SYNTHESIS AND CHARACTERIZATION OF [Cp$_2$Ti(CH$_3$CN)$_3$]$^{2+}$[AsF$_6^-$]$_2$ — ^{19}F NMR SPECTROSCOPY OF TITANOCENE HEXAFLUOROARSENATES*

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Abstract—Cp$_2$Ti(AsF$_6$)$_2$ (1) (Cp = η^5-C$_5$H$_5$) reacts with an excess of CH$_3$CN yielding quantitatively the new cationic titanocene complex [Cp$_2$Ti(CH$_3$CN)$_3$]$^{2+}$[AsF$_6^-$]$_2$ (2). 2 was characterized by elemental analysis, IR, ^{1}H NMR and ^{19}F NMR spectroscopy. Surprisingly, no reaction of 1 with CF$_3$CN could be observed. The ^{19}F NMR spectra of 1 at various temperatures are reported and discussed, too. The reaction behaviour of Cp$_2$TiCl$_2$ (3) towards ClF was investigated, and CpTiCl$_3$ (4) and traces of CpTiCl$_2$F (5) were shown to be the products of this reaction. Surprisingly, no evidence for the formation of Cp$_2$TiClF could be found. These results are discussed and can be understood easily on the basis of simple thermodynamic estimations.

The reaction of 3 with nitriles in the presence of suitable Lewis acids MCl$_n$, yields ionic complexes with one or two nitrile ligands bonded to the Ti. The complexes [Cp$_2$Ti(C$_8$H$_4$N$_2$)$_2$][SbCl$_6$]$_2$ (C$_8$H$_4$N$_2$ =phthalonitrile), [Cp$_2$Ti(Cl)(C$_3$H$_2$N$_2$)]$_4$[SnCl$_6$] (C$_3$H$_2$N$_2$ = malonitrile), and [Cp$_2$Ti(Cl)(CH$_3$CN)] [FeCl$_4$] have been isolated.[1-3] The N coordinated chelate complexes [Cp$_2$Ti(bipy)][CF$_3$SO$_3$]$_2$ and [Cp$_2$Ti(phen)][CF$_3$SO$_3$]$_2$ are also known.[4] Very recently we reported the synthesis of the first stable Lewis base free Cp$_2$Ti(MF$_6$)$_2$ (M = pnicogen) complexes where the MF$_6$ unit is directly co-coordinated to the Cp$_2$Ti fragment.[5,6] Whereas the mono-cyclopentadienyl species, CpTi(MF$_6$)$_3$, are unstable and till now were identified only at low temperature in solution,[7] Cp$_2$Ti(MF$_6$)$_2$ (M = As, Sb) are stable in the solid state and the structure of 1 was elucidated by single crystal X-ray diffraction.[6] The IR spectra and X-ray structure clearly show the covalent Cp$_2$Ti (|···F···AsF$_5$)$_2$ bond interaction in 1 with a bridging fluorine and reduced MF$_6$ symmetry.

As the ^{1}H NMR spectroscopy was not sufficient to elucidate the Cp$_2$Ti—MF$_6$ bond situation in solution,[5,6] we investigated this particular problem by temperature-dependent ^{19}F NMR spectroscopy. In addition to this it seemed to be of interest to discover whether stable 1 would react with neutral nitrile ligands, yielding cationic titanocene derivatives according to eq. (1). Ternary adducts of Ni(EF$_6$)$_2$ (E = Sb, Bi) like [Ni(CH$_3$CN)$_6$][EF$_6$]$_2$ have been reported quite recently.[8]

$$1+nR—CN \longrightarrow [Cp_2Ti(RCN)_n]^{2+}[AsF_6^-]_2. \quad (1)$$
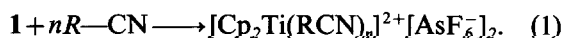
As 1 can be prepared either by reaction of 3 with AgAsF$_6$ or by reaction of Cp$_2$TiF$_2$ with AsF$_5$,[6] we were interested to achieve a simple synthesis of Cp$_2$TiF$_2$. This is of interest because of the high price for the commercially available AgAsF$_6$, which usually is prepared by fluorination of a mixture of elemental Ag or AgF and an excess of As$_2$O$_3$ with BrF$_3$.[9] One possible way seemed to be the reaction of 3 with ClF according to eq. (2) which was estimated to be thermodynamically favoured (see below),

$$3+2ClF \longrightarrow Cp_2TiF_2+2Cl_2. \quad (2)$$

The results of our investigations according to the goals outlined above are described in this paper.

