Reaction of [Ti(cp)$_2$(AsF$_6$)$_2$] (cp = η-C$_5$H$_5$) toward S$_4$N$_4$ and Se$_4$N$_4$: Identification in Solution of [Ti(cp)$_2$(S$_4$N$_4$)][AsF$_6$]$_2$; Synthesis and Characterization of [Ti(cp)$_2$F(AsF$_6$)], [Ti(cp)$_2$F$_2$]·AsF$_3$ and [Ti(cp)F$_3$]·AsF$_3$

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The reaction of [Ti(cp)$_2$(AsF$_6$)$_2$] **2** (cp = η-C$_5$H$_5$) with S$_4$N$_4$ in liquid sulphur dioxide gives [Ti(cp)$_2$F(AsF$_6$)] **4** and S$_4$N$_4$·AsF$_5$ **5**. The new complex **4** can be prepared in quantitative yield from [Ti(cp)$_2$F$_2$] **1** and AsF$_5$. Proton, ^{14}N and ^{19}F NMR spectroscopy reveals that SO$_2$ solutions of **2** and S$_4$N$_4$ or **4** and **5** contain [Ti(cp)$_2$(S$_4$N$_4$)][AsF$_6$]$_2$ **3**. In contrast Se$_4$N$_4$ is oxidized by **2** and leads to [(SeNSeNSe)$_2$][AsF$_6$]$_2$, N$_2$, AsF$_3$ and **1**. Complex **1** forms a stable adduct with AsF$_3$, [Ti(cp)$_2$F$_2$]·AsF$_3$, which was characterized by ^{1}H NMR, IR and mass spectroscopy and elemental analysis. The monocyclopentadienyl analogue [Ti(cp)F$_3$]·AsF$_3$ can also be prepared in quantitative yield from [Ti(cp)Cl$_3$] and Ag[AsF$_6$].

The complex [Ti(cp)$_2$(AsF$_6$)$_2$] **2**, prepared from [Ti(cp)$_2$F$_2$] **1** (cp = η-C$_5$H$_5$) and AsF$_5$, was the first structurally characterized metallocene hexafluoroarsenate complex containing a direct M···F···E interaction (E = P, As, Sb or Bi).[1] It fertilized both the high-oxidation-state organometallic chemistry of the early transition elements[2–4] and the chemistry of cationic metallocene species containing co-ordinated neutral Lewis bases.[5] As the AsF$_6$ unit in **2** can, owing to the high stability of the AsF$_6^-$ anion, be displaced easily even by weak Lewis bases and poor electron donors, we became interested in the reactivity of complex **2** towards tetrachalcogen tetranitrides. The well known precursor for cationic titanocene complexes [Ti(cp)$_2$(SO$_3$CF$_3$)$_2$] does not react either with S$_4$N$_4$ or with Se$_4$N$_4$[6–8] and no example of an organometallic complex containing a co-ordinated Y$_4$N$_4$ cage unit (Y = S or Se) has been reported in the literature. Adducts of S$_4$N$_4$ and CuCl or CuCl$_2$[9,10] and two complexes between S$_4$N$_4$ and TiCl$_4$[11] are known. On the other hand, [Ti(cp)$_2$(CO)$_2$] reacts with S$_4$N$_4$ to yield the heterocycles [Ti(cp)$_2$(NS)$_3$N] and [Ti(cp)$_2$(SSNSN)].[12,13] To our knowledge there are only two structurally characterized examples of a complex of S$_4$N$_4^{2-}$: [IrCl(CO)(S$_4$N$_4$)(PPh$_3$)][14] and [PtCl$_2$(S$_4$N$_4$)(PMe$_2$Ph)].[15,16]

Results and Discussion

Reactions of [Ti(cp)$_2$(AsF$_6$)$_2$] *with* S$_4$N$_4$.—The reaction of [Ti(cp)$_2$(AsF$_6$)$_2$] **2** with S$_4$N$_4$ in liquid sulphur dioxide produces [Ti(cp)$_2$F(AsF$_6$)] **4** and S$_4$N$_4$·AsF$_5$ **5** (Scheme 1).

$$\begin{tikzcd}
\underset{\mathbf{2}}{[Ti(cp)_2(AsF_6)_2]} + S_4N_4 \arrow[r] & \underset{\mathbf{3}}{[Ti(cp)_2(S_4N_4)][AsF_6]_2} \arrow[d, shift left, "- S_4N_4\cdot AsF_5\ \mathbf{5}"] \\
\underset{\mathbf{1}}{[Ti(cp)_2F_2]} + AsF_5 \arrow[r] & \underset{\mathbf{4}}{[Ti(cp)_2F(AsF_6)]} \arrow[u, shift left, "+\mathbf{5}"]
\end{tikzcd}$$

Scheme 1

Alternatively **4** can be made in SO$_2$ in quantitative yield by reaction of [Ti(cp)$_2$F$_2$] **1** and 1 equivalent of AsF$_5$ (Scheme 1). However, an equimolar mixture of compound **2** and S$_4$N$_4$ contains [Ti(cp)$_2$(S$_4$N$_4$)][AsF$_6$]$_2$ **3** as the major product. Therefore an equilibrium of **4** and **5** with **3** (Scheme 1) would be consistent with our observations.

