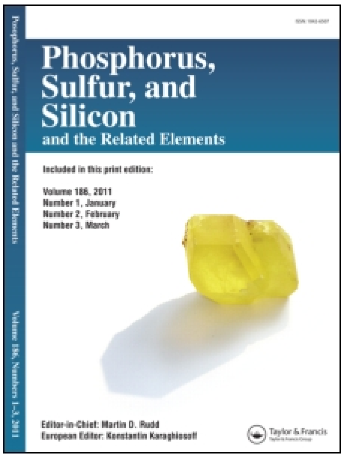

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REACTIVITY OF $Cp_2Ti(AsF_6)_2$ TOWARDS S_4N_4, Se_4N_4 AND As_2Me_4

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Abstract The reactivity of $Cp_2Ti(AsF_6)_2$ (**1**) ($Cp = \eta^5 - C_5H_5$) towards E_4N_4 ($E = S, Se$) and As_2Me_4 in liquid sulfur dioxide is reported. Complex **1** reacts with S_4N_4 to give $Cp_2TiF(AsF_6)$ (**2**) and $S_4N_4 \cdot AsF_5$ (**3**). In contrast, Se_4N_4 is oxidized by **1** and leads to $[(SeNSeNSe)_2]^{2+}[AsF_6]^-_2$ (**4**). The reaction of **1** with As_2Me_4 afforded $[Cp_2Ti(As_2Me_4)]_2^{4+}[AsF_6]_4^-$ (**5**). All compounds have been characterized by means of NMR (^1H, ^{14}N, ^{19}F) and IR spectroscopy and elemental analysis. The structure of **3** was elucidated by a single crystal X-ray diffraction study.

INTRODUCTION

The reactivity of $Cp_2Ti(AsF_6)_2$ (**1**) in comparison with the reactivity of AsF_5 is one part of our investigations. The behaviour of AsF_5 as well as a Lewis acid towards nitrogen bases and as a powerful oxidizing agent is well known.[1-3] Equation 1 represents some examples of the reactivity of AsF_5 acting as a Lewis acid.[3-6] On the other hand there are various examples for the reactivity of AsF_5 as a powerful oxidizer[2,7,8] as shown in equation 2.

$$AsF_5 + L \longrightarrow AsF_5 \cdot L \qquad (1)^{3-6}$$
$L = CH_3CN;\ S_4N_4;\ ClCN;\ BrCN;\ ICN$

$$12\,AsF_5 + 3\,Se_4N_4 \longrightarrow 4\,[Se_3N_2]^{2+}[AsF_6]^-_2 + 4\,AsF_3 + 2\,N_2 \qquad (2)^7$$

In consideration of these results it was interesting to investigate the behaviour of complex **1**, which can be regarded as a Lewis acid Lewis base adduct of Cp_2TiF_2 and AsF_5.[9] On the one hand the AsF_6 units are easily displaced by Lewis bases and compound **1** behaves as a precursor for new cationic titanocene complexes containing uncoordinated AsF_6^- ions (eq. 3).[10-13]

$$Cp_2Ti(AsF_6)_2 + 2\,RCN \longrightarrow [Cp_2Ti(RCN)_2]^{2+}[AsF_6]_2^- \qquad (3)^{10}$$
$R = CH_3, H, I$

On the other hand **1** can also generate AsF_5 and therefore **1** can behave as a mild source of AsF_5 . During our investigations we found out that **1** can react similar to free AsF_5.

In the present paper we want to report on the reactivity of **1** as an oxidizer, a source of the Lewis acid AsF_5 and a precursor for the preparation of a cationic titanocene heterocycle. Therefore we describe the synthesis of the first cationic dinuclear titanadiarsa metallacycle containing an intact As_2Me_4 unit.[12] It is also reported on the reactivity of **1** towards the chalcogene nitrides S_4N_4 and Se_4N_4.[13]

RESULTS AND DISCUSSION

The heterocycle $[Cp_2Ti(As_2Me_4)]_2^{4+}[AsF_6]_4^-$ (**5**) was prepared according to equation 4.

