Cationic Titanium(IV) Complexes *via* Halide Abstraction from $[Ti(C_5H_5)Cl_3]$: Crystal and Molecular Structure of $[Ti(C_5H_5)(MeCN)_5][SbCl_6]_3{\cdot}2MeCN$ †

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Treatment of $[Ti(cp)Cl_3]$ (cp = η^5-C_5H_5) with $SbCl_5$ as chloride abstractor in acetonitrile provided hexachloroantimonate(V) salts of $[Ti(cp)Cl_2]^+$, $[Ti(cp)Cl]^{2+}$ and $[Ti(cp)]^{3+}$ respectively. With 1:1 stoichiometry red-brown crystals of $[Ti(cp)Cl_2(MeCN)_3][SbCl_6]$ **1** are obtained and with 1:2 stoichiometry light blue crystals of $[Ti(cp)Cl(MeCN)_4][SbCl_6]_2$ **2**. Complete removal of chloride ion from $[Ti(cp)Cl_3]$ requires a six-fold excess of $SbCl_5$ when purple-blue crystals of $[Ti(cp)(MeCN)_5][SbCl_6]_3$ **3** can be isolated. These products were characterised by analytical and spectroscopic (IR, ^1H NMR) data and, in the case of **3**, by a crystal structure determination. Proton NMR studies indicate the presence of intermediate halide-bridged $[Ti(\mu\text{-}Cl)_2Sb]$ species in solution during the sequential halide abstractions **1** $\longrightarrow$ **2** $\longrightarrow$ **3**. Crystals of complex **3**, obtained as the bis(solvate) from recrystallisation in acetonitrile, are monoclinic and X-ray structural analysis confirmed the formulation. The crystal structure [space group *Cc*, $a = 19.650(4)$, $b = 19.182(4)$, $c = 12.958(3)$ Å, $\beta = 91.612(3)°$, $Z = 4$, $R = 0.0386$, $R' = 0.0406$] shows discrete cations and anions and a pseudo-octahedral co-ordination sphere for the Ti^{IV}. A significant *trans* influence of the cyclopentadienyl ligand affects Ti–N bond lengths in the complex.

Cationic Group 4 metal species as represented by $[M(cp)_2(X)L_a]^+$ and $[M(cp)_2L_b]^{2+}$ [M = Ti, Zr or Hf; X = R or halide; cp = η^5-C_5H_5; L = donor solvent, *e.g.* MeCN or tetrahydrofuran (thf)] are of current interest both from their potential as highly reactive Lewis-acid substrates[1] and, more specifically (X = R), as role models for the organotitanium cation species invoked as active catalytic intermediates in the Ziegler–Natta catalysed $\{[Ti(cp)_2Cl_2]\text{–}AlRCl_2]\}$ polymerisation of olefins.[2] Synthetic routes utilised for such cationic titanium species include halide elimination (as salt) using sodium tetraphenylborate *e.g.* $[Ti(cp)_2MeCl] \longrightarrow [Ti(cp)_2Me(MeCN)][BPh_4]$,[1a,b] oxidation of a titanium(III) precursor using silver tetraphenylborate, *e.g.* $[Ti(\eta^5\text{-}C_5Me_5)_2Me] \longrightarrow [Ti(\eta^5\text{-}C_5Me_5)_2Me(thf)][BPh_4]$[3] and protolysis (with elimination of CH_4) of $[TiR_2Me_2]$ (R = indenyl or cp) using $[HNR_3][BPh_4]$ where R = $C_6H_5NMe_2$,[4] Et[5] or Bu^n.[6]

Our observations that Sb^{III} and Sb^V can effectively and selectively remove halide ion(s) from early transition-metal halides represent another convenient route to these discrete cationic metal species particularly appropriate in the case of titanium, *e.g.* $TiCl_4\text{–}SbCl_5\text{–}MeCN \longrightarrow$ *fac* $[TiCl_3(MeCN)_3][SbCl_6]$,[7] $[Ti(cp)_2Cl_2]\text{–}SbCl_5\text{–}MeCN \longrightarrow [Ti(cp)_2Cl(MeCN)][SbCl_6] \longrightarrow [Ti(cp)_2(MeCN)_2][SbCl_6]_2$.[8] Berhalter and Thewalt[9] have reported similar halide abstraction for the reactions $[Ti(cp)_2Cl_2]\text{–}SbCl_5\text{–}C_8H_4N_2 \longrightarrow [Ti(cp)_2(C_8H_4N_2)_2][SbCl_6]_2$ ($C_8H_4N_2$ = phthalonitrile) and $[Ti(cp)_2Cl_2]\text{–}SnCl_4\text{–}C_3H_2N_2 \longrightarrow [Ti(cp)_2Cl(C_3H_2N_2)]_2[SnCl_6]$ ($C_3H_2N_2$ = malonitrile); $[Ti(cp)_2Cl(MeCN)][FeCl_4]$ has been isolated using iron(III) chloride as halide abstractor.[10] Cationic titanium(IV) complexes involving chelated ligands are also known *viz.* $[Ti(cp)_2(bipy)][CF_3SO_3]_2$ (bipy = 2,2'-bipyridine), $[Ti(cp)_2(phen)][CF_3SO_3]_2$ (phen = 1,10-phenanthroline)[11] and $[Ti\{\eta^5\text{-}C_5(SiMe_3)_2H_3\}(acac)_2][CF_3SO_3]$ (acac = acetylacetonate).[12]