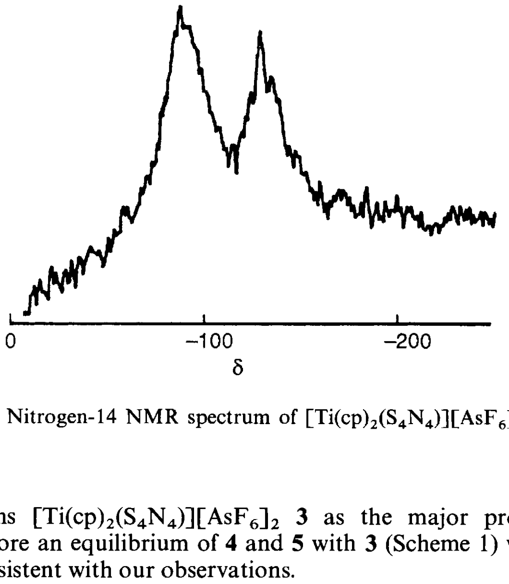


Fig. 1 Nitrogen-14 NMR spectrum of [Ti(cp)$_2$(S$_4$N$_4$)][AsF$_6$]$_2$ **3** in SO$_2$

According to ^{1}H NMR data the ratio **3**:**4** in SO$_2$ is approximately 5:1. To verify the equilibrium we prepared compound **4** according to Scheme 1 and treated it with S$_4$N$_4$·AsF$_5$, which was prepared from S$_4$N$_4$ and AsF$_5$.[17,18] The same ratio of **3**:**4** was obtained according to NMR data.

The identification of compound **3** containing the novel [Ti(cp)$_2$(S$_4$N$_4$)]$^{2+}$cation was based on ^{1}H, ^{14}N and ^{19}F NMR spectra. The ^{1}H NMR spectrum in SO$_2$ solution shows one sharp singlet (δ 6.80) shifted to high field (low frequency) from **2** (δ 7.30) and **4** (δ 7.10). This is in agreement with the donor ability of the co-ordinated S$_4$N$_4$ base. The AsF$_6^-$ ions were shown by means of ^{19}F NMR spectroscopy not to be co-ordinated to the metallocene centre but to exist in undistorted octahedral symmetry (quadruplet due to ^{19}F–^{75}As coupling). The appearance of two singlets of equal intensity in the ^{14}N NMR spectrum of compound **3** (Fig. 1) (δ −91, −133) clearly indicates that two of the four N atoms of the S$_4$N$_4$ cage are co-ordinated to the titanocene fragment. The low-field (high-frequency) shift compared with S$_4$N$_4$ (δ −244, relative to

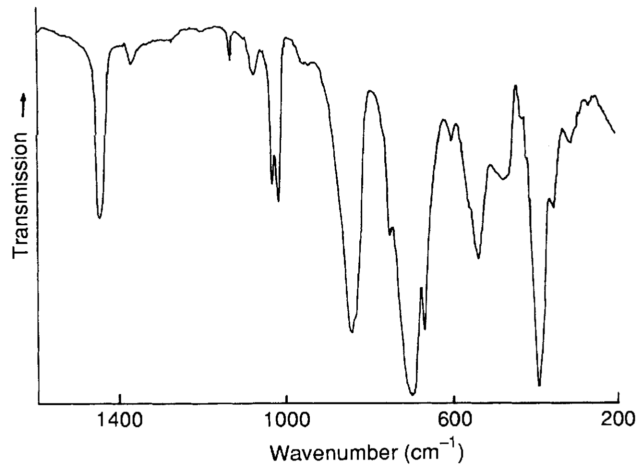
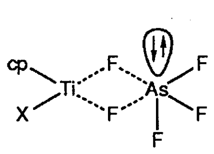


Fig. 2 Infrared spectrum of [Ti(cp)$_2$F(AsF$_6$)] **4** (see Experimental section)



7 X = cp
8 X = F

Fig. 3

MeNO$_2$, $\Delta\nu_{\frac{1}{2}}$ = 550 Hz)[19,20] is indicative of the positive charge and the donor function of the S_4N_4 unit in **3**. Because of the equilibrium in Scheme 1 we were unable to obtain a reliable molecular weight of **3** in solution, therefore we cannot state whether the species has a monomeric or dimeric structure.

