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Facile Synthesis and Structural Characterization of $[Cp_2Ti^{IV}(NCX)_2][AsF_6]_2$ Complexes: Adducts of $Cp_2Ti(AsF_6)_2$ with Halogen Cyanides (X = Cl, Br, I)

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A series of adducts between the highly reactive dicationic $Cp_2Ti^{IV\,2+}$ center and the weak Lewis base halogen cyanides (ClCN, BrCN, ICN) have been prepared in a facile synthesis and in quantitative yields from the reaction of $Cp_2Ti(AsF_6)_2$ with ClCN, BrCN, or ICN in liquid SO_2. The extremely air-sensitive $Cp_2Ti(NCX)_2(AsF_6)_2$ (X = Cl (**1**), Br (**2**), I (**3**)) complexes were characterized using IR and ^{1}H, ^{14}N, ^{19}F, and ^{75}As NMR spectroscopy, as well as X-ray diffraction. The structures of **1**−**3** were determined using X-ray diffraction techniques. The synthetic route employed should generally be applicable for the synthesis of a range of new cationic $Cp_2Ti^{IV}L_2{}^{2+}$ (L = neutral ligand) species using anhydrous conditions and demonstrates the usefulness of liquid SO_2 as a solvent for such systems. Compounds **1**−**3** are the first structurally characterized $Cp_2Ti^{IV}L_2(EF_6)_2$ (L = neutral ligand; E = As, Sb) complexes with the weakly coordinating AsF_6^- anion and are also the first adducts between cationic Cp_2M^{x+} (M = transition metal) centers and the halogen cyanides, which are weak Lewis bases in comparison with other nitriles such as CH_3CN.

Introduction

Although cationic bis(cyclopentadienyl)titanium(IV) complexes have been of interest for several years due to their catalytic properties,[1] the chemistry of dicationic Cp_2Ti^{IV}-containing species is still in its infancy. By contrast, related complexes of the group IV metals in the lower III oxidation state have been well investigated and extensively reported in the literature.[2] Extensive investigations by Thewalt and co-workers of complexes of the type $Cp_2Ti(CF_3SO_3)_2$[3] and $Cp_2Ti(NO_3)_2$[4] showed that the bonding in these complexes is predominantly covalent. Using more weakly coordinating anions, $Cp_2Ti(PF_6)_2$[5] was synthesized and characterized in solution, and notably, $Cp_2Ti(AsF_6)_2$[6] and $Cp_2Ti(SbF_6)_2$[7] were synthesized and structurally characterized by Klapötke, Thewalt, and co-workers, which opened up this area of chemistry. Whereas salts containing the AsF_6^- or SbF_6^- counteranions were prepared on a gram scale by the straightforward reaction of Cp_2TiCl_2 with $AgEF_6$ (E = As, Sb) in SO_2 solution (eq 1),[6,7] attempts to isolate $Cp_2Ti(PF_6)_2$ and $Cp_2Ti(BF_4)_2$ derived from the weaker Lewis acids BF_3 and PF_5 in the solid state were unsuccessful.[8]

$$Cp_2TiCl_2 + 2\,AgEF_6 \rightarrow Cp_2Ti(EF_6)_2 + 2\,AgCl \qquad (1)$$

The solid-state structure of the $Cp_2Ti(AsF_6)_2$ and $Cp_2Ti(SbF_6)_2$ salts showed the presence of strong fluorine bridges between the EF_6^- (E = As, Sb) and Cp_2Ti^{2+} groups.[6,7] However, the ability of $Cp_2Ti(AsF_6)_2$ to coordinate neutral ligands forming complexes of the type $Cp_2TiL_2(AsF_6)_2$ (L = neutral ligand) was demonstrated by the synthesis and spectroscopic characterization of $Cp_2Ti(NCX)_2(AsF_6)_2$ (X = H, I)[9] and $Cp_2Ti(As_2Me_4)(AsF_6)_2$.[9] The solid-state structures of these or other complexes of the type $Cp_2TiL_2(AsF_6)_2$ were not described, and the ability of the $Cp_2Ti(EF_6)_2$ (E = As, Sb) complexes to act as Lewis acids to coordinate neutral Lewis base molecules has not been well investigated.

It is worthwhile to note that the related complex $Cp_2Ti(SbCl_6)_2$ has yet to be unambiguously identified in the solid state, although the reaction of Cp_2TiCl_2 and $SbCl_5$ with the stronger Lewis base NCC_6H_4CN has resulted in the structural characterization of one compound of the type $Cp_2Ti(NCR)_2(SbCl_6)_2$ in the complex $Cp_2Ti(NCC_6H_4CN)_2(SbCl_6)_2$.[10] Further

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[1] (a) Ellis, W. W.; Gavrilova, A.; Liable-Sands, L.; Rheingold, A. L.; Bosnich, B. *Organometallics* **1999**, *18*, 332. (b) Hollis, T. K.; Robinson, N. P.; Bosnich, B. *Organometallics* **1992**, *11*, 2745. (c) Hollis, T. K.; Bosnich, B. *J. Am. Chem. Soc.* **1995**, *117*, 4570. (d) Hollis, T. K.; Robinson, N. P.; Bosnich, B. *Tetrahedron Lett.* **1992**, *33*, 6423. (e) Hollis, T. K.; Robinson, N. P.; Whelan, J.; Bosnich, B. *Tetrahedron Lett.* **1993**, *34*, 4309.