Having established the cation formation sequence $[Ti(cp)_2Cl_2] \longrightarrow [Ti(cp)_2Cl]^+ \longrightarrow [Ti(cp)_2]^{2+}$ using antimony(V) chloride as halide acceptor, we have now turned our attention to the monocyclopentadienyl complex $[Ti(cp)Cl_3]$ in anticipation of a similar pattern of halide abstraction. In this report we describe the synthesis and spectroscopic characterisation of the three cationic monocyclopentadienyltitanium(IV) complexes obtained from the $[Ti(cp)Cl_3]\text{–}SbCl_5\text{–}MeCN$ system and the crystal structure determination of one of these.

Experimental

Manipulations of materials were carried out using a conventional Schlenk system and/or a dinitrogen filled glove-box. Solvents were stored over CaH_2 and subsequently P_4O_{10} and freshly distilled under dinitrogen prior to use. Antimony(V) chloride (Aldrich) was used as supplied commercially; $[Ti(cp)Cl_3]$ was prepared following the method of Cardoso *et al.*[13]

The IR spectra were recorded as mulls between CsI plates using a Perkin-Elmer 580B spectrometer, ^1H NMR spectra on a Perkin-Elmer R34 spectrometer (220 MHz) with samples in sealed tubes and UV/VIS spectra on a Shimadzu UV35 spectrometer using MeCN solutions sealed in quartz cells, with a light path of 1 cm. Elemental analyses were performed by Medac Ltd., Brunel University, Uxbridge, Middlesex.

Preparation of Complexes.—$[Ti(cp)Cl_2(MeCN)_3][SbCl_6]$ **1**. A bright orange solution of $[Ti(cp)Cl_3]$ (1.56 g, 7.1 mmol) in acetonitrile (50 cm^3) was added dropwise to a chilled (0 °C) solution of $SbCl_5$ (2.122 g, 7.1 mmol) in acetonitrile (30 cm^3). The resulting dark red-brown solution was stirred at room temperature for 24 h. Removal of solvent *in vacuo* gave a dark red solid which was washed with benzene (3 × 30 cm^3) and then hexane (3 × 30 cm^3) and pumped dry *in vacuo* for several hours. This product was recrystallised from $MeCN\text{–}CH_2Cl_2$ (50:50) to give red-brown platelets of complex **1** (3.96 g, 87%) (Found: C, 20.0; H, 2.1; Cl, 44.1; N, 6.5. $C_{11}H_{14}Cl_8N_3SbTi$ requires C, 20.6; H, 2.2; Cl, 44.2; N, 6.6%). δ_H(CD_3CN with

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

tetramethylsilane as internal reference) 7.40 (5 H, s, C_5H_5) and 1.95 (9 H, s, CH_3CN). $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 349vs (Sb–Cl), 2321, 2291vs (CN). λ_{max} (MeCN) 36 859 cm^{-1}.

$[Ti(cp)Cl(MeCN)_4][SbCl_6]_2$ **2**. *Method* (*a*). A bright orange solution of $[Ti(cp)Cl_3]$ (0.97 g, 4.4 mmol) in acetonitrile (50 cm^3) was treated dropwise with a solution of $SbCl_5$ (2.64 g, 8.8 mmol) in acetonitrile (25 cm^3). The resulting solution became blue whilst being stirred at room temperature for 12 h. Removal of solvent *in vacuo* gave a blue solid which was washed with dichloromethane (3 × 30 cm^3) and hexane (2 × 30 cm^3) and pumped dry *in vacuo* for several hours. Recrystallisation from $MeCN-CH_2Cl_2$ (50 : 50) gave light blue cube-like crystals of complex **2** (3.94 g, 91%) (Found: C, 15.4; H, 1.6; Cl, 46.9; N, 5.8. $C_{13}H_{17}Cl_{13}N_4Sb_2Ti$ requires C, 15.9; H, 1.7; Cl, 47.0; N, 5.7%). $\delta_H(CD_3CN)$ 7.15, 7.40, 7.53 at room temperature. $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 348vs (SbCl), 2319, 2291vs (C≡N). λ_{max}(MeCN) 36 880 cm^{-1}.

