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Synthesis of $[Ti(\eta^6\text{-}1,3,5\text{-}C_6H_3{}^iPr_3)_2][BAr_4]$ (Ar = C_6H_5, p-C_6H_4F, 3,5-$C_6H_3(CF_3)_2$), the First Titanium(I) Derivatives

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Summary: The oxidation of $Ti(\eta^6\text{-}1,3,5\text{-}C_6H_3{}^iPr_3)_2$ *with* $FeCp_2[BAr_4]$, *Ar* = C_6H_5, p-C_6H_4F, 3,5-$C_6H_3(CF_3)_2$, *affords good yields of the paramagnetic derivatives of titanium(I),* $[Ti(\eta^6\text{-}1,3,5\text{-}C_6H_3{}^iPr_3)_2][BAr_4]$*; these compounds have been characterized by conventional methods, including single-crystal X-ray diffractometry of* $[Ti(\eta^6\text{-}1,3,5\text{-}C_6H_3{}^iPr_3)_2][B(p\text{-}C_6H_4F)_4]$.

$Ti(\eta^6\text{-arene})_2$ (arene = benzene, toluene, and mesitylene) complexes were first prepared in 1975 by cocondensation of metal atoms with the required aromatic hydrocarbon;[1] by a similar procedure, bis(η^6-naphthalene)titanium(0) was also obtained.[2] Some years later, X-ray diffractometry of $Ti(\eta^6\text{-arene})_2$, arene = benzene and toluene, showed the titanium atom to be sandwiched between the two aromatic rings with eclipsed ring carbon atoms and diametrically opposed methyl groups.[3]

More recently, $Ti(\eta^6\text{-}1,3,5\text{-}C_6H_3{}^tBu_3)_2$ has been prepared,[4] and thermochemical and *ab initio* quantum chemical studies on this molecule have appeared.[5]

Although $Ti(\eta^6\text{-arene})_2$, arene = toluene and mesitylene, can also be obtained by reducing $TiCl_3(THF)_3$ with potassium in THF in the presence of the parent aromatic hydrocarbon,[6] conventional syntheses of bis(η^6-arene) derivatives of titanium(0) were achieved only recently by Ellis and co-workers[7] and by Bönnemann and co-workers[8] by reducing $TiCl_4(THF)_2$ with arene radical anions[7a] or $KC_{10}H_8$[7b] or by sonication in the presence of both $KBEt_3H$ and arene.[8]

Reduction to the $[Ti(\eta^6\text{-arene})_2]^-$ anion (arene = benzene, toluene) was achieved with potassium or potassium hydride,[9] while loss of the coordinated aromatic ligand results from oxidation of the metal center: $Ti(acac)_3$, Ti_2S_3, or $[TiCp_2Cl]_2$ have been obtained by reaction of $Ti(\eta^6\text{-toluene})_2$ with acacH, H_2S (or S_8), or $TiCp_2Cl_2$, respectively.[10] With CO_2, $Ti(\eta^6\text{-toluene})_2$ was mentioned to give a low-valent titanium oxalate in an unspecified oxidation state.[11]

To expand upon the earlier results by some of us on the one-electron oxidation of bis(arenes) of vanadium(0) or niobium(0) with ferricinium cations to the corresponding monovalent cations,[12] we now wish to report the oxidation by a ferricinium derivative $FeCp_2[BAr_4]$, Ar = Ph, p-C_6H_4F, 3,5-$C_6H_3(CF_3)_2$, of the new, thermally stable (both in the solid state and in solution) bis(arene) derivative of titanium(0), $Ti(\eta^6\text{-}1,3,5\text{-}C_6H_3{}^iPr_3)_2$.[13]

The paramagnetic (μ_{eff} (293 K) = 2.01 μ_B (Ar = p-C_6H_4F), 1.94 μ_B (3,5-$C_6H_3(CF_3)_2$) derivatives of titanium(I), namely $[Ti(\eta^6\text{-}1,3,5\text{-}{}^iPr_3C_6H_3)_2][BAr_4]$,[14] which are the first examples of fully characterized derivatives of titanium(I),[15] were obtained according to eq 1. The solubility in toluene and the stability of these compounds strongly depend on the substituents on the