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EXPERIMENTAL

All techniques have been described in ref. 6. Cp_2TiCl_2 (3)[10] and $Cp_2Ti(AsF_6)_2$ (1)[6] were prepared as described in the works cited. Sulphur dioxide, ClF, AsF_5, CH_3CN and CF_3CN were purified by distillation. SO_2 and CH_3CN were dried over CaH_2. Silver fluoride (Alfa, 10125) was used without further purification. All reactions took place in an atmosphere due to the vapour pressure of SO_2, CH_3CN or CF_3CN, respectively.

Preparation of silver hexafluoroarsenate(V) [AgAsF₆]

In a 50 cm^3 thick-walled glass reaction vessel incorporating a "Young" valve (POR-10), 8 g of AsF (63.06 mmol) were suspended in 20 cm^3 of CO_2 (1). After cooling this mixture to $-196°C$, 13 g of AsF_5 (76.51 mmol) were condensed onto the frozen SO_2. The reaction mixture was allowed to warm to room temperature and was stirred at RT in the dark for 12 h. After the solvent had been evaporated, the remaining white residue was dried *in vacuo* at RT for 4 h. Yield: 18.69 g (99.87%). IR: v (cm^{-1}) (Nujol mull) 700 vs (v_3), 385 s (v_4); (cf. ref. 11).

Preparation of bis(η^5-cyclopentadienyl)tris(acetonitrile)bis(hexafluoroarsenato)titanium(IV) [Cp₂Ti(CH₃CN)₃][AsF₆]₂ (complex 2)

0.0691 g (0.1243 mmol) of 1 were dissolved in 5 cm^3 of CH_3CN and stirred at RT for 1 h. The solvent was condensed into a second vessel ($\Delta T \approx 10°C$, 5–10 h) and the remaining microcrystalline deep red residue was dried *in vacuo* at RT for 24 h. Yield: 0.0841 g, 0.1238 mmol (99.60%). Found: C, 27.9; H, 2.7; N, 6.1. Calc. for $C_{16}H_{19}As_2F_{12}N_3Ti$ (679.05) C, 28.3; H, 2.8; N, 6.2%. ^1H NMR (SO_2) δ (ppm) (int.) 7.28 (10.00) s, 2.69 (8.85) s, relative to TMS. ^{19}F NMR (CD_3CN) δ (ppm) (int.) -49.7 (1), -59.6 (1), -69.8 (1), -79.4 (1), relative to $CFCl_3$. $\Delta v = 929 \pm 25$ Hz. IR: v (cm^{-1}) (Nujol mull) 3128 m (v-CH, Cp), 2320 m ($v_3 + v_4$, CH_3CN), 2293 s (v-CN, v_2-CH_3CN), 1128 w, 1028 sh and 1018 m (δ-CH, Cp), 957 w, 858 s (γ-CH, Cp), 698 vs (v-AsF, v_3-AsF_6), 398 s (δ-AsF, v_4-AsF_6).

Attempted synthesis of [Cp₂Ti(CF₃CN)ₙ]²⁺[AsF₆⁻]₂ (n = 2, 3)

1.00 g (10.52 mmol) of CF_3CN (g) was condensed at $-196°C$ onto 0.2561 g (0.4607 mmol) of 1 and this was allowed to warm up to room temperature.

As 1 is insoluble in CF_3CN (under high pressure) a suspension was formed. After 2 h at RT the reaction mixture was recooled to $-78°C$ and the volatiles were pumped off at this temperature *in vacuo*. The remaining solid (0.2558 g) was identical with 1 (^1H NMR and IR data).