[2] (a) Melmed, K. M.; Coucouvanis, D.; Lippard, S. J. *Inorg. Chem.* **1973**, *12*, 232. (b) Sekutowski, D. G.; Stucky, C. D. *Inorg. Chem.* **1975**, *14*, 2192. (c) Seewald, P. A.; White, G. S.; Stephan, D. W. *Can. J. Chem.* **1988**, *66*, 1147. (d) Bochmann, M.; Jaggar, A. J.; Wilson, L. M.; Hursthouse, M. B.; Montevalli, M. *Polyhedron* **1989**, *8*, 1838. (e) Ahlers, W.; Temme, B.; Erker, G.; Frohlich, R.; Zippel, F. *Organometallics* **1997**, *16*, 1440. (f) Ohff, A.; Kempe, R.; Baumann, W.; Rosenthal, U. *J. Organomet. Chem.* **1996**, *520*, 241.

[3] Thewalt, U.; Klein, H. *Z. Kristallogr.* **1980**, *153*, 307.

[4] Klein, H. P.; Thewalt, U. *J. Organomet. Chem.* **1981**, *206*, 69.

[5] Clark, H. C.; Shaver, A. *J. Coord. Chem.* **1975**, *4*, 243.

[6] Klapötke, T. M.; Thewalt, U. *J. Organomet. Chem.* **1988**, *356*, 173.

[7] (a) Klapötke, T. M. *Polyhedron* **1988**, *7*, 1221. (b) Gowik, P.; Klapötke, T. M.; Thewalt, U. *J. Organomet. Chem.* **1990**, *385*, 345.

[8] Christe, K. O.; Dixon, D. A.; McLemore, D.; Wilson, W. W.; Sheehy, J. A.; Boatz, J. A. *J. Fluor. Chem.* **2000**, *101*, 151.

[9] (a) Gowik, P.; Klapötke, T. M. *J. Organomet. Chem.* **1991**, *402*, 349. (b) Gowik, P.; Klapötke, T. M.; Cameron, T. S. *Phosphorus, Sulfur, Silicon* **1992**, *65*, 181.

[10] (a) Berhalter, K.; Thewalt, U. *J. Organomet. Chem.* **1987**, *332*, 123. (b) Klein, H.-P.; Thewalt, U. *Z. Anorg. Allg. Chem.* **1981**, *476*, 62. (c) Ellis, W. W.; Gavrilova, A.; Liable-Sands, L.; Rheingold, A. L.; Bosnich, B. *Organometallics* **1999**, *18*, 332. (d) Thewalt, U.; Berhalter, K. *J. Organomet. Chem.* **1986**, *302*, 193. (e) Honold, B.; Thewalt, U. *J. Organomet. Chem.* **1986**, *318*, 291. (f) Thewalt, U.; Honold, B. *J. Organomet. Chem.* **1988**, *291*, 348. (g) Merola, J. S.; Campo, K. S.; Gentile, R. A.; Modrick, M. A. *Inorg. Chim. Acta* **1989**, *165*, 87.

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similar structurally characterized mononuclear dicationic $Cp_2Ti^{IV}L_2^{2+}$ complexes are very scarce and, to the best of our knowledge, comprise only a few examples.[10] Monocationic bis(cyclopentadienyl)titanium(IV) complexes of the type Cp_2TiR^+ have also been reported, e.g., $Cp^*_2Ti(OCHNMe_2)Cl^+CF_3SO_3^-$,[11] $Cp_2TiCl(NCCH_3)^+FeCl_4^-$,[11] and $[Cp_2Ti(Cl)NCCH_2CN)]_2SnCl_6$,[11] and are of importance in Ziegler−Natta catalysis.[12] In addition, a multitude of reports exist in the literature regarding $Cp_2Ti^{III}L_2^+$ complexes.[4] An excellent review of cationic Lewis acid−transition metal complexes with weakly coordinating anions can be found in ref 13. Establishing the existence and structure of a complex of the type $Cp_2TiL_2(EF_6)_2$ (E = As, Sb) would naturally be highly desirable, in particular if the Lewis acidity of the metal center could be probed through the coordination of weak Lewis bases such as the halogen cyanides. Herein, we wish to report the synthesis and characterization of $Cp_2Ti(NCCl)_2(AsF_6)_2$ (**1**), $Cp_2Ti(NCBr)_2(AsF_6)_2$ (**2**), and $Cp_2Ti(NCI)_2(AsF_6)_2 \cdot SO_2$ (**3**), which are the first structurally characterized examples of $Cp_2TiL_2(EF_6)_2$ (L = neutral ligand; E = As, Sb) complexes, which contain weak Lewis bases coordinated to the titanium(IV) center, as well as the weakly coordinating hexafluoropnicogenate anions.

