Synthesis and characterization of a chelating 2-dimethylsilylpyridine complex of titanocene(III)

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The complex $Cp_2Ti[2\text{-}SiMe_2(C_5H_4N)]$ 1, the first example of a chelating silyl, and a tertiary silyl complex of Cp_2Ti(III), is prepared by reaction of $2\text{-}SiHMe_2(C_5H_4N)$ with Cp_2TiMe_2, and its X-ray structure, EPR spectrum and reactions with C_5H_5N and PMe_3 are reported.

Titanocene silyl complexes have been implicated as intermediates in a number of catalytic reactions of hydrosilanes.[1–3] Although several such complexes with primary, secondary and unsubstituted silyl ligands have been synthesised and characterised, they still remain quite rare.[4–8] To our knowledge, only two titanocene complexes with tertiary silyl ligands have been reported, both of which are titanocene(IV) compounds.[9,10] We report here the first example of a tertiary silyl titanocene(III) complex in which the silyl group is part of a chelating ligand.

Reaction of Cp_2TiMe_2 with 2-(dimethylhydrosilyl)pyridine (2.2 equiv.) in hexane resulted in a slow evolution of CH_4, identified by the characteristic rotational fine structure in its gas phase infrared spectrum, and a color change of the solution from orange to purple over a period of 2 to 3 days. Upon cooling to −20 °C for 24 h, deep purple crystals of **1** precipitated and were isolated in 63% yield. In solution ([$^2H_8$]toluene), **1** gave no discernible ^1H or ^{29}Si NMR resonances, as is often the case with strongly paramagnetic Ti(III) complexes. The EPR spectra of **1** (Fig. 1) in solution at both low (−20 °C) and room temperature exhibit a well resolved triplet at $g = 1.9872$ with $a_N = 1.9$ G, due to coupling of a single unpaired electron to the ^{14}N nucleus ($I = 1$) in the pyridine, and satellites due to hyperfine interactions with Ti nuclei [$I = 7/2$, ^{49}Ti (5.5%); $I = 5/2$, ^{47}Ti (7.75%)] with $a_{Ti} = 8.8$ G.

The single crystal X-ray structure of a molecule of **1** shows that this complex is mononuclear (Fig. 2).† The geometry about the titanium center is very similar to those found in the analogous non-chelating silyl(tertiaryphosphine) complexes with the exception of the very acute N–Ti–Si angle of 64.72(7)° compared to the P–Ti–Si angles [84.8(1) to 86.2(2)°] in the latter complexes.[4] The bonding parameters are close to those observed for other titanocene(III) silyl complexes.[4]

Solutions of **1** are air sensitive, but relatively stable at room temperature under inert atmosphere. They decompose slowly over a period of days to give an unidentified paramagnetic product (broad single EPR resonance; $g = 1.9778$). Such a signal is often observed in the decomposition products of titanocene(III) complexes.[1] The enhanced thermal stability of the chelating tertiary silylpyridine complex **1** is in sharp contrast to the analogous non-chelating silyl(tertiarylphosphine) complexes $Cp_2Ti(PMe_3)(SiHRR')$ (R = H or Ph, R′ = Ph) which are stable only for minutes at ambient temperature.[4,5] We attribute the unusual stability of **1** to the absence of the Si–H hydrogens for further dehydrocoupling reactions.[5]

The pyridine ligand in **1** is labile and can be replaced by other donor ligands as shown in eqn. (1). Solutions of **1** treated with excess PMe_3 in toluene give **2a** [eqn. (1)] identified by its characteristic EPR spectrum which displayed a simple doublet at $g = 1.9936$ with $a_P = 29.3$ G, $a_{Ti} = 7.7$ G (*cf.* ref. 4) and observed by a color change of the solution from purple to bright violet. This reaction is reversible. Removal of the solvent along with the volatile PMe_3 by pumping, followed by redissolution of the residue, gave the starting complex **1**. Similarly, reaction of **1** with excess pyridine gave the silyl(pyridine)titanocene complex **2b**.‡

