Synthesis of η^5-Cyclopentadienyl- and η^8-Cyclo-octatetraenyl-titanacarboranes of Titanium-(II), -(III), and -(IV)

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Summary Treatment of the organometallic chlorides $LTiCl_x$ ($L = C_5H_5$, $x = 2$ or 3; $L = C_8H_8$, $x = 1$) with the sodium salts of carborane dianions, $Na_2C_2B_nH_{n+2}$, gives the first mixed-ligand titanacarboranes, $[C_5H_5TiC_2B_{10}H_{12}]^-$, $[C_8H_8TiC_2B_nH_{n+2}]^-$, and $C_8H_8TiC_2B_nH_{n+2}$ ($n = 9$ or 10) with formal metal oxidation states of +2, +3, and +4, respectively.

WE recently described[1] the first organometallic complexes of the group IV and V transition metals which incorporate carboranes as π-bonded ligands. We now report the first mixed-ligand metallocarboranes of titanium with the metal in a variety of formal oxidation states.

Addition of $C_5H_5TiCl_x$ ($x = 2$ or 3) to a tetrahydrofuran (THF) solution of $Na_2C_2B_{10}H_{12}$ under argon gave a green solution presumably containing the neutral species $C_5H_5TiC_2B_{10}H_{12}$, or a solvated analogue. Treatment of the solution with zinc dust resulted in a colour change to red and $[Et_4N][4\text{-}(\eta^5\text{-}C_5H_5)\text{-}4,1,6\text{-}TiC_2B_{10}H_{12}]$ (I) was isolated as described previously;[1a] 60 MHz ^1H n.m.r. spectrum in CD_3CN: τ 4·33 (5H, s, C_5H_5) and 2·36 (2H, s br., carborane C-H), 80·5 MHz ^{11}B n.m.r. spectrum: −14·0, −0·6, +0·1, +13·3, and +26·0 p.p.m., doublets of relative area 1:3:3:2:1, relative to $Et_2O{\cdot}BF_3$.† The n.m.r. data are consistent with a fluxional complex resulting from incorporation of the $C_2B_{10}H_{12}$ carborane ligand.[1,2] Cyclic voltammetry‡ showed an irreversible oxidation at $E_{p/2} = +0{\cdot}51$ V and a reversible reduction at $-1{\cdot}78$ V. The red crystalline (I) is stable for a short period in the air and is unreactive toward 1 atm of N_2 or CO in solution.

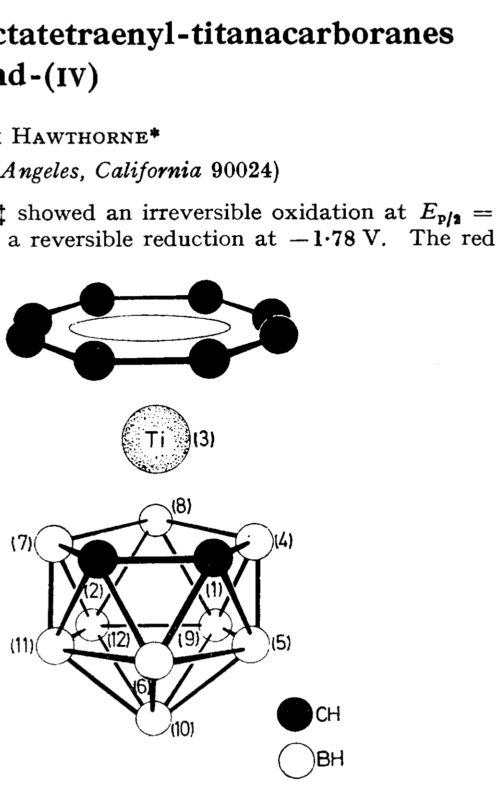

FIGURE. The proposed structure of (III).

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† Satisfactory elemental analyses were obtained for all the new metallocarboranes.

‡ MeCN solvent, 0·1 M $Et_4N^+PF_6^-$, Pt button electrode. Potentials are measured with reference to S.C.E.

The reaction of $(C_8H_8TiCl)_2$ with $Na_2C_2B_9H_{11}$ in THF yielded a green solution from which air-sensitive paramagnetic yellow-green crystals of $[Et_4N][3$-(η^8-C_8H_8)-3,1,2-$TiC_2B_9H_{11}]$ (II) were isolated. A reversible oxidation was observed for (II) at −0·91 V. Treatment of (II) with H_2O_2 gave the greenish-brown, crystalline, neutral species 3-(η^8-C_8H_8)-3,1,2-$TiC_2B_9H_{11}$ (III), ^1H n.m.r. spectrum in $(CD_3)_2CO$: τ 2·28 (s, C_8H_8) and 6·72 (s br., carborane C-H) of relative areas 4:1; ^{11}B n.m.r. spectrum: doublets of relative areas 1:2:2:2:2 at −8·9, +5·1, +5·9, +15·8, and +17·4 p.p.m. The cyclic voltammogram‡ of (III) showed a reversible reduction at −0·87 V. I.r. spectra of (II) and (III) were consistent with η^8-C_8H_8 ligands,[3] exhibiting absorptions at 915m, 835w, 882w, 780m, and 765s; and 920m, 810m, 793m, 772m, and 746vs cm^{-1}, respectively. The proposed structure for (III) is shown in the Figure, and is similar to that crystallographically found[4] for $C_8H_8TiC_5H_5$. These complexes represent the first metallocarboranes containing the C_8H_8 ligand; therefore it is pertinent to note that (III) is air stable to 300 °C and can be purified by liquid chromatography on silica.

The homologous metallocarboranes $[4$-(η^8-C_8H_8)-4,1,6-$TiC_2B_{10}H_{12}]^{n-}$ (n = 0 or 1) have also been prepared; the formal Ti^{IV} complex exhibited a reversible reduction at −0·55 V. A comparison of electrochemical data for all available B_9–B_{10} homologues[2,5] consistently shows lower reduction potentials (which are primarily metal in character[7]) for the $C_2B_{10}H_{12}$ complexes.

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