Experimental Section

General Procedures. All manipulations were undertaken using strictly anhydrous conditions due to the extreme moisture sensitivity of the $Cp_2Ti(AsF_6)_2$ starting material and compounds **1**−**3**. All solids were manipulated in a Braun drybox under a nitrogen atmosphere (<1 ppm O_2, <1 ppm H_2O). All samples were stored in sealed glass sample tubes under a nitrogen atmosphere at −28 °C, at which temperature no decomposition was observed after several months. $Cp_2Ti(AsF_6)_2$, BrCN, and ICN were prepared according to literature procedures.[6,14] ClCN (ICI) was used as supplied, and SO_2 (Messer-Griesheim) was dried over CaH_2 prior to use. All experimental manipulations were undertaken using standard two-bulb vessel techniques and a Monel vacuum line as have been described in the literature.[15] IR spectra were recorded as solids between KBr plates using a Perkin-Elmer Spectrum One FT-IR spectrometer. Multinuclear NMR spectra were recorded using a JEOL EX 400 FT-NMR spectrometer, operating at 399.78 MHz (^1H), 28.89 MHz (^{14}N), 276.17 MHz (^{19}F), and 46.26 MHz (^{75}As). Chemical shifts are given with respect to TMS (for ^1H), $MeNO_2$ (for ^{14}N), $CFCl_3$ (for ^{19}F), and $KAsF_6$ in D_2O (for ^{75}As) as external standards. No satisfactory C/H/N analyses were obtained for compounds **1**−**3** because of the extreme air sensitivity of these compounds, and decomposition of the solid samples was observed during preparation of the sample for analysis. The X-ray diffraction studies were carried out for compound **1** using a Nonius Kappa CCD diffractometer and for compounds **2** and **3** using a Siemens P4 instrument equipped with a CCD area detector. The structures of compounds **1**, **2**, and **3** were solved by direct methods using SHELXS 97[16] and refined by means of full-matrix least-squares procedures using SHELXL-97.[16] Melting points were determined by sealing the samples in capillaries under a nitrogen atmosphere. The halogen cyanides BrCN, ICN, and, in particular, ClCN are extremely toxic and should be handled with caution in a well-ventilated fume-cupboard. The use of SO_2 as a solvent requires the use of relevant protective clothing due to the vapor pressure of SO_2 at room temperature (3.3 atm).

$Cp_2Ti(NCCl)_2(AsF_6)_2$ (1). $Cp_2Ti(AsF_6)_2$ (0.556 g, 1.0 mmol) was loaded into a two-bulb vessel in the drybox. After evacuation of this vessel, approximately 5 mL of SO_2 was condensed in at −196 °C, and the reaction vessel was allowed to warm to room temperature, whereby a clear dark red-brown solution was observed. The reaction vessel was then cooled using liquid nitrogen, and a 5-fold excess of ClCN (10.0 mmol) was condensed in. On warming to room temperature, only a clear dark brown-red solution could be observed. After leaving the reaction mixture sitting for 30 min, the SO_2 solvent and excess ClCN were removed, leaving behind a dark brown-red extremely air-sensitive solid. The solid was isolated in the drybox and used for characterization. Yield: 0.64 g (94%). Crystals that were extremely air- and moisture-sensitive were obtained by slowly concentrating a saturated 10:1 (v/v) SO_2/ClCN solution.

IR (AgCl plates, RT, ν/cm^{-1}): 3126w (ν-CH, Cp), 2255m (ν-CN, ClCN), 1652m, 1582m, 1440m (ω-CC, Cp), 1341w, 1130w, 1077w, 1030m (δ-CH, Cp), 1018m, 992m, 845s (γ-CH, Cp), 699vs (ν-AsF, AsF_6^-), 675m, 396vs (δ-AsF, AsF_6^-). ^1H NMR (SO_2): δ 7.80 (s). ^{14}N NMR (SO_2): δ −191 (s, ν 1/2 = 545 Hz). ^{19}F NMR (SO_2): δ −58.49 (s). ^{75}As NMR (SO_2): δ −5 (s, ν 1/2 = 4539 Hz).