Method (*b*). A red-brown solution of complex **1** (4.36 g, 6.8 mmol) in acetonitrile (100 cm^3) was added dropwise to a chilled (0 °C) solution of $SbCl_5$ (2.03 g, 6.8 mmol) in acetonitrile (50 cm^3). The resulting dark blue solution was stirred at room temperature for 24 h. Removal of solvent provided the product as a dark blue solid which was washed with benzene (3 × 25 cm^3) and hexane (3 × 20 cm^3) and pumped dry *in vacuo* (5.94 g, 89%) (Found: C, 15.3; H, 1.7; Cl, 46.9; N, 5.7%). $\delta_H(CD_3CN)$ 7.15, 7.40, 7.53 at room temperature. $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 348vs (SbCl), 2319, 2291vs (CN). λ_{max}(MeCN) 36 887 cm^{-1}.

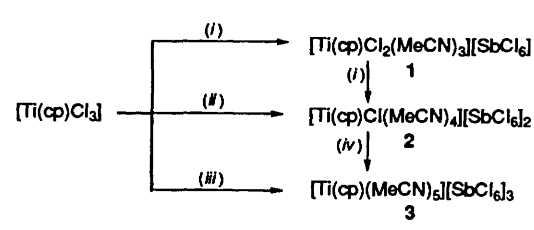
$[Ti(cp)(MeCN)_5][SbCl_6]_3$ **3**. An ice-cold solution of $[Ti(cp)Cl_3]$ (0.56 g, 2.6 mmol) in acetonitrile (50 cm^3) was treated dropwise with a solution of $SbCl_5$ (4.57 g, 15 mmol) in acetonitrile (30 cm^3). The resulting solution became deep blue over a period of 12 h with stirring at room temperature. Removal of solvent gave a purple-blue solid which was washed with dichloromethane (6 × 30 cm^3) and hexane (3 × 30 cm^3) and pumped *in vacuo* for several hours. This product was dissolved in the minimum of acetonitrile and layered with an equal volume of dichloromethane to provide deep blue block crystals of complex **3** (2.79 g, 83%) (Found: C, 13.8; H, 1.6; Cl, 48.6; N, 5.3. $C_{15}H_{20}Cl_{18}N_5Sb_3Ti$ requires C, 13.6; H, 1.5; Cl, 48.3; N, 5.3%). $\delta_H(CD_3CN)$ 7.15, 7.40, 7.45, 7.53 at room temperature; 7.69 at 76 °C. $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 348vs (SbCl), 2320, 2291vs (C≡N). λ_{max}(MeCN) 36 888 cm^{-1}.

X-Ray Crystallography.—Purple-blue cube crystals of complex **3**, as the 2MeCN solvate, suitable for X-ray diffraction studies were obtained following recrystallisation from acetonitrile. The chosen crystal was sealed in a Lindemann tube under an atmosphere of argon.

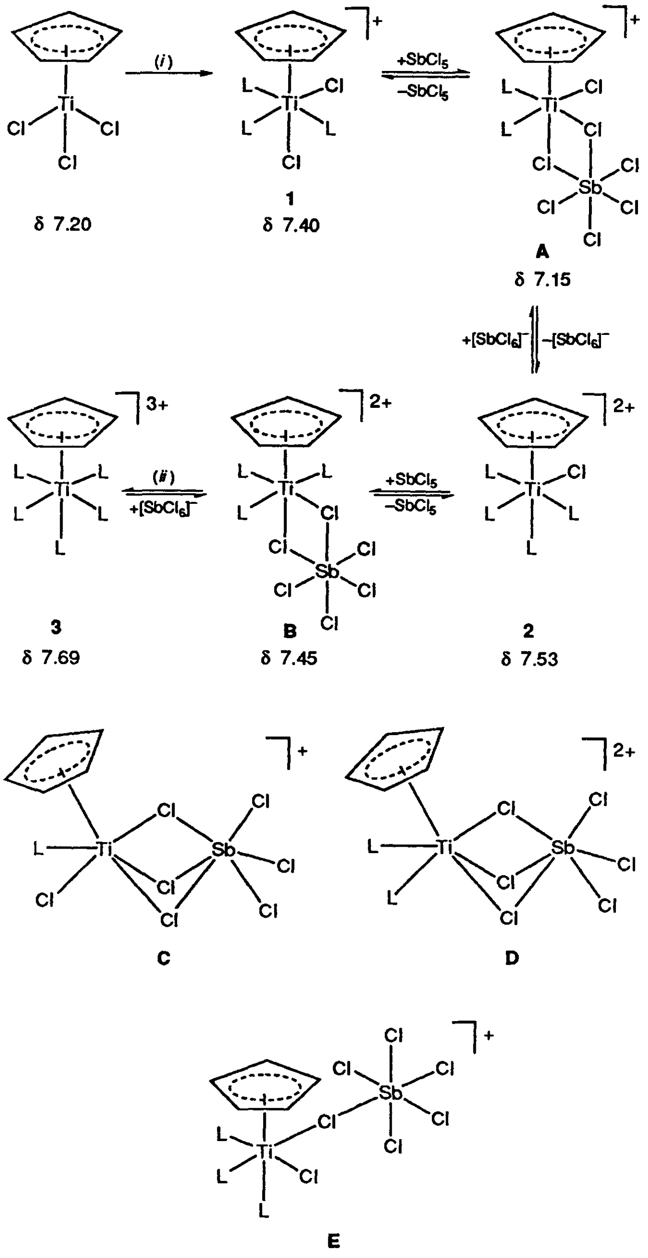
Crystal data. $C_{19}H_{26}Cl_{18}N_7Sb_3Ti$, $M = 1403.72$, monoclinic, space group *Cc*, $a = 19.650(4)$, $b = 19.182(4)$, $c = 12.958(3)$ Å, $\beta = 91.612(3)°$, $Z = 4$, $U = 4882.27$ Å^3, $D_c = 1.910$ g cm^{-3}, $F(000) = 2\,680$, $\mu(Mo\text{-}K\alpha) = 27.1$ mm^{-1}.

