti(NMe$_2$)]$_2$ and [(cp)Ti(NMe$_2$)$_2$]$_2$ are known but (cp)Ti(NMe$_2$)$_3$ was preferentially formed under conditions {*e.g.* reaction of (cp)$_2$TiCl$_2$ + 2LiNMe$_2$} favourable for the formation of (cp)$_2$Ti(NMe$_2$)$_2$. Moreover the reaction of [(cp)$_2$Ti(NMe$_2$)]$_2$ with hexamethyldisilazane gave an intractable mixture of products.[2] Since the bis(trimethylsilyl)amido-group has been shown to stabilise low coordination of transition metals and the lanthanides[3] we have attempted to prepare some bis(cyclopentadienyl)titanium bis(trimethylsilyl)amides and now report a remarkable reaction which led to the formation of the novel 4-membered heterocycle (I).



(I)

The compound was obtained as a deep-red solid which sublimes at *ca.* 110°/10^{-3} mm from the reaction involving (cp)$_2$TiCl$_2$ (1 mol) and LiN(SiMe$_3$)$_2$ (2 mol) in pentane. Elemental analyses and the mass spectrum showed that the formula was $C_{16}H_{27}NSi_2Ti$. Its i.r. spectrum showed bands characteristic of π-cyclopentadienyl and silylamide ligands but there was no evidence for Ti–H bonds thus ruling out (cp)$_2$Ti(H)[N(SiMe$_3$)$_2$]. A solution (benzene) molecular weight measurement showed that the compound was monomeric. The ^{1}H n.m.r. spectrum (C_6D_6/C_6H_6 ref.) which showed no temperature dependence (30° to −80°, in pentane) gave signals at τ 4·08 (10-H 2 π-cp groups); 6·89 (2-H, TiCH_2–Si); and a partially resolved doublet at 9·99 and 10·01 (intensities 11 : 5, SiMe_3 and SiMe_2 respectively). These data are consistent with the formula (I) and were confirmed by ^{13}C n.m.r. spectra (CDCl$_3$,Me$_4$Si) {δ 113·5 (cp), 71·9 (TiCH$_2$Si), 4·32 (NSiMe_3), and 2·05 (N–SiMe_2–CH$_2$) from Me$_4$Si} which clearly resolved the two types of methyl groups and gave reasonable assignments of the four types of carbon-atom environment.

Apart from the novelty of disclosing a 4-membered heterocycle containing four different elements including a transition metal these results are of significance in revealing an unprecedented reaction in which a stable Ti–C σ-bond is formed by deprotonation of a methyl group bound to silicon (*cf.* the deprotonation of the methylene group of CH$_2$SiMe$_3$ by Nb and Ta[4]). The mechanism of this reaction has not been elucidated but hexamethyldisilazane was isolated as a product and suggests the following stoicheiometry: (cp)$_2$TiCl$_2$ + 2LiN(SiMe$_3$)$_2$ → (I) + 2LiCl + HN(Si-

$Me_3)_2$. Although the compound is essentially diamagnetic, a solution in pentane gave an e.s.r. signal ($g = 1{\cdot}98$) showing titanium–nuclear hyperfine coupling which suggests the presence of a trace of a Ti^{III} compound, *e.g.* possibly $(cp)_2TiN(SiMe_3)_2$.

We thank Dr. L. Farnell for obtaining the ^{13}C spectra, Mr. P. Cook for the mass spectra, and S.R.C. for financial support.

(*Received*, 15*th October* 1973; *Com.* 1415.)

---

[1] E. C. Alyea, D. C. Bradley, M. F. Lappert, and A. R. Sanger, *Chem. Comm.*, **1969**, 1064; D. C. Bradley and A. H. Kasenally, *ibid.*, 1968, 1430.

[2] M. F. Lappert and A. R. Sanger, *J. Chem. Soc.* (*A*), 1971, 874; 1971, 1314.

[3] E. C. Alyea, D. C. Bradley, and R. G. Copperthwaite, *J.C.S. Dalton*, 1972, 1580; D. C. Bradley, J. S. Ghotra, and F. A. Hart, *ibid.*, 1973, 1021.

[4] W. Mowat and G. Wilkinson, *J.C.S. Dalton*, 1973, 1120.