Cationic ansa-(η^5-Cyclopentadienyl)(η^6-arene) Complexes of Titanium^{3+}

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The half-sandwich titanium trimethyl complex (η^5-C_5H_4CMeo_2Ar)TiMe_3 (Ar = 3,5-Me_2C_6H_3) reacts with the Lewis acid B(C_6F_5)_3 to give the ionic TiIV ansa-cyclopentadienyl-arene complex [(η^5-C_5H_4CMeo_2Ar)TiMe_2]-[MeB(C_6F_5)_3]. In bromobenzene solvent, addition of more TiMe_2 and MeB(C_6F_5)_3 leads to C_6F_5/Me exchange and, subsequently, to formation of an unusual dimeric TiIII dicationic species, [[[(η^5-C_5H_4CMeo_2Ar)TiBr(Me)][B(C_6F_5)Me]]_2, which was structurally characterized. Its formation involves reduction of the transition-metal center, solvent C–Br cleavage and perfluoroaryl-group scrambling.

Results and Discussion

The synthesis of the benzylic-cyclopentadienyl salt Li[C_5H_4CMeo_2Ar] (Ar = 3,5-dimethylphenyl) is straightforward, proceeding through addition of AlLi (obtained from ArBr and nBuLi) to 6,6-dimethylfulvene, analogous to the preparation of Li[C_5H_4CMeo_2Ph]. The 3,5-(dimethyl)phenyl group was chosen initially to provide a stronger donor interaction (in [Cp*MMe_2(arene)]^+ toluene is more strongly bound than benzene) and to make arene cyclo-metallation less favorable. Reaction of this Li salt with TiCl_4 in dichloromethane afforded (C_5H_4CMeo_2Ar)TiCl_3, which was methylated in benzene solvent using Me_2Mg(dioxane) to give the trimethyl derivative (C_5H_4CMeo_2Ar)TiMe_2.

In [D_2]-1,1,2,2-tetrachloroethane or [D_6]bromobenzene solvent, I reacts with 1 equiv. of the Lewis acid B(C_5F_9)_3 to give deep red solutions of a species that was identified by 1D and 2D NMR techniques as the ionic ansa-cyclopentadienyl-arene complex [(η^5,η^6-C_5H_4CMeo_2Ar)TiMe_2][MeB(C_6F_5)_3] (2, Scheme 1).

The resonances for the [MeB(C_5F_9)_3]^+ anion are consistent with those for a noncoordinated anion, and the resonances for the arene moiety show substantial coordination chemical shifts (downfield for o-C and p-C, upfield for m-C; the o-H proton resonances are found upfield shifted at δ = 5.91). The chemical shift difference between the two sets of Cp protons also increases strongly (Δδ = 1.59 in 2 and 0.14 in 1). Compound 2 is a 16-electron complex and does not readily react with propene or styrene at ambient temperature (as seen from NMR-tube-scale experiments). This suggests that the arene moiety is fairly strongly bound. Addition of a drop of [D_8]THF to a C_6D_5Br solution of 2 shows a shift of the Cp and aryl proton resonances back to C_6F_5 scrambling. This species subsequently undergoes a highly unusual transformation, resulting in a dicatonic dimeric TiIV complex. The crystal structure of this product represents the first structural characterization of an ansa-cyclopentadienyl-arene early transition-metal compound.

Introduction

Cationic titanium half-sandwich (mono-cyclopentadienyl) species show interesting catalytic activity, especially in the syndiotactic polymerization of styrenes and the polymerization of propene to high molecular weight atactic polypropene. There has been some debate in the literature about the nature of the actual active species in these systems, e.g. whether TiIV or TiIII species are involved, or both.[3] As the cationic species [(η^5-C_5Me_5)TiMe_2]^+ is highly electron-deficient we sought ways of stabilizing these, without resorting to strong heteroatom-based Lewis basic species. Baird et al. found that [(η^5-C_5Me_5)MMe_2]^+ cations (M = Ti, Zr, Hf) can bind arenes reversibly,[4] and that this interaction is significantly stronger for Zr and Hf (for which a related crystal structure has been reported)[5] thar for Ti. We thus set out to prepare half-sandwich titanium complexes with benzyl-substituted Cp-ligands to use these interactions in an intramolecular fashion. The feasibility of this was suggested by observations of Chien, Rausch et al. on the [(η^5-C_5Me_5(CH_2CH_2Ph))TiMe_2]^+ system, where NMR evidence was obtained for η^6-coordination of the arene moiety in the thermally labile cationic dimethyl species.[6] In this contribution we describe the synthesis of neutral and cationic titanium complexes with the benzyl-substituted cyclopentadienyl ligand [C_5H_4CMeo_2Ar]^+ (Ar = 3,5-dimethylphenyl).