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(13) Synthesis of $Ti(\eta^6\text{-}1,3,5\text{-}C_6H_3{}^iPr_3)_2$. In a typical experiment, titanium (2.3 g, 48 mmol) from an ingot of *ca.* 24 g at a power input of 0.58 kW was co-condensed with an excess of 1,3,5-triisopropylbenzene at 77 K over a 3 h period. After the reaction mixture was allowed to warm to room temperature, the reactor walls were washed with light petroleum ether (400 mL) and the resultant deep purple solution was filtered at 193 K. The light petroleum ether was evaporated under reduced pressure, and the excess ligand was removed by condensation on a cold finger cooled with liquid nitrogen under vacuum (10^{-5} atm). The residue was extracted with light petroleum ether, and the solution was filtered and cooled at 193 K, giving a black-purple solid. The solid was recovered by filtration and dried *in vacuo* (4.11 g, 19% yield with respect to the evaporated titanium). Anal. Calcd for $C_{30}H_{48}Ti$: C, 78.9; H, 10.6. Found: C, 79.5; H, 10.8. ^1H NMR (benzene-d_6, 500 MHz, 25 °C): δ 4.81 (s, 3 H), 2.67 (septet, J_{HH} = 7.0 Hz, 6 H), 1.20 (d, J_{HH} = 7.0 Hz, 18 H) ppm. $^{13}C\{^1H\}$ NMR (benzene-d_6, 125.7 MHz, 25 °C): δ 107.93 (C-$CH(CH_3)_2$), 82.29 (ring CH), 35.03 ($CH(CH_3)_2$), 25.75 ($CH(CH_3)_2$) ppm.

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$$\mathrm{Ti}(\eta^6\text{-}1,3,5\text{-}C_6H_3{}^i\mathrm{Pr}_3)_2 + \mathrm{FeCp_2[BAr_4]} \rightarrow [\mathrm{Ti}(\eta^6\text{-}1,3,5\text{-}C_6H_3{}^i\mathrm{Pr}_3)_2][\mathrm{BAr_4}] + \mathrm{FeCp_2}$$

$$\mathrm{Ar} = \mathrm{Ph},\ p\text{-}C_6H_4F,\ 3,5\text{-}C_6H_3(CF_3)_2$$

aromatic rings of the tetraarylborato anion; thus, $[Ti(\eta^6\text{-}1,3,5\text{-}C_6H_3{}^iPr_3)_2][B(C_6H_5)_4]$ decomposes at about 50 °C and has a limited solubility in aromatic hydrocarbons; $[Ti(\eta^6\text{-}1,3,5\text{-}C_6H_3{}^iPr_3)_2][B(p\text{-}C_6H_4F)_4]$ undergoes partial decomposition in boiling toluene and can be recrystallized from this medium. The substantially insoluble $[Ti(\eta^6\text{-}1,3,5\text{-}C_6H_3{}^iPr_3)_2][B(3,5\text{-}C_6H_3(CF_3)_2)_4]$ is stable in boiling toluene and can be handled in air over short periods of time in the solid state.

Recrystallization of $[Ti(\eta^6\text{-}1,3,5\text{-}C_6H_3{}^iPr_3)_2][B(p\text{-}C_6H_4F)_4]$ from toluene gave small orange platelets suitable for a single-crystal X-ray diffraction experiment.[16] Although the poor quality of the crystals did not allow accurate data collection to be carried out, the atom connectivity can be definitely established. The structure consists of $[Ti(\eta^6\text{-}1,3,5\text{-}C_6H_3{}^iPr_3)_2]^+$ cations (Figure 1) and $[B(p\text{-}C_6H_4F)_4]^-$ anions with two independent cationic moieties on inversion centers, *i.e.*, with necessarily coplanar arene ligands, and a tetrakis(*p*-fluorophenylborate) anion in a general position. The cation has an inversion center on the titanium atom and, therefore, a staggered conformation of the alkyl substituents on the aromatic rings. The ring centroid-to-titanium bond distance is 1.81 Å, compared with the values observed for $[V(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)_2][AlCl_4]$ (1.73.Å),[17] $[Cr(\eta^6\text{-}1,3,5\text{-}C_6H_3{}^iPr_3)_2]I$ (1.65 Å),[18] and $[Mn(\eta^6\text{-}C_6H_5Me)_2]I$ (1.56 Å).[19] The larger distance observed in the titanium(I) complex of the $3d^3$ configuration with respect to the systems of chromium(I), $3d^5$, or manganese(I), $3d^6$, is believed to be consistent with the presumably larger radius of titanium, due to a lower effective nuclear charge.