Data collection. Data were collected with a Philips PW1100 four-circle diffractometer in the range θ 3–25° by the method described previously,[14] with a constant scan speed of 0.05° s^{-1} and an ω-scan width of 0.90° for the crystal of dimensions 2.1 × 2.8 × 3.2 mm. Three reference reflections were measured at 5 h intervals and showed no significant changes in intensities. The data were corrected for Lorentz and polarisation factors and equivalent reflections were merged to give a total of 3184 unique data with $I > 3\sigma(I)$.

Structure solution and refinement.[15] The positions of two antimony and four chlorine atoms were deduced from a Patterson synthesis. The remaining non-hydrogen atoms were located from subsequent Fourier-difference syntheses; residual electron density was assigned to two severely disordered acetonitrile solvate molecules. Hydrogen atoms on methyl carbons of each co-ordinated acetonitrile were included in idealised positions (C–H 1.08 Å). Absorption corrections[16] were applied after refinement with isotropic thermal parameters for all atoms. In the final cycles of full-matrix least-squares refinement, the titanium, antimony and chlorine atoms were assigned anisotropic thermal parameters. Neutral scattering factors, corrected for the real and imaginary components of anomalous dispersion, were used throughout.[17] Individual weights of $1/\sigma^2(I)$ were assigned to each reflection and refinement converged at *R* 0.0386 and *R′* 0.0406 where $R' = \Sigma[|F_o| - |F_c|]w^{\frac{1}{2}}/\Sigma|F_o|w^{\frac{1}{2}}$. Final atomic coordinates are listed in Table 1 and selected bond lengths and angles in Table 2.



Scheme 1 (*i*) $SbCl_5$, MeCN; (*ii*) $2SbCl_5$, MeCN; (*iii*) $6SbCl_5$, MeCN; (*iv*) $4SbCl_5$, MeCN



Scheme 2 (*i*) $SbCl_5$, L = MeCN; (*ii*) high temperature

Table 1 Fractional atomic coordinates with estimated standard deviations in parentheses for $[Ti(cp)(MeCN)_5][SbCl_6]_3$

Atom	*x*	*y*	*z*
Ti	0.076 1(1)	0.779 9(1)	0.256 0(2)
N(1)	0.013 9(5)	0.691 7(6)	0.264 5(9)
C(11)	−0.018 3(7)	0.643 4(8)	0.266 5(11)
C(12)	−0.058 8(9)	0.581 0(10)	0.275 8(15)
N(2)	0.157 8(5)	0.709 7(5)	0.269 3(8)
C(21)	0.199 6(7)	0.670 6(7)	0.269 0(11)
C(22)	0.257 5(8)	0.623 8(8)	0.272 2(13)
N(3)	0.141 5(5)	0.849 0(6)	0.183 4(9)
C(31)	0.174 9(7)	0.883 8(7)	0.138 4(12)
C(32)	0.218 1(9)	0.930 7(9)	0.078 8(15)
N(4)	−0.004 3(5)	0.830 6(6)	0.177 6(9)
C(41)	−0.048 3(7)	0.858 1(8)	0.137 3(12)
C(42)	−0.104 8(9)	0.895 1(10)	0.082 2(16)
N(5)	0.081 8(6)	0.736 1(6)	0.100 8(10)
C(51)	0.084 9(7)	0.710 8(7)	0.024 9(12)
C(52)	0.092 1(10)	0.678 1(10)	−0.070 2(16)
C(1)	0.064 1(8)	0.760 8(8)	0.434 7(13)
C(2)	0.125 4(7)	0.798 8(8)	0.422 4(12)
C(3)	0.111 9(8)	0.864 0(9)	0.383 2(13)
C(4)	0.038 0(8)	0.868 7(9)	0.369 2(13)
C(5)	0.011 0(8)	0.804 1(8)	0.398 6(13)
Sb(1)	0	0.098 70(6)	0.25
Cl(11)	−0.071 9(3)	0.106 1(3)	0.102 4(5)
Cl(12)	−0.076 2(3)	0.016 8(2)	0.318 3(4)
Cl(13)	−0.060 0(3)	0.188 5(3)	0.329 8(5)
Cl(14)	0.068 5(3)	0.088 4(5)	0.399 9(6)
Cl(15)	0.074 2(3)	0.180 6(3)	0.182 4(4)
Cl(16)	0.059 4(3)	0.009 3(3)	0.172 0(6)
Sb(2)	0.159 54(7)	0.441 94(5)	0.086 38(12)
Cl(21)	0.103 8(2)	0.543 8(3)	0.138 4(4)
Cl(22)	0.217 0(3)	0.435 3(3)	0.247 9(4)
Cl(23)	0.217 2(2)	0.339 6(2)	0.036 6(4)
Cl(24)	0.103 5(2)	0.445 7(3)	−0.075 2(4)
Cl(25)	0.248 9(2)	0.508 6(3)	0.022 2(4)
Cl(26)	0.071 3(3)	0.372 8(3)	0.149 5(5)
Sb(3)	0.345 72(7)	0.900 22(5)	0.434 92(11)
Cl(31)	0.276 9(2)	0.979 8(2)	0.340 8(4)
Cl(32)	0.394 9(2)	0.994 3(2)	0.524 9(4)
Cl(33)	0.294 7(2)	0.807 7(2)	0.343 5(4)
Cl(34)	0.412 3(2)	0.820 9(2)	0.532 0(4)
Cl(35)	0.429 2(2)	0.905 8(2)	0.311 4(4)
Cl(36)	0.261 2(2)	0.892 6(2)	0.559 3(4)

