Preparation of the Titanium Bisthionylimide Complex $[Cp_2Ti(NSO)_2]$ and the Silyl Sulphur Di-imide Derivative $[Cp_2Ti(NSNSiMe_3)_2]$: Precursors of Novel Metallacycles. Crystal Structure of the Thionylimide (Cp = η^5-C_5H_5)

Herbert Plenio, Herbert W. Roesky,* Mathias Noltemeyer, and George M. Sheldrick

Institut für Anorganische Chemie der Universität Göttingen, Tammannstrasse 4, D-3400 Göttingen, Federal Republic of Germany

The bisthionylimide complex $[Cp_2Ti(NSO)_2]$ (Cp = η^5-C_5H_5) was prepared by reaction of $[Cp_2TiCl_2]$ and KNSO and its *X*-ray crystal structure determined; reaction of this compound with $LiN(SiMe_3)_2$ yielded $[Cp_2Ti(NSNSiMe_3)_2]$.

The chemistry of $[Cp_2TiCl_2]$ (Cp = η^5-C_5H_5) has been the subject of much research from a synthetic point of view.[1] Recently Oakley *et al.* reported the first examples of SN heterocyclic compounds incorporating Cp_2Ti units.[2] As part of our studies of S–N compounds co-ordinated to transition metals,[3] we report here the synthesis and structure of $[Cp_2Ti(NSO)_2]$, the second example of a potentially large class of transition-metal-bonded NSO compounds.[4] We had investigated the reactions of Me_3SiNSO and KNSO[5] with some metal halides as a possible general route to early transition metal d^0 complexes containing the thionylimide moiety. However, all our attempts to introduce the NSO unit *via* Me_3SiNSO were unsuccessful.

The reaction of $[Cp_2TiCl_2]$ with 2 equiv. of KNSO in MeCN proceeded at low temperatures to give yellow $[Cp_2Ti(NSO)_2]$ in 80% yield. It was purified by recrystallisation from MeCN (Scheme 1).† The i.r. spectrum contained the three typical -NSO absorptions (1235, 1075, and 525 cm^{-1}).[6] A crystal structure determination‡ confirmed the existence of two nitrogen-bonded NSO units (Figure 1). The long Ti–N bond indicates little multiple bonding; there are thus limited N–Ti p_π–d_π interactions if any. This bond is even longer than the Rh–N bond (198.9 pm) in $[Rh(NSO)(CO)(PPh_3)_2]$. The NSO angle and the N–S distance are similar to those in the isoelectronic SO_2 (119°; 143.1 pm).[7]

The -NSO groups are potential sites for a number of reactions,[8] and we are exploring the derivatization of the titanium-bonded thionylimide. Appel *et al.* have reported the transformation of RNSO (R = Et, Ph, or Bu^t) with $LiN(SiMe_3)_2$ to give monosilylated sulphur diimides.[9] It is possible to extend this reaction to $[Cp_2Ti(NSO)_2]$ (Scheme 2) and $[Cp_2Ti(NCO)_2]$. We were able to isolate and characterize pale yellow crystals of hexane-soluble $[Cp_2Ti(NSNSiMe_3)_2]$§ in 65% yield. Details of the synthesis of $[Cp_2Ti(NCNSiMe_3)_2]$ will be reported elsewhere.

$$[Cp_2TiCl_2] + 2KNSO \xrightarrow{0\,°C} [Cp_2Ti(NSO)_2] + 2\,KCl$$

Scheme 1

In principle four isomers (*E,E*, *E,Z*, *Z,E*, and *Z,Z*) are possible for each of the two sulphur diimide systems. $[Cp_2Ti(NSNSiMe_3)_2]$ gives rise to strongly temperature- and solvent-dependent n.m.r. spectra. In $CDCl_3$ (80 MHz; 32 °C) two singlets for the Cp and $SiMe_3$ groups are observed. In CD_3CN (80 MHz; 32 °C) all signals are broad, with two independent peaks in the $SiMe_3$ region. In the case of $[Cp_2Ti(NSO)_2]$ it is probably not possible to distinguish between the different isomers in solution by means of n.m.r. *Notes added after submission:* $[Cp_2Ti(NSO)_2]$ has been prepared independently by hydrolysis of $[Cp_2Ti(NSNBu^t)_2]$ on silica, and structurally characterized (M. Herberhold, personal communication).