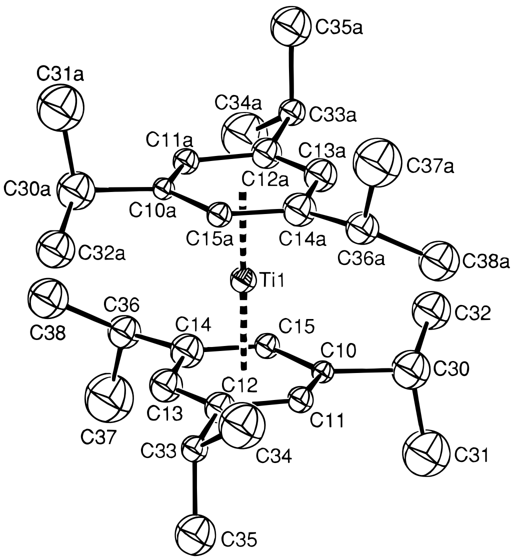

Figure 1. Structure of the $[Ti(\eta^6\text{-}1,3,5\text{-}C_6H_3{}^iPr_3)_2]^+$ cation in $[Ti(\eta^6\text{-}1,3,5\text{-}C_6H_3{}^iPr_3)_2][B(p\text{-}C_6H_4F)_4]$. Selected bond distances and angles: Ti−C, 2.27(2)−2.33(2) Å; C−C (ring), 1.34(3)−1.51(3) Å; $C_{ring}-C_{^iPr}$, 1.49(3)−1.54(3) Å; C−C (^{i}Pr), 1.49(3)−1.61(3); C−C−C (ring), 115(3)−123(2)°; $C_{ring}-C_{ring}-C_{^iPr}$, 117(2)−126(2)°.

The paramagnetic behavior of titanium is in agreement with the presence of one unpaired electron and may suggest the existence of a small orbital contribution consistent with the energy level scheme for sandwiched bis(arene) metal complexes characterized by a low-energy degenerate level.[6,20,21]

The compounds reported in this paper completes the series of the bis(η^6-arene)metal(I) cations from the d^6 manganese(I) to the d^4 vanadium(I) through the chromium(I) derivatives.

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Supporting Information Available: Tables of positional parameters of non-hydrogen atoms, positional parameters of hydrogen atoms, and bond distances and angles (9 pages). Ordering information is given on any current masthead page.