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Direct treatment of $[Ti(cp)Cl_3]$ with $SbCl_5$ in acetonitrile provides a convenient and direct route to the titanium(IV) (d^0) cations **1**–**3** following stepwise chloride abstraction (Scheme 1). Whereas **1** and **2** can be obtained directly from $[Ti(cp)Cl_3]$ following the required stoichiometry, *viz.* 1 : 1 and 1 : 2 respectively, total halide abstraction to give the triply charged cation **3** demands a large excess of $SbCl_5$ (approximately 1 : 6). Similarly, although **2** can be obtained in sequence from **1** using 1 equivalent of $SbCl_5$, the conversion **2**⟶**3** is only effected in the presence of an excess of $SbCl_5$. The red-brown (**1**), light blue (**2**) and purple-blue (**3**) complexes are extremely sensitive to air/moisture hydrolysis, especially when in solution, and must be handled continuously under an inert atmosphere of dinitrogen or argon.

The IR spectra indicate the presence of co-ordinated MeCN with a sharp doublet 2321, 2291 (**1**), 2319, 2291 (**2**) and 2320, 2291 cm^{-1} (**3**) representing a high-energy shift *ca.* 34–40 cm^{-1}, with respect to the free nitrile, typical for such solvated cationic species, *e.g.* $[Ti(cp)_2(MeCN)_2][PF_6]_2$ (2325, 2288 cm^{-1}).[18] An intense broad band at *ca.* 348 cm^{-1} is characteristic for the $SbCl_6^-$ anion, *cf.* $K[SbCl_6]$ with ν(SbCl) $[F_{1u}(\nu_3)]$ 346 cm^{-1},[19] but most likely incorporates some coupling between individual ν(SbCl) and ν(TiCl) stretching modes. The UV/VIS spectra (MeCN) show an intense charge-transfer band λ_{max} *ca.* 36 800 cm^{-1} diagnostic of $[SbCl_6]^-$ in solution.[8] The room-temperature ^1H NMR spectrum (CD_3CN) of **1** shows a singlet δ 7.40 (relative intensity 5) for the cp ring protons and another singlet δ 1.95 (relative intensity 9) for uncomplexed acetonitrile. This establishes the presence of three acetonitrile ligand molecules and that exchange between free and co-ordinated acetonitrile is rapid on the NMR time-scale. For **2** the room-temperature ^1H NMR spectrum shows three cp resonances at δ 7.15, 7.40 and 7.53; these collapse to one signal at δ 7.45 on addition of 1 equivalent of $SbCl_5$. Upon warming this solution to 76 °C the single resonance is retained but with a conspicuous downfield shift to δ 7.69. The ^1H NMR spectrum of **3** at room temperature features four cp resonances at δ 7.15, 7.40, 7.53 and 7.45 which collapse to a singlet at δ 7.69 as the temperature is raised to 76 °C. These observations are consistent with ligand exchange L(MeCN) ⟷ $SbCl_5$ and equilibria between cationic species involving halide-bridged intermediates (Scheme 2).