The cationic ansa-cyclopentadienylarene complex [(η^5,η^6-C_5H_4CMeo_2Ar)TiMe_2][MeB(C_6F_5)_3] was found to be quite stable in bromobenzene solution at ambient temperature, but it reacts with the Lewis acid B(C_5F_9)_3 via Me/
“normal” chemical shift ranges, indicating release of the arene moiety in the presence of a hard Lewis base to give a \([\eta^3, \eta^6-C_5H_4CM_{e2}Ar]TiMe_3(THF)x\)[MeB(C\(6\)F\(5\))]\(\text{-}\)species. Compound 2 is reasonably stable in C\(2\)D\(2\)Cl\(4\) or [D\(5\)]bromo-benzene and only very gradually decomposes at ambient temperature. Solutions of 2, prepared in situ in [D\(5\)]bromo-benzene, produced a few deep brown-green crystals upon standing at ambient temperatures for several days (vide infra).

The presence of one equivalent of excess B(C\(6\)F\(5\))\(\text{-}\)in bromobenzene solutions of 2 resulted in a reaction (complete in about 20–24 h at ambient temperature) forming MeB(C\(6\)F\(5\))\(\text{-}\)[11] and an organometallic species that, based on NMR spectroscopy, was identified as the mixed methyl/perfluoroaryl species \([\eta^3, \eta^6-C_5H_4CM_{e2}Ar]Ti(C\(6\)F\(5\))Me\][MeB(C\(6\)F\(5\))]\(\text{-}\) (3, Scheme 1). The \(^{19}\text{F}\) NMR spectrum shows a C\(6\)F\(5\) group with a downfield shifted o-F resonance, and the \(^{13}\text{C}\) NMR spectrum a triplet with J\(_{\text{CF}}\) 7.3 Hz at \(\delta = 102.7\) for the Ti–Me group. These features are consistent with a Ti(Me)(C\(6\)F\(5\)) species. [12] The \(^{1}\text{H}\) NMR resonances of 3 are broad at ambient temperature, but at –30 °C they reveal an asymmetric structure, and the retention of the \(\eta^3, \eta^6\)-coordination mode of the ancillary ligand. Thus the addition of an extra equivalent of the Lewis acid induces a scrambling of Ti-bound and B-bound hydrocarbyl groups. Upon standing at ambient temperature the solution produces brown-green crystals that (based on lattice parameters) are identical to those that are (more slowly) formed in solutions of 2.

An X-ray structure determination showed that these crystals are of the salt \([\eta^3, \eta^6-C_5H_4CM_{e2}Ar]Ti(\mu-\text{Br})_2][\text{B(C}6\text{F}5\text{)}4\text{]}\) (4, Figure 1).

In this compound a dicatonic dimeric Ti\(\text{IV}\) ansa-cyclopentadienyl-arene bromide complex is complemented by two tetrakis(pentafluorophenyl)borate anions. The dication is centrosymmetric, with nearly equivalent Ti–Br bond lengths in the Ti(\(\mu\)-Br), Ti bridge. The Ti–Br distances are, on average, 0.085 Å shorter than in the isoelectronic neutral \([C_4H_4Me]_2Ti(\mu-\text{Br})_2\) complex[12] and this, combined with the wider Br–Ti–Br’ angle, results in a Ti...Ti distance of 3.7858(9) Å in 4 that is 0.34 Å shorter than in the latter compound. The bend angle of the Cp-arene ligand backbone, C(5)...C(6)...C(7), is quite acute at 95.8(3)°, and the Cp(centroid)...Ti–Ar(centroid) angle is 125.0°. The arene ring does not deviate significantly from planarity, but the bonding to the Ti atom is highly asymmetric, with Ti–C(7), Ti–C(8) and Ti–C(12) being much shorter than the Ti–C(9), –C(10) and –C(11) distances. This results in a slight lengthening of the C(7)...C(8) and C(7)...C(12) bonds relative to the other arene C–C bonds.