$Cp_2Ti(NCBr)_2(AsF_6)_2$ (2). $Cp_2Ti(AsF_6)_2$ (0.556 g, 1.0 mmol) was loaded into a two-bulb vessel in the drybox. Into the second bulb, 0.212 g (2.0 mmol) of BrCN was added. After cooling the bulb containing the BrCN using liquid nitrogen, the vessel was evacuated and then 5 mL of SO_2 was condensed onto the BrCN. The reaction vessel was allowed to warm to room temperature, whereby only a colorless BrCN/SO_2 solution was observed, which was then poured onto the $Cp_2Ti(AsF_6)_2$ solid. A clear brown-red solution was observed, and no solid was visible. After the reaction mixture was stirred for 30 min at room temperature, the SO_2 solvent was removed in vacuo, leaving behind a dark brown-red extremely air-sensitive solid, which was isolated in the drybox and used for characterization. Yield: 0.73 g (95%). Crystals that were extremely air- and moisture-sensitive were obtained by slowly concentrating a saturated SO_2 solution.

IR (AgCl plates, RT, ν/cm^{-1}): 3122w (ν-CH, Cp), 2233m (ν-CN, BrCN), 1437m (ω-CC, Cp), 1383w, 1129w, 1028w (δ-CH, Cp), 1018m, 853s (γ-CH, Cp), 700vs (ν-AsF, AsF_6^-), 670m, 395vs (δ-AsF, AsF_6^-). ^1H NMR (SO_2): δ 7.59 (s). ^{14}N NMR (SO_2): δ −168 (s, ν 1/2 = 545 Hz). ^{19}F NMR (SO_2): δ −58.3 (s). ^{75}As NMR (SO_2): δ −2 (s, ν 1/2 = 3257 Hz).

$[Cp_2Ti(NCI)_2][AsF_6]_2 \cdot SO_2$ (3). $Cp_2Ti(AsF_6)_2$ (0.556 g, 1.0 mmol) was loaded into a two-bulb vessel in the drybox. Into the second bulb, 0.306 g (2.0 mmol) of ICN was added. After cooling the bulb containing the $Cp_2Ti(AsF_6)_2$ using liquid nitrogen, the vessel was evacuated, and approximately 5 mL of SO_2 was condensed onto the $Cp_2Ti(AsF_6)_2$. After allowing the reaction vessel to warm to room temperature the solution was then poured onto the solid ICN, whereby a brown-red solution formed and no solid could be observed. After leaving the reaction mixture stirring for 30 min, the SO_2 was removed under vacuum, leaving behind a dark brown-red extremely air-sensitive solid, which was isolated in the drybox and used for characterization. Yield: 0.81 g (94%). Crystals that were extremely air- and moisture-sensitive were obtained by slowly concentrating a saturated SO_2 solution.

IR (AgCl plates, RT, ν/cm^{-1}): 3120m (ν-CH, Cp), 2200m (ν-CN, ICN), 1445s (ω-CC, Cp), 1020s (δ-CH, Cp), 825s (γ-CH, Cp), 698vs (ν-AsF, AsF_6^-), 398vs (δ-AsF, AsF_6^-). ^1H NMR (SO_2): δ

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[11] (a) Honold, B.; Thewalt, U. *J. Organomet. Chem.* **1986**, *316*, 291. (b) Thewalt, U.; Berhalter, K.; Neuse, E. W. *Trans. Met. Chem.* **1985**, *10*, 1642. (c) Berhalter, K.; Thewalt, U. *J. Organomet. Chem.* **1987**, *332*, 123.

[12] Janiak, C.; Klapötke, T. M.; Meyer, H.-J. In *Moderne Anorganische Chemie*, 2nd ed.; Riedel, E., Ed.; Walter de Gruyter: Berlin, 2003.

[13] Beck, W.; Sünkel, K. *Chem. Rev.* **1988**, *88*, 1405.

[14] Brauer, G. *Handbuch der Präparativen Anorganischen Chemie*, 3rd. ed.; Ferdinand Enke: Stuttgart.

[15] Tornieporth-Oetting, I. C.; Klapötke, T. M. In *Inorganic Experiments*; Woollins, J. D., Ed.; VCH Verlagsgesellschaft: Weinheim, 1994; p 217.

[16] (a) Sheldrick, G. M. *SHELXS-97*, Structure Solving Program for Crystal Structure Determination; University of Göttingen: Göttingen, 1997. (b) Sheldrick, G. M. *SHELXS-97*, Program for the Refinement of Crystal Structures; University of Göttingen: Göttingen, 1997.

8.5 (s). ^{14}N NMR (SO_2): δ −145 (s, ν 1/2 = 912 Hz). ^{19}F NMR (SO_2): δ −57.4 (s). ^{75}As NMR (SO_2): δ −13 (s, ν 1/2 = 3251 Hz).