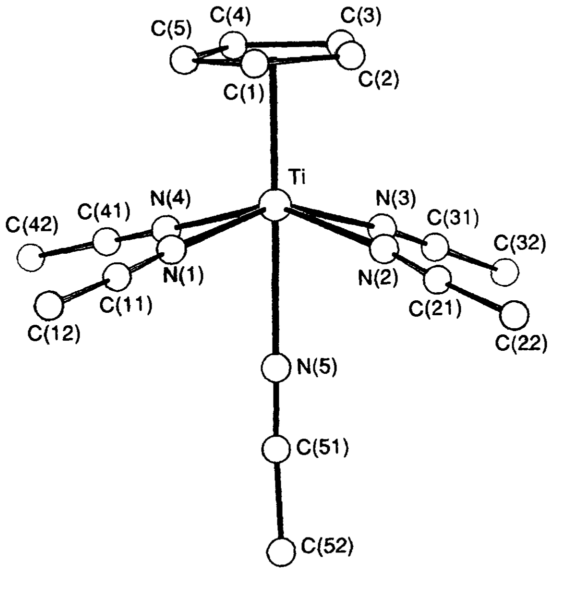


Fig. 1 The structure of the $[Ti(cp)(MeCN)_5]^{3+}$ cation showing the atom numbering scheme

The downfield shift of the characteristic cp resonance on going from neutral $[Ti(cp)Cl_3]$ through **1** ⟶ **2** ⟶ **3** is a direct reflection of the increasing cationic charge. The postulated intermediates **A** and **B** are depicted as doubly halide-bridged species involving edge–edge sharing of (pseudo) octahedral, solvated chloro(cyclopentadienyl)titanium (IV) and antimony(V) units. The triply halide-bridged arrangements **C** and **D** based on face–face sharing of such octahedral units can equally be invoked as acceptable alternatives to **A** and **B** respectively. Single halide bridging, *i.e.* apex–apex sharing as depicted in **E**, seems much less likely bearing in mind the rapacious Lewis acidity of Sb^V and Ti^{IV}. It is interesting that the cp resonance of each of the intermediates **A** and **B** is shifted upfield from that of the 'parent' cation, *viz.* **1** and **2** respectively. Presumably the side-on attachment of an $SbCl_5$ unit, which brings an 'extra' chlorine atom into the metal co-ordination sphere at the expense of a solvent (MeCN) molecule, provides

Table 2 Selected bond lengths (Å) and angles (°) for $[Ti(cp)(MeCN)_5][SbCl_6]_3$

Ti–N(1)	2.092(11)	Ti–N(2)	2.098(10)
Ti–N(3)	2.089(11)	Ti–N(4)	2.094(11)
Ti–N(5)	2.185(12)	Ti–C(1)	2.36(2)
Ti–C(2)	2.37(2)	Ti–C(3)	2.40(2)
Ti–C(4)	2.38(2)	Ti–C(5)	2.32(2)
N(1)–C(11)	1.12(2)	C(11)–C(12)	1.45(2)
N(2)–C(21)	1.11(2)	C(21)–C(22)	1.45(2)
N(3)–C(31)	1.11(2)	C(31)–C(32)	1.47(2)
N(4)–C(41)	1.13(2)	C(41)–C(42)	1.48(2)
N(5)–C(51)	1.10(2)	C(51)–C(52)	1.39(2)
C(1)–C(2)	1.42(2)	C(1)–C(5)	1.40(2)
C(2)–C(3)	1.37(2)	C(3)–C(4)	1.46(2)
C(4)–C(5)	1.41(2)		
N(2)–Ti–N(1)	85.6(4)	N(2)–Ti–N(5)	76.7(4)
N(4)–Ti–N(1)	88.2(4)	N(4)–Ti–N(5)	77.8(4)
N(4)–Ti–N(2)	154.6(4)	N(3)–Ti–N(1)	154.8(4)
N(3)–Ti–N(5)	77.4(4)	N(3)–Ti–N(2)	88.0(4)
N(3)–Ti–N(4)	87.2(4)	N(5)–Ti–N(1)	77.5(4)
C(11)–N(1)–Ti	178(1)	C(21)–N(2)–Ti	175(1)
C(31)–N(3)–Ti	175(1)	C(41)–N(4)–Ti	179(1)
C(51)–N(5)–Ti	176(1)	N(1)–C(11)–C(12)	176(2)
N(2)–C(21)–C(22)	176(1)	N(3)–C(31)–C(32)	179(2)
N(4)–C(41)–C(42)	178(2)	N(5)–C(51)–C(52)	177(2)
C(5)–C(1)–C(2)	107(1)	C(3)–C(2)–C(1)	111(1)
C(4)–C(3)–C(2)	107(1)	C(5)–C(4)–C(3)	107(1)
C(4)–C(5)–C(1)	109(1)		

an increased σ/π donation thereby 'softening' the effective charge at the metal centre.