Whereas compound **4** was detected in the ^{1}H NMR spectrum of the equilibrium mixture of **4** (15%) and **5** (85%), the four chemically non-equivalent N atoms of **5** could not be observed in the ^{14}N NMR spectrum due to quadrupole broadening and low concentration.

After evaporating the solvent from the reaction of compounds **2** and S_4N_4 (Scheme 1) a bright red solid formed which contained both **4** and **5**. However, crystals grown over a period of 10 d from the same mixture in SO$_2$ at −50 °C led to **5**, which was identified by Raman spectroscopy[17] and a single-crystal X-ray structure determination.[18]

Reactions of [Ti(cp)$_2$(AsF$_6$)$_2$] *with* Se_4N_4.—Surprisingly compound **2** reacts with Se_4N_4 in a 1:1 stoichiometry under N$_2$ evolution according to equation (1). However, only traces of **1** were identified (^{1}H NMR spectroscopy) as it forms a stable adduct with AsF$_3$ yielding the hitherto unknown species [Ti(cp)$_2$F$_2$]·AsF$_3$ **7** [equation (2)] (see below). According to equation (1), compound **2** acts as an oxidizing agent owing to the formation of AsF$_5$ (intermediate). Therefore, it is likely that the reaction of **2** with Se_4N_4 occurs in the same way as the reaction with S_4N_4. However, Se_4N_4·AsF$_5$ is unstable as Se_4N_4 does not form stable adducts with AsF$_5$ but is oxidized to give **6**. Compound **6** was recently reported by Passmore and co-workers[21] and has been prepared by the reaction of Se_4N_4 and AsF$_5$ in liquid sulphur dioxide [equation (3)]. [NB If compound **2** is regarded as an equivalent to **1** and two AsF$_5$ the stoichiometry of reaction (1) is identical with that of reaction (3).]

$$3\,\mathbf{2} + 3\,Se_4N_4 \longrightarrow 3\,\mathbf{1} + 2\,N_2 + 2\,AsF_3 + \underset{\mathbf{6}}{2\,[(SeNSeNSe)_2][AsF_6]_2} \qquad (1)$$

$$\mathbf{1} + AsF_3 \longrightarrow \underset{\mathbf{7}}{[Ti(cp)_2F_2]\cdot AsF_3} \qquad (2)$$

$$3\,Se_4N_4 + 6\,AsF_5 \longrightarrow 2\,\mathbf{6} + 2\,N_2 + 2\,AsF_3 \qquad (3)$$

Preparation of [Ti(cp)$_2$F(AsF$_6$)] **4**, [Ti(cp)$_2$F$_2$]·AsF$_3$ **7** *and* [Ti(cp)F$_3$]·AsF$_3$ **8**.—The attempt to isolate compound **3** in the solid state led instead to **4** and **5** (see above, Scheme 1). Subsequently **4** was synthesized quantitatively in liquid SO$_2$ according to Scheme 1. The new titanocene complex **4** was characterized by means of ^{1}H NMR and IR spectroscopy. As expected in the ^{1}H NMR spectrum in SO$_2$ solution the resonance of **4** (δ 7.10) appears between that of **2** (δ 7.30)[1] and that of **1** (δ 6.43).[22] The IR spectrum of **4** (Fig. 2) shows in addition to the terminal Ti–F stretching mode [ν(Ti–F) 545 cm^{-1}] a broad absorption at 475 cm^{-1} which can be assigned to the Ti···F···AsF$_5$ stretch (*cf.* IR spectrum of **2**, refs. 1 and 23). The ν_3 and ν_4 modes of the AsF$_6$ unit are split in agreement with the lowered symmetry of the co-ordinated AsF$_6$ unit (*cf.* refs. 24–26).