Reaction of 3 with ClF

Onto a frozen solution of 0.270 g (1.08 mmol) of 3 in 5 cm^3 of SO_2, 0.118 g (2.17 mmol) of ClF were condensed at $-196°C$. After warming up and stirring for 12 h at RT, the solvent and the volatiles were pumped off *in vacuo* also at RT. Yield: 0.220 g (93%, calc. for $CpTiCl_3$). ^1H NMR ($CDCl_3$) δ (ppm) 7.07 s, relative to TMS. MS (50°C, 70 eV): m/z (int.), 218 (100) $CpTiCl_3^+$, 202 (11) $CpTiCl_2F^+$, 183 (76) $CpTiCl_2^+$, 148 (34) $CpTiCl^+$, 118 (36) $TiCl_3^+$, 109 (19) $CpTiCl_3^{2+}$, 83 (53) $TiCl^+$.

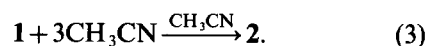## ^{19}F NMR of 1

^{19}F NMR (SO_2) δ (ppm) $T = 20°C$: -57.02 s, $b_{1/2} = 200$ Hz, $T = -70°C$: -61.53 s, $b_{1/2} = 350$ Hz; relative to $CFCl_3$.

RESULTS AND DISCUSSION

Preparative aspects

The reaction of 1 with an excess of CH_3CN (solvent) led in 100% yield to the preparations of 2 according to eq. (3).

$$1 + 3CH_3CN \xrightarrow{CH_3CN} 2. \qquad (3)$$

The identity of 2 was proved by elemental analysis, IR, ^1H and ^{19}F NMR spectroscopy (see Experimental and below).

Whereas some related cationic titanocene derivatives with one and two via N coordinated neutral ligands are known (see above and refs 1–4), 2 contains three CH_3CN molecules, thus realizing the coordination number five. The 12-electron fragment Cp_2Ti^{2+} obtains the noble gas configuration by coordinating three two-electron donor ligands. In the MO scheme of Cp_2Ti^{2+} two of the three unoccupied orbitals lowest in energy are bonding ($2a_1$ and b_2), while one is non-bonding ($1a_1$).[12] This is in agreement with the experimental result that one of the three CH_3CN ligands can be removed by pumping off 2 at a higher temperature for several days according to eq. (4).

$$2 \xrightarrow[\text{40–50°C}]{\text{dyn. vac.}} [Cp_2Ti(CH_3CN)_2]^{2+}[AsF_6^-]_2. \qquad (4)$$

The loss of one equivalent of CH_3CN was proved by weight change.

Surprisingly, **1** does not react with an excess of CF_3CN, yielding a cationic complex by analogy to the observed reaction with CH_3CN. **1** also crystallizes from SO_2 (l) as the covalent species and does not contain coordinated SO_2. Assuming that the crystal lattice energies of **2** and the CF_3CN analogue are more or less identical, the gaining of energy due to coordination of CF_3CN to Cp_2Ti^{2+} is less than the sum of the energy terms due to entropy and $Ti \cdots AsF_6$-bond interaction, which are working against the salt formation.

The preparation of Cp_2TiF_2 from **3** and ClF according to eq. (2) was not successful, surprisingly $CpTiCl_3$ was the reaction product [eq. (5)] and was identifed by ^1H NMR and mass spectroscopy.

$$3 + ClF \xrightarrow{SO_2} CpTiCl_3 + \text{``CpF''}. \qquad (5)$$
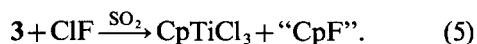
According to eq. (6) the preparation of $AgAsF_6$ in 100% yield was shown to be very convenient. In this reaction all of the expensive AsF_5 is converted into $AgAsF_6$. Silver fluoride can be prepared from Ag_2O by using HF.[13] Equation (7) also describes a common method to prepare $AgAsF_6$.

$$AgF + AsF_5 \xrightarrow{SO_2} AgAsF_6 \qquad (6)$$

$$2Ag + 3AsF_5 \longrightarrow 2AgAsF_6 + AsF_3. \qquad (7)$$
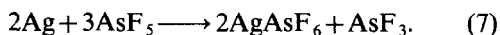
Vibrational spectroscopy

In the IR spectrum (see Fig. 1) of **1** the strong, broad absorption at 530 cm^{-1} was assigned to the Ti—F symmetric and asymmetric stretching mode.[5,6] The disappearance of this band indicates that also in the solid state there is no direct bonding interaction between the $[Cp_2Ti(CH_3CN)_3]^{2+}$ cation and the $[AsF_6^-]$ anions.