Structural Considerations.—Complexes of the generic type $[Ti(cp)_2(X)_aL_{2-a}]^{(2-a)+}$ (a = 0 or 1) have a formal 16e$^-$ classification with a four-co-ordinate pseudo-tetrahedral metal geometry in accord with theoretical predications, *viz.* of the three lowest-energy unoccupied orbitals in the molecular orbital description of a bent metallocene $Ti(cp)_2$ fragment two are bonding ($2a_1 + b_2$) whilst the other is non-bonding ($1a_1$).[20]

The present complexes belong to the generic type $[Ti(cp)(X)_aL_{5-a}]^{(3-a)+}$ where a = 2 (**1**), 1 (**2**) and 0 (**3**) which features a six-co-ordinate pseudo-octahedral metal geometry again assuming the cyclopentadienyl ligand as unidentate; the expansion in co-ordination number but retention of an effective 16-valence-electron configuration on going from $[Ti(cp)_2(X)_aL_{2-a}]^{(2-a)+}$ to $[Ti(cp)(X)_aL_{5-a}]^{(3-a)+}$ is seen simply as a result of steric relaxation coincident with the removal of a large bulky cyclopentadienyl group. Structure **3** is the first example of this particular series; the triflate salt, $[Ti\{\eta^5\text{-}C_5(SiMe_3)_2H_3\}(acac)_2][CF_3SO_3]$[12] features a monocyclopentadienyl titanium(IV) cation with a formal 14e$^-$ electronic configuration. The parent molecule $[Ti(cp)Cl_3]$ has a 'piano-stool' structure based on a tetrahedral metal geometry.[21]

The structure of the bis(acetonitrile) solvate of complex **3** shows a discrete $[Ti(cp)(MeCN)_5]^{3+}$ cation, three $[SbCl_6]^-$ counter anions and two non-associated (and disordered) acetonitrile molecules in the asymmetric unit. Selected bond lengths and angles are given in Table 2. The cation is six-co-ordinate; the metal co-ordination sphere comprises five *N*-bonded acetonitrile ligands and an η^5-bonded cyclopentadienyl anion, and shows significant distortion from idealised octahedral geometry (Fig. 1). The cyclopentadienyl ring is symmetrically bonded to the metal with a ring centroid–Ti distance (2.04 Å) comparable to those found for neutral $[Ti(cp)Cl_3]$ (2.01 Å)[21] and cationic $[Ti(cp)_2Cl(C_3H_2N_2)]^+$ [2.00(3), 2.03(2) Å] and $[Ti(cp)_2(C_8H_4N_2)_2]^{2+}$ (2.01, 2.02 Å).[9] The four 'equatorial' nitrogen atoms are coplanar to within 0.01 Å. The metal lies 0.46 Å above the N_4 equatorial plane and consequently N–Ti–N angles between these equatorial nitrogens and that *trans* to the cyclopentadienyl ring are in the range 76.7(4)–77.8(4)°, significantly smaller than the ideal. The Ti–N bond lengths in the equatorial plane, in the range 2.089(11)–2.098(10) Å, are significantly shorter than those in the six-co-ordinate $[TiCl_3(MeCN)_3]^+$ monocation[7] and in four-co-ordinate titanocenes featuring *N*-bonded nitrile ligands.[9,10,22] This shortening may be attributed to the markedly higher charge of the trication **3**. Interestingly, the bond length to the nitrogen *trans* to the cyclopentadienyl ring in the titanium(IV) co-ordination sphere [Ti–N(5) 2.185(12) Å] is significantly longer than the equatorial Ti–N distances and is attributed to a *trans* influence from the η^5-cyclopentadienyl ligand. Since this appears to be the first example of an octahedral cyclopentadienyltitanium(IV)–acetonitrile complex suitable comparisons with related complexes are not possible.

The hexachloroantimonate(V) counter anions possess geometries close to ideal octahedral; observed bond angles lie in the range 88.6(4)–91.1(4)°, within 2° of the ideal, and Sb–Cl bond lengths in the range 2.321(5)–2.365(4) Å.