Various attempts to prepare [Ti(cp)$_2$(Se$_4$N$_4$)][AsF$_6$]$_2$ led instead to the formation of **7**. This molecular adduct was prepared essentially quantitatively according to equation (2), and led naturally to the attempted synthesis of the AsF$_3$ adduct of [Ti(cp)F$_3$]. Surprisingly [Ti(cp)F$_3$]·AsF$_3$ was quantitatively prepared by reaction of [Ti(cp)Cl$_3$] with 1 equivalent of Ag[AsF$_6$]. Presumably [Ti(cp)Cl$_2$(AsF$_6$)] is initially formed [equation (4)] but rearranges to the thermodynamically more stable **8** [equation (5)]. The new species **7** and **8** were identified by microanalyses, ^{1}H, IR and mass spectra. The vibrational data for both complexes are indicative of a distorted pseudo-octahedral geometry at the As atom. Therefore, it can be assumed that the As atoms are co-ordinated by five F atoms and the lone pair of electrons. This is also in agreement with the shift to lower wavenumbers of the Ti–F stretching mode of **7** and **8** compared with the ν(Ti–F) mode of **1** (see above).[23,27]

$$[Ti(cp)Cl_3] + Ag[AsF_6] \longrightarrow [Ti(cp)Cl_2(AsF_6)] + AgCl \qquad (4)$$

$$[Ti(cp)Cl_2(AsF_6)] \longrightarrow \underset{\mathbf{8}}{[Ti(cp)F_3]\cdot AsF_3} + Cl_2 \qquad (5)$$

The ^{1}H NMR data also confirm the suggested structure for compounds **7** and **8**. In both cases the resonances are shifted to lower field (high frequency) compared with **1** and [Ti(cp)F$_3$] (see Experimental section). Whereas in the spectrum of **7** the cp resonance appears as a singlet, the signal is split into a doublet in the case of **8** due to ^{1}H–^{19}F coupling of the cp protons with the one non-bridging fluorine atom. (NB The yellow solution of **1** in SO$_2$ shows a well resolved triplet in the ^{1}H NMR spectrum, δ 6.48.[22])

Although the deep red and microcrystalline species **7** and **8** are stable at room temperature even in a dynamic vacuum, they dissociate under the conditions in a mass spectrometer (see Experimental section) and peaks due to the ions [Ti(cp)$_2$F$_2$]$^+$ and [Ti(cp)F$_3$]$^+$ appear with the highest *m*/*z* values; AsF$_3$$^+$ and all fragments of arsenic trifluoride as well as [Ti(cp)$_2$F$_2$]$^+$ (spectrum of **7**) or [Ti(cp)F$_3$]$^+$ (spectrum of **8**) also appear as intense signals. In both cases the base peak can be attributed to the $C_5H_5{}^+$ cation.

Experimental

All manipulations were performed under an inert atmosphere (N$_2$, Ar) in pre-dried solvents. The compounds [Ti(cp)$_2$(AsF$_6$)$_2$] **2**,[1] S_4N_4,[28] Se_4N_4[29] and S_4N_4·AsF$_5$[17] were prepared by literature methods; AsF$_5$ (Air Products) and AsF$_3$ (T. J. Baker) were used as supplied.

Fluorine-19 (Varian SXP-100), ^{14}N (Varian XL-200) and ^{1}H NMR spectra (Varian EM 360 and Bruker WP 80) were obtained in SO_2 solution at room temperature and are referred to $CFCl_3$, $MeNO_2$ or $SiMe_4$, respectively. Infrared spectra were recorded as pressed KBr discs, Nujol mulls or powdered samples between KBr discs using a Perkin-Elmer 580 B instrument, Raman spectra on a Ybin Yvon Ramanor U 1000 (Spectra Physics krypton laser, excitation line 647.09 nm). Mass spectra were recorded on a Varian MAT 311 A spectrometer in the electron impact mode (70 eV, *ca.* 1.12×10^{-17} J). Elemental analyses were provided by the microanalytical service at TU Berlin.

CAUTION: S_4N_4 and Se_4N_4 are explosives; AsF_5 is a powerful oxidizer and fluorinator.

Reaction of Compound **2** *with* S_4N_4.—A suspension of S_4N_4 (0.200 g, 1.08 mmol) in SO_2 (10 cm^3) was treated at room temperature with a solution of compound **2** (0.550 g, 1.08 mmol) in SO_2 (10 cm^3) and stirred for 2 h. The deep red solution was concentrated to 10 cm^3 and NMR spectra were recorded. After cooling the solution to −50 °C for 10 d, red crystalline **5** precipitated and was filtered off. The solvent was then evaporated in a dynamic vacuum and compound **4** was identified in the remaining solid by ^{1}H NMR and IR spectroscopy (see below).

NMR spectra of the reaction solution: ^{19}F, $\delta = -59$ (q, $^{1}J_{AsF} = 930$ Hz); ^{1}H, δ 6.80 (s, 85%, **3**) and 7.10 (s, 15%, **4**); ^{14}N, $\delta = -91$ (s, $\Delta\nu_{\frac{1}{2}} = 464$) and −133 (s, $\Delta\nu_{\frac{1}{2}} = 419$ Hz) (**3**). Raman spectrum of compound **5**: 139m, 176s, 187s, 221w, 258s, 279w, 320w, 339m, 362s, 384vs and 613s cm^{-1}.