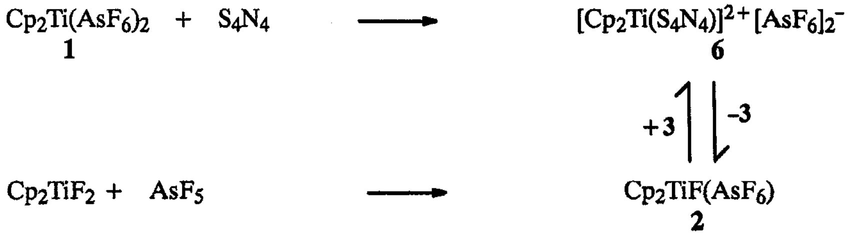
$$\underset{\mathbf{1}}{2\,Cp_2Ti(AsF_6)_2} + 2\,As_2Me_4 \longrightarrow \underset{\mathbf{5}}{[Cp_2Ti(As_2Me_4)]_2^{4+}[AsF_6]_4^-} \qquad (4)$$

Compound **5** was characterized by elemental analysis, by IR spectroscopy[12] and by temperature dependent ^1H NMR spectroscopy in SO_2 solution.

Two singular resonances appeared at room temperature due to the equivalence of the Cp protons on one side and the Me protons on the other side [δ_{Cp} = 6.87 ppm s (10), δ_{Me} = 1.63 ppm s (12); cf. **1**: δ_{Cp} = 7.33 ppm s, As_2Me_4: δ_{Me} = 1.20 ppm s].

In the temperature dependent ^1H NMR spectra **5** shows a reversible dynamic effect. The methyl resonance is split into two sharp signals essentially equal in their intensity at low temperatures. This is nicely in agreement with the non-equivalent axial and equatorial methyl groups in a six-membered ring in chair conformation (Fig. 1). The apparent equivalence of the Cp protons (no signal splitting) is also observed in the six-membered $[Cp_2TiSe_2]_2$ and can be explained by a very similar chemical shift of the axial and equatorial Cp protons in these distorted rings.[14] The estimated coalescence temperature is T_c = -15^o C (258 K) and the signal splitting is $\Delta\nu$ = 20 Hz. Therefore the free activation enthalpy can be estimated to $\Delta G^{\#}_c$ = 13 Kcal/mol (54 KJ/mol).[15]

The reaction of **1** with S_4N_4 in SO_2 gives **2** and **3**, the latter of which could be identified by means of Raman spectroscopy[5] and a single crystal X-ray diffraction study (Fig. 2).[6] Complex **2** also was prepared by reaction of Cp_2TiF_2 and AsF_5. Based on ^1H, ^{14}N, ^{19}F NMR investigations we could show that a solution of **1** and S_4N_4 (or **2** and **3**) contains **6** as the main product. So it is possible to formulate an equlibrium between **6**, which is stable in solution only, and **2** and **3** as shown in Scheme 1.



SCHEME 1 Reaction behaviour of **1** towards S_4N_4, formation of **2** and **3** (**3** = $S_4N_4 \cdot AsF_5$).

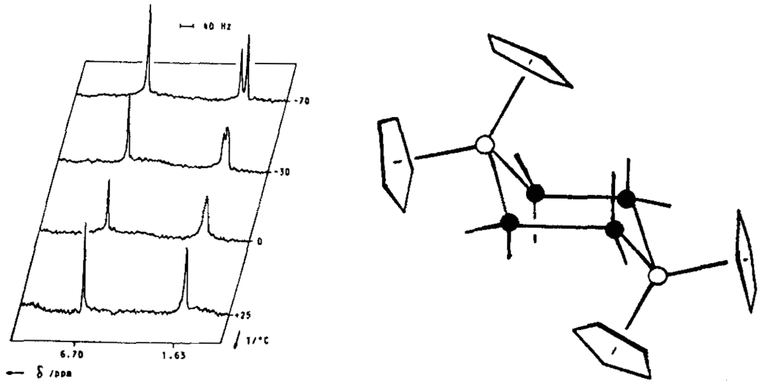


FIGURE 1 Temperature dependent ^1H NMR spectrum of **5** in SO_2 solution and suggested structure.