The formation of compound 4 is remarkable for at least two reasons: a) the reaction of a Ti\(\text{IV}\) cation with a Lewis acid in a halogenated solvent yields a Ti\(\text{III}\) halide species, and b) starting from a cation with the [MeB(C\(6\)F\(5\))]\(\text{-}\)counterion, a product is formed with [B(C\(6\)F\(5\))]\(\text{-}\)counterions. This indicates that the reaction involves a reduction of the...
metal center, cleavage of the solvent C–Br bond, and a
scrambling of the substrates on the borane/borate species.
In C6D5Br solvent, formation of CH3C6D5 is seen (GC/MS).
The isolated yield of 4 is rather low (18%) and precise
reactive pathways in this transformation are, as yet, unclear,
but the observations made so far are of interest. For in-
stance, they may shed some light on the way in which TiIV
centers can be generated by the reaction of TiIV alkyls
with an excess of Lewis acid activator (note that Grassi et al. use
chlorobenzene as solvent for their ESR experiments with
Cp*TiMe3 and Lewis acids[3b]). It also demonstrates the dy-
namic nature of perfluoroarylborate “weakly coordinating”
anions, in which tetraarylborates may be formed from alkyl-
triarylboranes (an interesting contrast to the aryl abstrac-
tion from the [B(C6F5)4]– anion, recently reported by Boch-
nard et al.[21]).
An interesting contrast to the aryl abstraction is the
namic nature of perfluoroarylborate “weakly coordinating”
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triarylboranes (an interesting contrast to the aryl abstrac-
tion from the [B(C6F5)4]– anion, recently reported by Boch-
nard et al.[21]).

In conclusion, we have observed the formation of a cat-
onic ansa-Cp-arene titanium dimethyl species, hydrocarbyl
ligand scrambling on this species induced by the presence
of excess Lewis acid, and a highly unusual degradation of
a cationic TiIV species in bromobenzene to produce a TiII
complex, the first structurally characterized ansa-Cp-arene
early transition-metal derivative. These observations pro-
vide an interesting insight into the possible activation and
degradation processes in titanium-based half-sandwich ol-
efin polymerization catalysts, and we are presently studying
related hemilabile monocyclopentadienyl TiIV species to in-
crease our understanding of this chemistry.

Experimental Section

General: All experiments were performed under a nitrogen atmo-
sphere with standard Schlenk and glove-box techniques. Deu-
terated solvents (Aldrich, Acros) were either degassed and dried over
molecular sieves (C2D2Cl4, C6D5Br, CD2Cl2) or dried over
Na/K alloy and vacuum transferred before use. Dichloromethane was
distilled from P2O5, CH3Br from Ca chips, other solvents were dis-
tilled from Na/K alloy or Na (toluene) before use. – NMR spectra
were recorded on Varian Gemini 200/300, Inova 400 and Unity 500
spectrometers. The 1H-NMR spectra were referenced to resonances
at low temperature to yield analytically pure material. – 1H NMR
([D6]benzene): δ = 6.94 (s, 2 H, o-H), 6.69 (s, 1 H, p-H), 5.95 (ps.
t, 2 H, Cp), 5.81 (ps. t, 2 H, Cp), 2.15 (s, 6 H, Ar–C), 1.45 (s, 6 H, C
(C6H5)3). – 13C{1H} NMR (C6D5Br): δ = 70.2 (s, 1 H, p-H), 6.74 (ps.
t, 2 H, Cp), 5.91 (ps. t, 2 H, Cp), 2.10 (s, 6 H, Ar–C), 1.07 (6, C(CH3)3) + 3 H B–C) 0.34 (s, 6 H, Ti–C). – 19F NMR (C2D2Cl4, –40°C): δ = 155.2 (s, Ar C), 151.2 (d, JCF = 236 Hz, o-CF), 140.3 (d, JCF = 236 Hz, p-CF), 139.2 (d, JCF = 236 Hz, m-CF), 138.0 (s, Cp C), 135.3 (d, JCF = 166 Hz, Ar–C), 131.4 (s, Ar–C). – 19F NMR (C6D5Br): δ = –132.8 (o-F), –164.1 (p-F), –166.7 (m-F).