Reaction of Compounds **4** *and* **5**.—At room temperature compound **5** (0.100 g, 0.28 mmol) was treated in SO_2 (10 cm^3) with **4** (0.109 g, 0.28 mmol) and stirred for 1 h. The reaction mixture was concentrated to 5 cm^3 and characterized by ^{1}H NMR spectroscopy: δ 6.80 (s, 87%, **3**) and 7.10 (s, 13%, **4**).

Reaction of Compound **2** *with* Se_4N_4.—A suspension of Se_4N_4 (0.154 g, 0.414 mmol) in SO_2 (10 cm^3) was treated at 0 °C with a solution of compound **2** (0.230 g, 0.414 mmol) in SO_2 (10 cm^3). Spontaneously N_2 was evolved. The reaction mixture was stirred for 4 h, producing a red-brown solution over a dark brown solid. The dark brown solid was separated by filtration and purified as described previously.[18] Elemental analysis (Se, N and F) fitted well with the given formulation of compound **6**. The solvent from the red-brown solution was removed and the remaining solid recrystallized several times from SO_2. Finally red, microcrystalline **7** was identified by means of ^{1}H NMR and mass spectroscopy (see below).

Preparation of Compound **4**.—At −196 °C AsF_5 (0.393 g, 2.31 mmol) was condensed onto a frozen solution of compound **1** (0.500 g, 2.31 mmol) in SO_2 (15 cm^3). The mixture was warmed to room temperature and stirred for 1 h, producing a deep red solution. The solvent was removed, and the remaining red-brown solid recrystallized from SO_2 (0.749 g, 1.94 mmol, 84%) (Found: C, 30.9; H, 2.6. $C_{10}H_{10}AsF_7Ti$ **4** requires C, 31.1; H, 2.6%). ^{1}H NMR: δ 7.10 (s). IR (powder or Nujol mull): 3125s, 1445s, 1033m, 1018s, 845vs, 708(sh), 699vvs, 670vs, 545s, 475m (br), 435 (sh), 395vs and 360(sh) cm^{-1}.

Preparation of Compound **7**.—At room temperature AsF_3 (0.305 g, 2.31 mmol) was dissolved in SO_2 (5 cm^3) and treated with a solution of compound **1** (0.500 g, 2.31 mmol) in SO_2 (10 cm^3). The colour of the reaction mixture changed spontaneously from yellow **1** to deep red **7**. The mixture was stirred for 1 h and the solvent slowly evaporated at room temperature yielding compound **7** as a bright red microcrystalline solid (0.773 g, 2.22 mmol, 96%) (Found: C, 34.4; H, 2.8. $C_{10}H_{10}AsF_5Ti$ requires C, 34.5; H, 2.9%). ^{1}H NMR: δ 7.15 (s). IR (KBr): 3118s, 1448s, 1028 (sh), 1020m, 890 (sh), 865 (sh), 830vs, 548m, 420 (sh), 398m and 372m cm^{-1}. Mass spectrum (160 °C): $m/z = 216$ [58, $Ti(cp)_2F_2$], 197 [50, $Ti(cp)_2F$], 178 [65, $Ti(cp)_2$], 151 [12, $Ti(cp)F_2$], 132 (28, AsF_3), 113 (15, AsF_2) and 65 (100%, C_5H_5).

Preparation of Compound **8**.—A solution of $[Ti(cp)Cl_3]$ (0.400 g, 1.82 mmol) in SO_2 (10 cm^3) was treated at room temperature with a solution of $Ag[AsF_6]$ (0.541 g, 1.82 mmol) in SO_2 (10 cm^3) and stirred for 1 h, producing a red solution over precipitated AgCl. After filtration the solvent was evaporated slowly at room temperature yielding red microcrystalline compound **8** (0.505 g, 1.67 mmol, 92%) (Found: C, 19.7; H, 1.6. $C_5H_5AsF_6Ti$ requires C, 19.9; H, 1.7%). ^{1}H NMR: δ 7.57 (d, $J = 2.5$ Hz). IR (KBr): 3130m, 1445s, 1028m, 845vs, 795 (sh), 705vs, 675m, 560s (br), 395vs and 370 (sh) cm^{-1}. Mass spectrum (260 °C): $m/z = 170$ [58, $Ti(cp)F_3$], 151 [48, $Ti(cp)F_2$], 132 (20, AsF_3), 113 (13, AsF_2), 105 (5, TiF_3), 86 (15, TiF_2) and 65 (100%, C_5H_5).

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