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References

1 See, for example, (*a*) M. Bochmann and L. M. Wilson, *J. Chem. Soc., Chem. Commun.*, 1986, 1610; (*b*) M. Bochmann, L. M. Wilson, M. B. Hursthouse and R. L. Short, *Organometallics*, 1987, **6**, 2556; (*c*) M. Bochmann, L. M. Wilson, M. B. Hursthouse and M. Motevalli, *Organometallics*, 1988, **7**, 1148; (*d*) T. K. Hollis, N. P. Robinson and B. Bosnich, *J. Am. Chem. Soc.*, 1992, **114**, 5464; (*e*) S. L. Borkowsky, N. C. Baenziger and R. F. Jordan, *Organometallics*, 1993, **12**, 486; (*f*) R. F. Jordan, C. S. Bajgur, W. E. Dasher and A. L. Rheingold, *Organometallics*, 1987, **6**, 1041; (*g*) R. F. Jordan and A. S. Guram, *Organometallics*, 1990, **9**, 2116, 2190; (*h*) S. L. Borkowsky, R. F. Jordan and G. D. Hinch, *Organometallics*, 1991, **10**, 1268; (*i*) Y. W. Alelyunas, R. F. Jordan, S. F. Echols, S. L. Borkowsky and P. K. Bradley, *Organometallics*, 1991, **10**, 1406; (*j*) A. S. Guram and R. F. Jordan, *Organometallics*, 1991, **10**, 3470; (*k*) W. E. Piers, L. Koch, D. S. Ridge, L. R. MacGillivray and M. Zaworotko, *Organometallics*, 1992, **11**, 3148; (*l*) Z.-Y. Guo, P. K. Bradley and R. F. Jordan, *Organometallics*, 1992, **11**, 2690; (*m*) Y. W. Alelyunas, Z.-Y. Guo, R. E. LaPointe and R. F. Jordan, *Organometallics*, 1993, **12**, 544; (*n*) Y. Hong, B. A. Kuntz and S. Collins, *Organometallics*, 1993, **12**, 964; (*o*) R. F. Jordan, *Adv. Organomet. Chem.*, 1991, **32**, 325.

2 L. Clawson, J. Soto, S. L. Buckwald, M. L. Steigerwald and R. L. Grubbs, *J. Am. Chem. Soc.*, 1985, **107**, 3377; J. J. Eisch, A. M. Piotrowski, S. K. Brownstein, E. J. Gabe and F. L. Lee, *J. Am. Chem. Soc.*, 1985, **107**, 7219; C. A. Jolly and D. S. Marynick, *J. Am. Chem. Soc.*, 1989, **111**, 7968; R. Benn and W. Hermann, *Angew. Chem., Int. Ed., Engl.*, 1991, **30**, 426; J. J. Eisch, K. R. Caldwell, S. Werner and C. Kruger, *Organometallics*, 1991, **10**, 3417; J. C. W. Chien, G. H. Llinas, M. D. Rausch, G.-Y. Lin, H. H. Winter, J. L. Atwood and S. G. Bott, *J. Am. Chem. Soc.*, 1991, **113**, 8569 and refs. therein.

3 M. Bouchmann, A. J. Jaggar, L. M. Wilson, M. B. Hursthouse and M. Motevalli, *Polyhedron*, 1989, **8**, 1838; M. Bochmann, A. J. Jaggar, M. B. Hursthouse and M. Mazid, *Polyhedron*, 1990, **9**, 2097.

4 R. Taube and L. Krukowka, *J. Organomet. Chem.*, 1988, **347**, C9.

5 M. Bochmann, A. J. Jaggar and J. C. Nichols, *Angew. Chem., Int. Ed., Engl.*, 1990, **29**, 780; M. Bochmann and S. J. Lancaster, *J. Organomet. Chem.*, 1992, **434**, C1.

6 J. J. W. Eshuis, Y. Y. Tan and J. H. Teuben, *J. Mol. Catal.*, 1990, **62**, 277.

7 P. P. K. Claire, G. R. Willey and M. G. B. Drew, *J. Chem. Soc., Chem. Commun.*, 1987, 1100.

8 P. N. Billinger, P. P. K. Claire, H. Collins and G. R. Willey, *Inorg. Chim. Acta*, 1988, **149**, 63.

9 K. Berhalter and U. Thewalt, *J. Organomet. Chem.*, 1987, **332**, 123.

10 U. Thewalt, K. Berhalter and E. W. Neuse, *Transition Met. Chem.*, 1985, **10**, 393.

11 U. Thewalt and K. Berhalter, *J. Organomet. Chem.*, 1986, **302**, 193.
12 C. H. Winter, X.-X. Zhou and M. J. Heeg, *Organometallics*, 1991, **10**, 3799.
13 A. M. Cardoso, R. J. H. Clark and S. Moorhouse, *J. Chem. Soc., Dalton Trans.*, 1980, 1156.
14 M. K. Cooper, P. A. Duckworth, K. Henrick and M. McPartlin, *J. Chem. Soc., Dalton Trans.*, 1981, 2357.
15 G. M. Sheldrick, SHELX 76 program system, University of Cambridge, 1976.
16 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A, 1983,* **39**, 158.
17 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.
18 M. R. M. Bruce and D. R. Tyler, *Organometallics*, 1985, **4**, 528; R. F. Jordan and S. F. Echols, *Inorg. Chem.*, 1987, **26**, 383.
19 M. Burgard and J. MacCordick, *Inorg. Nucl. Chem. Lett.*, 1970, **6**, 599.
20 J. W. Lauher and R. Hoffmann, *J. Am. Chem. Soc.*, 1976, **98**, 1729.
21 L. M. Engelhardt, R. I. Papasergio, C. L. Raston and A. H. White, *Organometallics*, 1984, **3**, 18.
22 H. Aslan, S. H. Eggers and R. D. Fischer, *Inorg. Chim. Acta*, 1989, **159**, 55.

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