Results and Discussion

The synthesis and characterization of the Lewis acid−Lewis base adducts between $Cp_2Ti(AsF_6)_2$ and the halogen cyanides XCN (X = Cl, Br, I), which are weak Lewis bases, was achieved using liquid SO_2 as the solvent (eq 2). The general synthetic procedure used involved the reaction of the previously synthesized and structurally characterized $Cp_2Ti(AsF_6)_2$ salt[6] with the corresponding halogen cyanide in liquid SO_2 at room temperature (eq 2).

$$Cp_2Ti(AsF_6)_2 + 2\ XCN \rightarrow Cp_2Ti(NCX)_2(AsF_6)_2 \qquad (2)$$

$$(X = Cl,\ solvent = ClCN/SO_2;\quad X = Br, I,\ solvent = SO_2)$$

In the case of ClCN, only two ClCN moieties were coordinated to the titanium center, even though an excess of ClCN was present and used in combination with liquid SO_2 to act as the solvent. It is interesting to note that even though the Lewis basicity of ClCN is relatively low, the adducts between all three halogen cyanides and $Cp_2Ti(AsF_6)_2$ were formed. All reactions occurred to completion within a few minutes and resulted in essentially quantitative yields of compounds **1**−**3**. The compounds were found to be very soluble in SO_2, but insoluble in CH_2Cl_2. All three compounds were found to be extremely air- and moisture-sensitive and required handling under an inert atmosphere to prevent very fast decomposition. This is in stark contrast to $Cp_2Ti(bipy)(CF_3SO_3)_2$[10] and $Cp_2Ti(phen)(CF_3SO_3)_2$,[10] which are stable for days in air and do not appear to decompose in aqueous solution.

As the highly reactive compounds **1**−**3** were found to react with both KBr and CsI plates, IR spectra were recorded of the solids between AgCl plates. In the IR spectra of compounds **1**−**3**, a significant shift of the ν(CN) stretching vibration to higher wavenumbers by approximately 30 cm^{-1} (ν(CN) = 2255 cm^{-1} (**1**); 2233 cm^{-1} (**2**); 2200 cm^{-1} (**3**)) in comparison with the free halogen cyanide (ν(CN) = 2206 cm^{-1} (ClCN);[17] 2189 cm^{-1} (BrCN);[17] 2169 cm^{-1} (ICN)[17]) was observed. This shift is of the same order of magnitude as has been observed for the coordination of the halogen cyanides to strong Lewis acids such as AsF_5 (ν(CN)/cm^{-1}: 2297, $ClCN{\cdot}AsF_5$; 2269, $BrCN{\cdot}AsF_5$; 2236, $ICN{\cdot}AsF_5$).[18] A shift to higher wavenumbers for the stretching vibrations of neutral ligands coordinated to cationic transition metal centers has been particularly well investigated and discussed in the cationic transition metal carbonyl cations, examples of which include $[Pt(CO)_4]^{2+}$, $[Fe(CO)_6]^{2+}$, $[Rh(CO)_4]^{2+}$, and $[Ag(CO)_2]^+$ by the groups of Willner, Aubke, and Strauss.[19] It has been shown in these complexes that the π-back-bonding from the cationic metal center to the neutral CO ligand is significantly reduced in comparison with the neutral homoleptic metal carbonyl complexes.[20] The coordination of the XCN group (X = Cl, Br, I) via the N atom is also reflected in the ^{14}N NMR spectra, which show a marked upfield shift for the XCN (X = Cl, Br, I) nitrogen atom in comparison with that observed for free XCN (X = Cl, Br, I) in SO_2 solution (^{14}N NMR δ/ppm; −146, ClCN; −191, $Cp_2Ti(NCCl)_2(AsF_6)_2$; −203, $ClCN{\cdot}AsF_5$ −122, BrCN; −168 $Cp_2Ti(NCBr)_2(AsF_6)_2$; −183 $BrCN{\cdot}AsF_5$; −98, ICN; −145, $Cp_2Ti(NCI)_2(AsF_6)_2$; −164, $ICN{\cdot}AsF_5$).[18] For compounds **1**−**3**, the ^1H NMR shows a very high-field peak for the Cp-ring hydrogen atoms. This upfield shift has also been observed for the parent compound $Cp_2Ti(AsF_6)_2$[6] (^1H NMR δ/ppm = 7.8 ppm (**1**); 7.6 ppm (**2**); 8.5 ppm (**3**); 7.30 ppm ($Cp_2Ti(AsF_6)_2$);[6] 7.25 ppm ($Cp_2Ti(SbF_6)_2$)[7]). On redissolving compounds **1**−**3** in liquid SO_2 and recording the multinuclear NMR spectra, a small amount of decomposition product was observed in the ^1H NMR spectra of compounds **1**−**3**, which highlights the extremely sensitive nature of these compounds. It is worthwhile to mention that compound **1** was found to be the most sensitive, which is reflected in the NMR spectra, and corresponds to the adduct with ClCN.