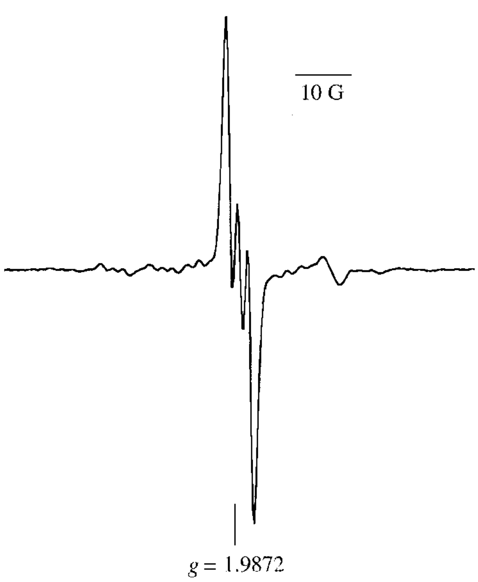


Fig. 1 EPR spectrum of **1** (−20 °C; toluene)

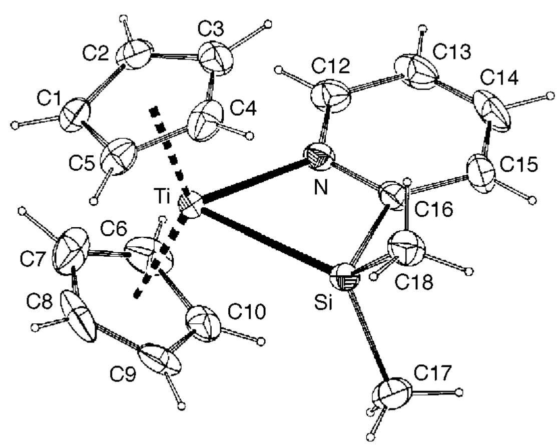
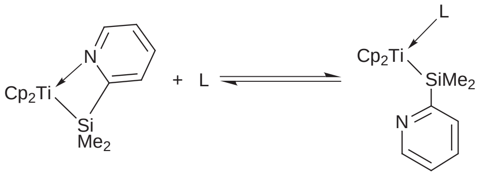


Fig. 2 A view of the structure of **1** (30% probability ellipsoids). Selected bond lengths (Å) and bond angles (°): Ti–N 2.229(2), Ti–Si 2.651(2), N–C(12) 1.340(4), N–C(16) 1.360(4), Si–C(16) 1.922(3), Si–C(17) 1.901(3); N–Ti–Si 64.72(7), Cp(cent)–Ti–Cp(cent) 137.2(1), Ti–N–C(16) 110.0(2), Ti–Si–C(16) 79.64(9), N–C(16)–Si 105.6(2).



1 **2**

(**2a**, L = PMe_3; **2b**, L = pyridine)

(1)

We are continuing to explore the reactions with group 4 metallocenes by modifying the chelating ligand and preparing other novel group 14/15 chelating ligands.

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Notes and References

† *Crystal data* for **1**: $C_{17}H_{20}NSiTi$, M = 314.33, monoclinic, space group $P2_1/c$, a = 14.786(9), b = 7.814(3), c = 14.488(4) Å, β = 106.48(4)°, V = 1605(1) Å^3, Z = 4, D_c = 1.301 g cm^{-3}, $F(000)$ = 660, μ = 5.130 mm^{-1}, crystal size: 0.49 × 0.36 × 0.05 mm. Data were collected at 220 K on an Enraf Nonius CAD4 diffractometer using Cu-Kα radiation (λ = 1.54056 Å) in the $\omega/2\theta$ scan mode. A total of 11485 reflections were measured in the range 3.11° < θ < 69.96° of which 2638 with $I > 2\sigma(I)$ were considered observed. The structure was solved by direct methods using SHELXS96 and refined by full-matrix least-squares on F^2 using SHELXL-96.[11] R = 0.0599 [for $I > 2\sigma(I)$] and $wR2$ = 0.1695 (for all data). CCDC 182/982.

Elemental analysis of **1**: Calc. for $C_{17}H_{20}NSiTi$: C: 64.97; H: 6.37; N: 4.46. Found C: 65.25; H: 7.08; N: 4.42%.

‡ EPR data for **2b** in toluene at 20 °C: g = 1.9878, a_{Ti} = 9.5 G, a_N = 2.0 G.

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