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(14) Synthesis of $[Ti(\eta^6\text{-}1,3,5\text{-}C_6H_3{}^iPr_3)_2][BAr_4]$, Ar = C_6H_5, $p\text{-}C_6H_4F$; $3,5\text{-}C_6H_3(CF_3)_2$. Only the preparation of $[Ti(\eta^6\text{-}1,3,5\text{-}C_6H_3{}^iPr_3)_2][B(p\text{-}C_6H_4F)_4]$ is described in detail, the other compounds were prepared in a similar manner. $Ti(\eta^6\text{-}1,3,5\text{-}C_6H_3{}^iPr_3)_2$ (0.33 g, 0.73 mmol) was added to a suspension of $FeCp_2[B(p\text{-}C_6H_4F)_4]$ (0.40 g, 0.69 mmol) in toluene (40 mL) at 243 K. An immediate reaction took place. After 12 h of stirring at room temperature, the solid was recovered by filtration, washed with toluene (5 mL) and heptane (5 mL), and dried *in vacuo*. It was analytically and spectroscopically identified as $[Ti(\eta^6\text{-}1,3,5\text{-}C_6H_3{}^iPr_3)_2][B(p\text{-}C_6H_4F)_4]$ (0.37 g, 63% yield). Anal. Calcd for $C_{54}H_{64}BF_4Ti$: C, 74.6; H, 7.5; Ti, 5.6. Found: C, 75.9; H, 7.2; Ti, 5.2. IR (poly(chlorotrifluoroethylene), PCTFE and Nujol mull): 2965 (s), 2930 (m), 2873 (w), 1594 (s), 1582 (m s), 1493 (s), 1461 (m), 1385 (w), 1365 (w), 1232 (m s), 1207 (m), 1157 (m s), 837 (w), 812 (s), 548 (w m) cm^{-1}. The compound readily loses included solvent (toluene) by drying *in vacuo*. $[Ti(\eta^6\text{-}1,3,5\text{-}C_6H_3{}^iPr_3)_2][B(C_6H_5)_4]$: red-orange, 63% yield. Anal. Calcd for $C_{54}H_{68}BTi$): C, 83.5; H, 8.8; B, 1.5; Ti, 6.2. Found: C, 82.9; H, 8.0; B, 1.5; Ti, 5.7. IR (PCTFE and Nujol mull): 3055 (w m), 3032 (w), 2968 (s), 2929 (m), 2872 (w), 1601 (vw), 1581 (w), 1484 (w m), 1461 (m), 1424 (w), 1306 (m), 1262 (m), 1068 (m), 733 (s), 704 (s), 613(m) cm^{-1}. ^1H NMR (acetonitrile-d_3 in the presence of air, 200 MHz, 25 °C): δ 7.3 (m, 26 H), 2.86 (septet, $J_{HH} = 7.0$ Hz, 6 H), 1.21 (d, $J_{HH} = 7.0$ Hz, 36 H) ppm. μ_{eff} (293 K): 2.01 μ_B ($\chi^M{}_{corr} = 1710 \times 10^{-6}$ cgsu, diamagnetic correction = -553×10^{-6} cgsu). $[Ti(\eta^6\text{-}1,3,5\text{-}C_6H_3{}^iPr_3)_2][B(3,5\text{-}C_6H_3(CF_3)_2)_4]$: green-brown, 50% yield. Anal. Calcd for $C_{62}H_{60}BF_{24}Ti$: C, 56.4; H, 4.5; Ti, 3.6. Found: C, 55.2; H, 4.3; Ti, 4.5. IR (PCTFE and Nujol mull): 3050 (w), 3030 (w), 2967 (m), 2928 (m), 2873 (w), 1610 (w), 1580 (w), 1354 (s), 1279 (vs), 1228 (m), 1168 (vs), 1138 (vs), 896 (m), 723 (s), 683 (s) cm^{-1}. μ_{eff} (293 K): 1.94 μ_B ($\chi^M{}_{corr} = 1593 \times 10^{-6}$ cgsu, diamagnetic correction = -729×10^{-6} cgsu).

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(16) Crystals of $[Ti(\eta^6\text{-}1,3,5\text{-}C_6H_3{}^iPr_3)_2][B(p\text{-}C_6H_4F)_4]$ were obtained from toluene as thin elongated platelets (0.9 × 0.2 × 0.06 mm) and quickly transferred in a stream of cold nitrogen ($T = -90$ °C). Intensity data collection determination resulted in mostly weak reflections. Due to the limited number of observations, phenyl carbon atoms were refined isotropically. Crystal data for $[Ti(\eta^6\text{-}1,3,5\text{-}C_6H_3{}^iPr_3)_2][B(p\text{-}C_6H_4F)_4]\cdot C_7H_8$: $C_{61}H_{72}BF_4Ti$, fw 939.96, orange platelets, $T = 183$ K, $P\bar{1}$ (No. 2), $Z = 2$, $a = 10.74(1)$ Å, $b = 12.66(1)$ Å, $c = 21.26(2)$ Å, $\alpha = 102.06(5)°$, $\beta = 97.20(8)°$, $\gamma = 109.25(8)°$, V = 2608(4) Å^3, λ (Cu Kα) = 1.5418 Å, $\mu = 17.89$ cm^{-1}, $D_c = 1.197$ $g\cdot cm^{-3}$, $F(000) = 1002$. Of the 8759 measured and empirically absorption-corrected reflections ($\omega-\theta$ scan type; scan range $4° < \theta < 49°$), 1651 independent reflections with $I > 1.5\sigma(I)$ and 267 variables for 140 atoms were considered for the refinement ($R = 0.147$, $R_w = 0.116$, GOF = 1.830).

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