Despite using an excess of ClCN in a ClCN/SO_2 solvent mixture as the solvent for the preparation of $Cp_2Ti(NCCl)_2(AsF_6)_2$, only a coordination number of 4 was observed for the central titanium atom with only two ClCN moieties coordinated, in contrast to the dinuclear $[TiCl_4(NCCH_3)]_2$, where a coordination number of 6 has been observed.[21] The coordination number of 4 for the central titanium atom in the Cp_2Ti unit through the coordination of two Lewis base nitrogen atoms from the XCN (X = Cl, Br, I) nitriles is in agreement with that observed for the $Cp_2Ti(NCC_6H_4CN)_2^{2+}$ cation,[10] where although one $C_6H_4(CN)_2$ unit could coordinate twice through the two CN groups present in each $C_6H_4(CN)_2$ molecule, two $C_6H_4(CN)_2$ molecules are coordinated and the central titanium atom maintains a coordination number of 4. Whereas $Cp_2Ti(NCC_6H_4CN)_2(SbCl_6)_2$ is soluble in organic solvents, compounds **1**−**3** are insoluble in, or react with, common organic solvents. It is interesting to note that the attempted preparation of $Cp_2Ti(NCCF_3)_x(AsF_6)_2$ (x = 2, 3) was reported in the literature by the reaction of $Cp_2Ti(AsF_6)_2$ in CF_3CN; however, the weak Lewis base CF_3CN was not found to coordinate to the $Cp_2Ti(AsF_6)_2$.[22] As the electronegativity and chemical reactivity of the CF_3 group is often compared to that of Cl, it is interesting to note here that, in contrast to CF_3CN, ClCN has been successfully coordinated to the $Cp_2Ti(AsF_6)_2$. For the new $Cp_2Ti(NCX)_2(AsF_6)_2$ salts (X = Cl, Br, I), SO_2 is an excellent choice of solvent because of the high solubility and unreactive nature of these adducts with SO_2. Many other solvents are unsuitable because they either coordinate to the Cp_2Ti^{2+} center (e.g., CH_3CN) or react with the $Cp_2Ti(NCX)_2(AsF_6)_2$ product (X = Cl, Br, I) or $Cp_2Ti(AsF_6)_2$ starting material (e.g., CH_2Cl_2); however, liquid SO_2 has been shown to possess neither of these disadvantages. In fact, even for the “parent compound” $Cp_2Ti(AsF_6)_2$, which was prepared in SO_2 solution, no coordination of SO_2 solvent was observed. This is in contrast to the preparation of $Cp_2Zr(NCCH_3)_3(BPh_4)_2$, which is prepared by

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[17] Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; J. Wiley: New York, 1986.

[18] Broschag, M. Klapötke, T. M. *Polyhedron* **1992**, *11*, 443.

[19] (a) Lupinetti, A. J.; Havighurst, M. D.; Miller, S. M.; Anderson, O. P.; Strauss, S. H. *J. Am. Chem. Soc.* **1999**, *121*, 11920. (b) Hurlburt, P. K.; Rack, J. J.; Luck, J. S.; Dec, S. F.; Webb, J. D.; Anderson, O. P.; Strauss, S. H. *J. Am. Chem. Soc.* **1994**, *116*, 10003. (c) Hurlburt, P. K.; Anderson, O. P.; Strauss, S. H. *J. Am. Chem. Soc.* **1991**, *113*, 6277. (d) Hwang, G.; Bodenbinder, M.; Willner, H.; Aubke, F. *Inorg. Chem.* **1993**, *32*, 4667. (e) Bley, B.; Willner, H.; Aubke, F. *Inorg. Chem.* **1997**, *36*, 158. (f) von Ahsen, B.; Bach, C.; Berkei, M.; Köckerling, M.; Willner, H.; Hägele, G.; Aubke, F. *Inorg. Chem.* **2003**, *42*, 3801. (g) Willner, H.; Bodenbinder, M.; Bröchler, R.; Hwang, G.; Rettig, S. J.; Trotter, J.; von Ahsen, B.; Westphal, U.; Jonas, V.; Thiel, W.; Aubke, F. *J. Am. Chem. Soc.* **2001**, *123*, 588.

[20] (a) Willner, H.; Aubke, F. *Organometallics* **2003**, *22*, 3612. (b) Willner, H.; Aubke, F. *Chem. Eur. J.* **2003**, *9*, 1668. (c) Lupinetti, A. J.; Strauss, S. H.; Frenking, G. *Prog. Inorg. Chem.* **2001**, *49*, 1. (d) Willner, H.; Aubke, F. *Inorg. Chem. Highlights* **2002**, 195. (e) Willner, H.; Aubke, F. *Angew. Chem. Int. Ed.* **1997**, *36*, 2402.

[21] Gauch, E.; Hoppe, H.; Strähle, J. *J. Organomet. Chem.* **2000**, *593*, 175.

[22] Klapötke, T. *Polyhedron* **1989**, *8*, 311.