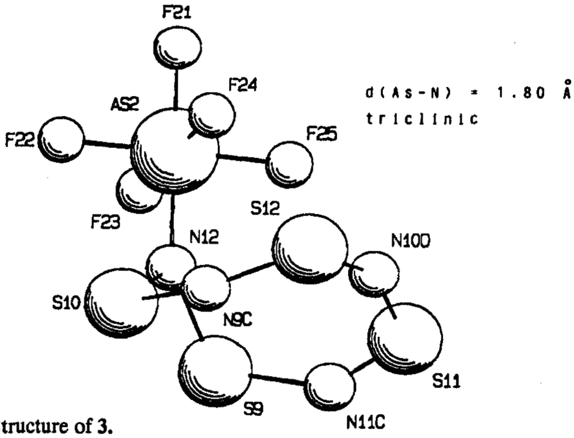


FIGURE 2 Structure of **3**.

In every case the ^1H NMR spectra show that the ratio of **2** : **6** in SO_2 solution is approximately 5 : 1, and the sharp singlet (δ = 6.80 ppm) shifted to high field from **1** (δ = 7.30 ppm) and **2** (δ = 7.10 ppm) can be assigned to **6**.

The ^{19}F NMR spectrum shows the typical quadruplet of uncoordinated AsF_6^- ions due to ^{19}F - ^{75}As coupling (δ = -59 ppm; $^1J_{As\text{-}F}$ = 930 Hz). The appearance of two singlets of equal intensity in the ^{14}N NMR spectrum of **6** (δ = -91 ppm, $\Delta\nu_{1/2}$ = 469 Hz and -133 ppm, $\Delta\nu_{1/2}$ = 419 Hz) indicated that two N atoms of the S_4N_4 cage are coordinated to the metal center (uncoordinated S_4N_4: δ = -244 ppm, $\Delta\nu_{1/2}$ = 550 Hz).

Se_4N_4 shows a completely different reactivity towards **1**. Under similar conditions (in contrast to S_4N_4) N_2 evolution and the formation of a dark brown paramagnetic solid (**4**) was observed (eq.5). By means of ^1H NMR spectroscopy we could identify traces of Cp_2TiF_2 and the adduct $Cp_2TiF_2 \cdot AsF_3$ (**7**) (δ_7 = 7.13 ppm) (eq. 6).

These three different types of reactivity of $Cp_2Ti(AsF_6)_2$ towards Lewis bases like S_4N_4, Se_4N_4 and As_2Me_4 demonstrate the manifold possible applications as a starting reagent in

$$3\,Cp_2Ti(AsF_6)_2 + 3\,Se_4N_4 \longrightarrow 3\,Cp_2TiF_2 + 2\,N_2 + 2\,AsF_3 + 2\,\underset{\mathbf{4}}{[(SeNSeNSe)_2]^{2+}[AsF_6]_2^-} \quad (5)$$

$$Cp_2TiF_2 + AsF_3 \longrightarrow \underset{\mathbf{7}}{Cp_2TiF_2 \cdot AsF_3} \quad (6)$$

preparative chemistry. Compound **1** acts like a Lewis acid towards S_4N_4 to form **6** which is stable in solution only, yielding **2** and **3** in the solid state. Therefore it is likely that the reaction of **1** with Se_4N_4 occurs in the same way. However, $Se_4N_4 \cdot AsF_5$ is unstable as Se_4N_4 does not form stable adducts with AsF_5 but is oxidized to give **4**.

In the light of these results the formation of the heterocycle **5** was really surprising because thermodynamical estimations show that the oxidation of As_2Me_4 by AsF_5 to form $AsMe_2F$ and AsF_3 according to equation 7 is allowed by about 57 Kcal/mol (240 KJ/mol). [B. E.(As–As) = 35, (As^{III}–F) = 97, (As^{V}–F) = 116 Kcal/mol].[16]

$$As_2Me_4 + AsF_5 \longrightarrow 2\,AsMe_2F + AsF_3 \quad (7)$$

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