Reaction of 2 with [D5]THF: To a deep red solution of 2 in C6D5Br,
preserved as described above, was added a drop of [D5]THF; re-
sulting in a red solution of [n⁴-C6H4Me2Ar]Ti–Me–CF3)[Br][MeB(C6F5)2] – 1H NMR (C6D5Br/[D5]THF): δ = 6.72 (s, 2H, o-H), 6.66 (s, 1H, p-H), 6.14 (ps. t, 2H, Cp), 6.04 (ps. t, 2H, Cp), 2.14 (s, 6H, Ar–C), 1.37 (6H, C(CH3)3) + 6 H, Ti–C). 1.04 (br, 3 H, B–CH3).

Reaction of 2 with B(C6F5)3: In an NMR tube with a Teflon
(Young) valve, a solution of 2 was prepared as described above, but
using two equivalents of B(C6F5)3 per Ti. The tube was allowed to
stand at ambient temperature, and was monitored at regular inter-
vals by 1H and 19F NMR. After 24 h all of 2 had disappeared, giving 3 and MeB(C6F5)3.
132.9 (α-F, B–Ar), –149.9 (p-F, Ti–Ar), –159.5 (m-F, Ti–Ar), –164.7 (p-F, B–Ar), –167.3 (m-F, B–Ar).

MeB(C6F5)2: 1H NMR (CD2Cl2, 20 °C): δ = 1.52 (quint., J1/2 = 2 Hz, B–Me). – 19F NMR (CD2Cl2, –30 °C): δ = –129.9 (α-F), –147.5 (p-F), –161.5 (m-F).

Formation of [[η5,η5-C8H8CMe2Ar]Ti(μ-Br)2][B(C6F5)4]2 (4): A solution of 1 (0.120 g, 0.39 mmol) in 5 mL of bromobenzene was added to B(C6F5)3 (0.40 g, 0.78 mmol). Over a period of 3 weeks at ambient temperature green-brown crystals separated from the solution. The supernatant was decanted and the crystals rinsed twice with 10 mL of pentane. Yield: 0.070 g (34% solution. The supernatant was decanted and the crystals rinsed at ambient temperature green-brown crystals separated from the solution. The supernatant was decanted and the crystals rinsed twice with 10 mL of pentane. Yield: 0.070 g (34 μmol, 18%) of analytically pure 4. – C80H38B2Br2F40Ti2 (2036.3): calcd. C 47.19, H 2.22, Ti 4.58. Found C 47.03, H 2.22, Ti 4.58.

Crystal Structure Analysis of 4: Enraf–Nonius CAD4-F diffractometer, Mo-Kα radiation (λ = 0.71073 Å), T = 130 K; monoclinic, P21/n. a = 13.616(2), b = 16.014(1), c = 17.702(2) Å, β = 109.01(1), V = 3649.4(7) Å³, Z = 2, D = 1.853 g cm⁻³, μ = 14.7 cm⁻¹. The structure was solved by direct methods. A final refinement on F² converged at wR(F²) = 0.1143 for 7118 reflections with Fo ≥ 0 and R(F) = 0.0415 for 5390 reflections with Fo ≥ 4σ(Fo) and 644 parameters.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-135683. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Note Added in Proof (February 28, 2000): During the processing of this contribution a paper was published describing the generation and NMR-spectroscopic characterization (in CD2Cl2 solvent at –60 °C of the cation [η5,η5-C8H8CMe2Ph]TiMe2]ⁿ⁺.[14]

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