Table 1. Crystallographic Data for $Cp_2Ti(NCCl)_2(AsF_6)_2$ (1), $Cp_2Ti(NCBr)_2(AsF_6)_2$ (2), and $Cp_2Ti(NCI)_2(AsF_6)_2{\cdot}SO_2$ (3)

	$Cp_2Ti(NCCl)_2(AsF_6)_2$	$Cp_2Ti(NCBr)_2(AsF_6)_2$	$Cp_2Ti(NCI)_2(AsF_6)_2{\cdot}SO_2$
formula mass (amu)	678.82	767.78	925.82
cryst syst	orthorhombic	orthorhombic	monoclinic
space group	*Pnma*	*Pnma*	$P2_1/c$
a (Å)	18.1491(3)	17.987(2)	9.022(1)
b (Å)	8.1751(1)	8.3387(8)	14.845(2)
c (Å)	14.3414(2)	14.622(2)	19.141(2)
α (deg)	90	90	90
β (deg)	90	90	103.328(2)
γ (deg)	90	90	90
V (Å^3)	2127.84(5)	2193.1(4)	2494.5(5)
Z	4	4	4
T (K)	200	193	193
cryst size (mm)	0.09 × 0.08 × 0.04	0.20 × 0.20 × 0.20	0.10 × 0.10 × 0.20
ρ_{calcd} (g cm^{-3})	2.119	2.325	2.465
μ(Mo Kα) (mm^{-1})	3.846	7.132	5.638
R1 [$I > 2\sigma(I)$], wR2 (all data)	0.0713, 0.2069	0.0545, 0.1398	0.0514, 0.1163

Table 2. Selected Structural Parameters for $Cp_2Ti(NCCl)_2(AsF_6)_2$ (1), $Cp_2Ti(NCBr)_2(AsF_6)_2$ (2), and $Cp_2Ti(NCCl)_2(AsF_6)_2{\cdot}SO_2$ (3)

parameter d/Å, ∠/deg	$Cp_2Ti(NCCl)_2(AsF_6)_2$	$Cp_2Ti(NCBr)_2(AsF_6)_2$	$Cp_2Ti(NCI)_2(AsF_6)_2{\cdot}SO_2$
d(Ti1−N1)	2.117(9)	2.11(1)	2.115(9)
d(Ti1−N2)	2.126(9)	2.106(9)	2.099(8)
d(N1−C1)	1.15(1)	1.10(1)	1.12(1)
d(N2−C2)	1.14(1)	1.15(1)	1.15(1)
d(C1−X1)	1.59(1)	1.82(1)	1.99(1)
d(C2−X2)	1.60(1)	1.76(1)	1.980(9)
d(As−F$_{aver.}$)	1.662	1.593	1.692
d(S−O$_{av}$)			1.401
∠(Ti1−N1−C1)	174.5(8)	173(1)	176.3(9)
∠(N1−C1−X1)	178(1)	179(1)	177.8(9)
∠(N1−Ti−N2)	85.4(4)	84.7(4)	91.4(3)
∠(O1−S1−O2)			114(3)

the reaction of Cp_2ZrI_2 and $AgBPh_4$ in CH_3CN solution, whereby coordination of the CH_3CN was observed.[23] Due to the strong Lewis base nature of the CH_3CN solvent, coordination is observed. In the solid state, the three structures are not isomorphic.

Compounds **1** and **2** are orthorhombic (Figures S1 and S2, Tables 1 and 2), whereas compound **3** is monoclinic (Figure 1, Tables 1 and 2) with a disordered SO_2 solvent molecule in the lattice. In all three compounds, there are discrete AsF_6^- monoanions with no significant cation−anion contacts, in contrast to the parent molecule $Cp_2Ti(AsF_6)_2$, which displays strong Ti−F−As bridges.[6] In addition, in the IR spectra of compounds **1**−**3** there is no peak at 530 cm^{-1}, which has previously been assigned to Ti−F stretching modes.[17] The $Cp_2Ti(NCX)_2^{2+}$ cations (X = Cl, Br, I) adopt a tetrahedral structure, as would be expected, containing two essentially linear XCN moieties (linear within the esd's) with X−C bond lengths similar to those observed in the free XCN molecules (X = Cl, Br, I) (d(X−C) = 1.57(1) Å, ClCN;[24] 1.596 Å (average, **1**); 1.79 Å, BrCN;[25] 1.791 Å (average, **2**); 1.987 Å (average, **3**)). The I−C and C≡N bond lengths in ICN were not reported, and only the length of the ICN molecule was given in the literature.[26] The CN bond lengths in the coordinated XCN moieties are also similar to those of the uncoordinated XCN molecules (X = Cl, Br, I) (d(C≡N) = 1.16(2) Å, ClCN;[24] 1.143 Å (average, **1**); 1.15 Å, BrCN;[25] 1.126 Å (average, **2**); 1.138 Å (average, **3**)). The N−Ti bond lengths compounds **1**−**3** are all similar (d(Ti−N) average = 2.122 Å, **1**; 2.108 Å, **2**; 2.107 Å, **3**) and correspond well to those observed in $Cp_2Ti(C_6H_4(CN)_2)_2(SbCl_6)_2$ (d(Ti−N) = 2.13 Å),[10] but are significantly longer than those observed in the neutral four-coordinated bis(cyclopentadienyl)titanium(IV) compounds $Cp_2Ti(NCO)_2$ (d(Ti−N) = 2.007(3), 2.018(3) Å)[27] and $Cp_2Ti(N_3)_2$ (d(Ti−N) = 2.03(1) Å).[28] The presence of the AsF_6^- anion was established by both IR and ^{19}F and ^{75}As NMR spectra.