$$[Cp_2Ti(NSO)_2] + 2LiN(SiMe_3)_2 \rightarrow [Cp_2Ti(NSNSiMe_3)_2] + 2LiOSiMe_3$$

Scheme 2

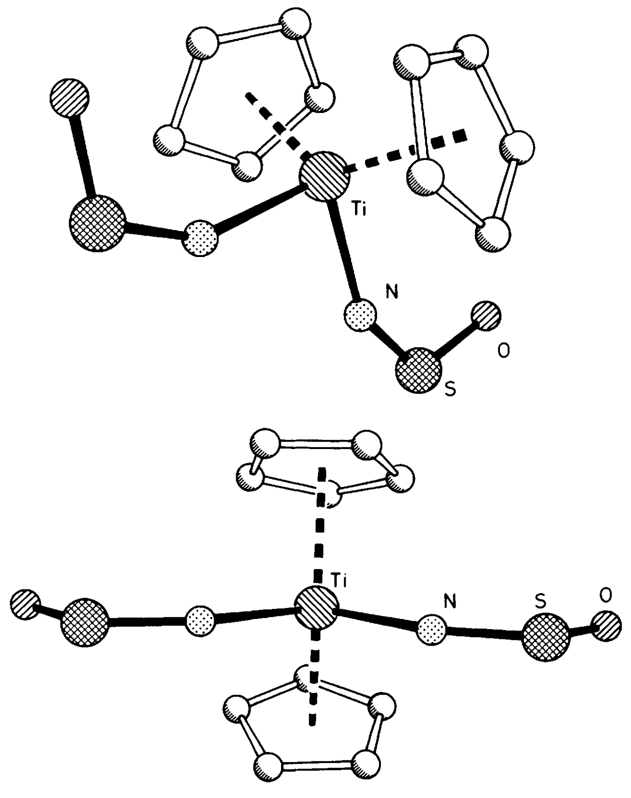

Figure 1. Molecular structure of $[Cp_2Ti(NSO)_2]$; important bond lengths (pm) and angles (°): Ti–N 201.3(2), N–S 147.4(2), S–O 145.2(3), Ti–X 2.055(1), N–Ti–N 96.0(1), Ti–N–S 150.8(2), N–S–O 119.1(2), X–Ti–X 132.3(1), X–Ti–N (mean) 105.7(2) (X is the centroid of the C_5 ring).

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† $[Cp_2Ti(NSO)_2]$ ^{1}H n.m.r. δ 6.38, i.r. 3110, 1235, 1075, 830, 525, 430, and 400 cm^{-1} (Found: C, 38.6; H, 3.2; N, 9.2. $C_{10}H_{10}N_2O_2S_2Ti$ requires C, 39.7; H, 3.3; N, 9.3%).

‡ $[Cp_2Ti(NSO)_2]$ crystallises in space group *Fdd*2 with a = 2917.0(6), b = 1413.9(2), c = 618.8(2) pm; Z = 8. An η-refinement[10] [η = −1.01(9)] showed that the co-ordinates had to be inverted[11] in the point 1/8, 1/8, 0 to obtain the absolute structure reported here. The final *R*-value was 0.035 for 1540 unique data with $F > 3\sigma(F)$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ $[Cp_2Ti(NSNSiMe_3)_2]$ ^{1}H n.m.r. (CD_3CN) δ 6.22, 0.24, and 0.08], *m/z* (e.i.) 444 (M^+) (Found: C, 42.5; H, 6.0. $C_{16}H_{28}N_4S_2Si_2Ti$ requires C, 43.2; H, 6.3%).

$[Cp_2Ti(NSO)_2]$ can also be prepared by reaction of $Hg(NSO)_2$ with $[Cp_2TiCl_2]$ or $[Cp_2Ti(CO)_2]$ (J. D. Woollins, personal communication).

Very recently the synthesis and structure of $[(Ph_3P)_2Pt(NSO)_2]$ have been described. The distances and the angles within the NSO unit are similar to those reported here (R. Short, M. B. Hursthouse, T. G. Purcell, and J. D. Woollins, *J. Chem. Soc., Chem. Commun.*, 1987, 407).

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