Free acetonitrile (liquid) shows the C—N stretching mode (v_2) at 2254 cm^{-1}.[14] In **2** this band is shifted to 2293 cm^{-1}. This result may indicate that **2** has strong σ-donor ($CH_3CN \rightarrow Ti$) but weak π-acceptor (back) bonding (cf. CN^-: 5σ, weakly antibonding; $2p\pi^*$ antibonding[15]).

NMR spectroscopy

The integration of the proton NMR spectrum of **2** in SO_2 solution clearly shows the composition of the complex as $[Cp_2Ti(CH_3CN)_3]^{2+}$ (see Fig. 2). The chemical shift in the ^1H NMR spectrum of **2** in SO_2 is similar to that observed for **1** in SO_2 solution.[6] However, CH_3CN in solution is also still coordinated as the only methyl singlet appears at 2.67 ppm, whereas free acetonitrile in SO_2 has a chemical shift of 2.05 ppm (own results).

The ^{19}F NMR spectra of **1** in SO_2 and **2** in SO_2 and CD_3CN show this effect, also. For instance, the
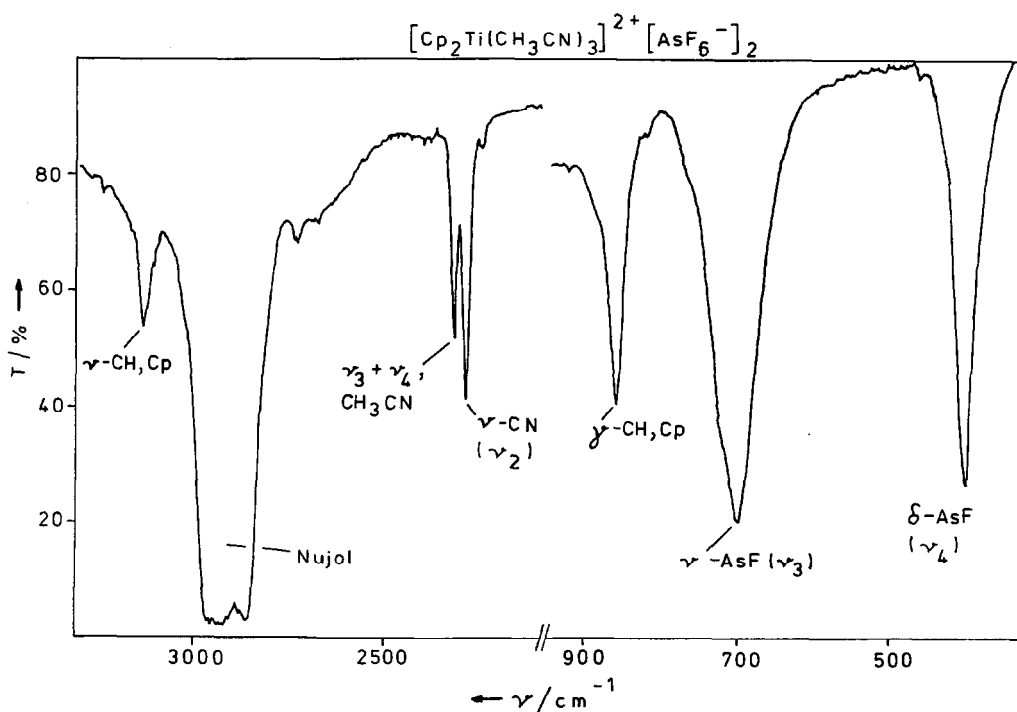

Fig. 1. IR spectrum of **2** in the regions 200–1000 cm^{-1} and 2000–3300 cm^{-1}.

$$\left[Cp_2Ti(CH_3CN)_3\right]^{2+}\left[AsF_6^-\right]_2$$

Fig. 2. ^{1}H NMR spectrum of **2** in SO_2, 20°C.