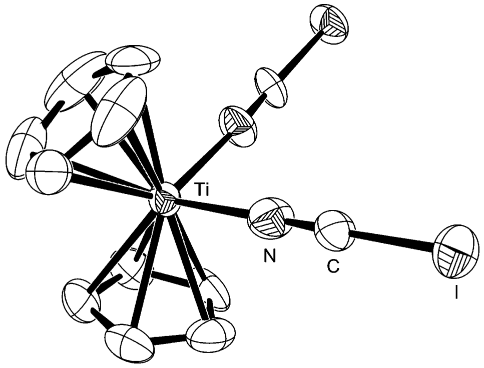

Figure 1. Molecular structure of the cation in **3** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

The IR spectra for compounds **1**−**3** are very similar, as would be expected, with a strong, symmetrical characteristic band between 695 and 700 cm^{-1} which corresponds to ν_3(AsF) AsF_6^-, whereas for the parent Lewis acid, AsF_5, the band in this region is distinctly broader and asymmetrical.[17] A further band that is characteristic for the AsF_6^- moiety at 395 cm^{-1} corresponds to δ(AsF) AsF_6^-. The bands in the IR spectra that are characteristic for the $Cp_2Ti(NCX)_2^{2+}$ cations (X = Cl, Br, I) were discussed above. In the ^{75}As NMR spectra, only one broad peak centered around 1 ppm is observed for all three

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(23) Jordan, R. F.; Echols, S. F. *Inorg. Chem.* **1987**, *23*, 383.

(24) (a) Heiart, R. B.; Carpenter, G. B. *Acta Crystallogr.* **1956**, *9*, 889. (b) Heiart, R. B.; Carpenter, G. B. *Acta Crystallogr.* **1954**, *7*, 639.

(25) Geller, S.; Schawlaw, A. L. *J. Chem. Phys.* **1955**, *23*, 779.

(26) Katelaar, J. A. A.; Zwartsenberg, J. W. *Recl. Trav. Chim. Pays-Bas* **1939**, *58*, 449.

(27) Anderson, S. J.; Brown, D. S.; Norbury, A. H. *J. Chem. Soc., Chem. Commun.* **1974**, 996.

(28) de Gil, E. R.; de Burguera, M.; Rivera, A. V. *Acta Crystallogr.* **1977**, *B33*, 578.

compounds ($\nu_{1/2}$ = 4539 Hz (**1**); 3257 Hz (**2**); 3251 Hz (**3**)) with a chemical shift similar to the $KAsF_6$ standard, which is a further indication that the AsF_6^- moiety is present (^{75}As NMR δ ppm, −5 ppm (**1**); −2 ppm (**2**); −13 ppm (**3**)). The presence of the AsF_6^- anion was clearly shown in the solid-state structures of compounds **1**−**3**; however the AsF_6^- anion in compound **1** is disordered, which is a relatively common problem when highly symmetrical AsF_6^- ions are present. However, the sharp ν_3(AsF) band in the IR spectrum and the peak at −5 ppm in the ^{75}As NMR spectrum of compound **1** provide convincing evidence for the presence of the AsF_6^- counteranions in compound **1**.

Conclusion

The synthesis and characterization of three new dicationic $Cp_2Ti^{IV}(NCX)_2^{2+}$ complexes has been achieved. Compounds **1**−**3** are the first examples of structurally characterized $Cp_2TiL_2(AsF_6)_2$ compounds, as well as the first structurally characterized $Cp_2M(NCX)_2^{2+}$ (M = transition metal; X = halogen) moieties reported in the literature. The aim of this work has been not only to unambiguously establish the existence of the conceptually simple $Cp_2TiL_2(AsF_6)_2$ class of compounds but also to demonstrate the usefulness of $Cp_2Ti(AsF_6)_2$ to generate new, simple cationic $Cp_2TiL_2^{2+}$ complexes, which opens up for further investigations the chemistry of the cationic bis(cyclopentadienyl)titanium(IV) complexes. It is hoped that the cationic chemistry of the Cp_2Ti^{IV} can now be fully investigated.

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Supporting Information Available: X-ray crystallographic files for $Cp_2Ti(NCCl)_2(AsF_6)_2$ (**1**), $Cp_2Ti(NCBr)_2(AsF_6)_2$ (**2**), and $Cp_2Ti(NCI)_2(AsF_6)_2 \cdot SO_2$ (**3**) are available in CIF format. ORTEP plots of compounds **1** and **2** as well as the NMR spectra of compounds **1**−**3** are also available. This material is available free of charge via the Internet at http://pubs.acs.org.

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