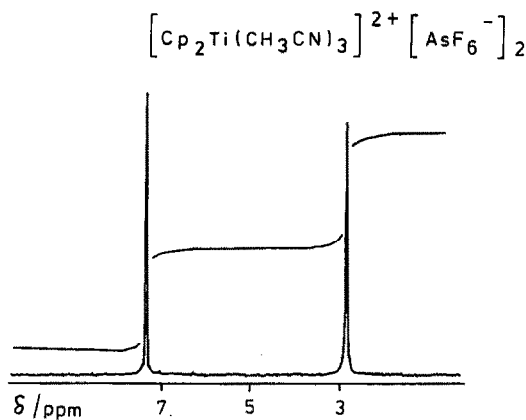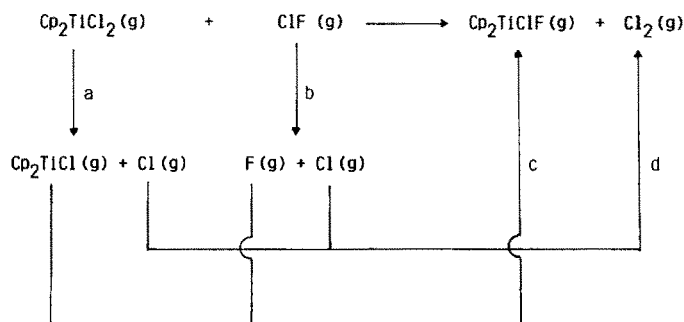$$\left[Cp_2Ti(CH_3CN)_3\right]^{2+}\left[AsF_6^-\right]_2$$

Fig. 3. ^{19}F NMR spectrum of **2** in CD_3CN, −40°C.

^{19}F NMR spectrum of **2** in CD_3CN, even at low temperatures. (−40°C), consists of a nicely dissolved four-line pattern due to the As—F couplings (I, $^{75}_{33}$As = 3/2) in the octahedral AsF_6^- anion (see Fig. 3).

On the other hand, **1** dissolved in SO_2 shows at RT in the ^{19}F NMR spectrum only one peak which does not split into the expected pattern even at low temperatures (−70°C). This indicates free highly symmetric AsF_6^- ions in the first case (**2**), whereas this group is coordinated to the Ti centre in the second case (**1**), showing rapid exchange (pseudorotation) even at low temperatures (otherwise no singlet in the proton NMR spectrum could be expected).

Thermodynamic aspects

By the reaction of **3** with ClF neither Cp_2TiClF nor Cp_2TiF_2, but only $CpTiCl_3$ (with traces of $CpTiCl_2F$) was identified as the product. Nevertheless the reaction according to eq. (8) should be exothermic, $\Delta H_8 = -144$ kJ mol^{-1}, as was estimated in Scheme 1.

$$3 + ClF \longrightarrow Cp_2TiClF + Cl_2. \qquad (8)$$

However, a reaction according to eq. (9) was estimated to be even more thermodynamically favourable (see Scheme 2), $\Delta H_9 = -358$ kJ mol^{-1}.

$$3 + ClF \longrightarrow CpTiCl_3 + \text{"CpF"}. \qquad (9)$$
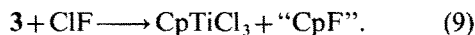
Therefore one can easily understand why a process, shown by eq. (9) and not as indicated by eq. (8), occurs. Moreover, the sums of the bond energies of Ti—Cl (429 kJ mol^{-1})[16,17] and C—F (485 kJ mol^{-1})[19] on one side and Ti—F (585 kJ mol^{-1})[19] and C—Cl (327 kJ mol^{-1})[19] on the other side, explain that $CpTiCl_3$ is formed as the main product and only a small amount of $CpTiCl_2F$ was found.

It seems likely that some of the bond strength estimation data may either bear some experimental error or may be slightly inaccurate, as only ΔH but no ΔS values were estimated. However, this simple

Scheme 1. Thermodynamic cycle to estimate the heat of reaction 8. (a) Ti—Cl bond energy in **3**: 429 kJ mol^{-1};[17] (b) Cl—F bond energy in ClF: 255 kJ mol^{-1};[18] (c) Ti—F bond energy in TiF$_4$: 585 kJ mol^{-1};[19] (d) Cl—Cl bond energy in Cl$_2$: 243 kJ mol^{-1}.[18]
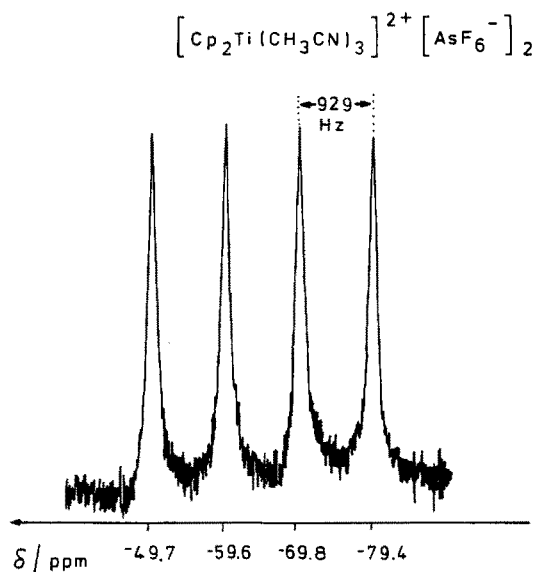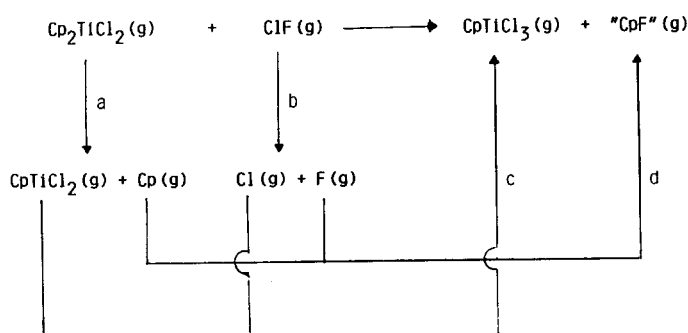
$$Cp_2TiCl_2 (g) \quad + \quad ClF(g) \quad \longrightarrow \quad CpTiCl_3 (g) \quad + \quad "CpF" (g)$$

$$\Big\downarrow a \qquad\qquad \Big\downarrow b \qquad\qquad\qquad \uparrow c \qquad\qquad \uparrow d$$

$$CpTiCl_2 (g) + Cp (g) \qquad Cl (g) + F (g)$$

Scheme 2. Thermodynamic cycle to estimate the heat of reaction 9. (a) Ti—Cp bond energy in **3**: 301 kJ mol^{-1};[17] (b) Cl—F bond energy in ClF: 255 kJ mol^{-1};[18] (c) Ti—Cl bond energy in **3**: 429 kJ mol^{-1};[17] (d) C—F bond energy: 485 kJ mol^{-1}.[19]

thermodynamic analysis clearly shows that a synthesis of Cp_2TiF_2 from **3** and ClF according to eq. (2) seems to be very unlikely or even impossible.

CONCLUSIONS

Quite recently we described the first synthesis and characterization of stable titanocene derivatives containing MF_6^- groups (M = pnicogen) directly coordinated to the Cp_2Ti centre.[5,6] In the present work the preparation of the ionic $[Cp_2Ti(CH_3CN)_3]^{2+}[AsF_6^-]_2$ (**2**) is reported, in which three nitrile ligands are bonded to the Cp_2Ti^{2+} fragment. This also clearly shows the importance of the "covalent" hexafluoroarsenates mentioned above as useful reagents in the synthesis of cationic metallocene complexes. These compounds (neutral and cationic) are of interest not only on account of their structure in solution and in crystals, but also in respect of their transition metal fluorine bond situation and the rapid exchange processes of the coordinated hexafluoropnictogenate ligands. In addition, the highly hydrophilic (and water soluble) cationic species may well open up a new form of chemotherapeutics, as compounds containing the Cp_2Ti group often show antiproliferative activity, but their application is limited by their low solubility in polar solvents.[20]

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