Reaction of $Ta_2Cp'_2Cl_4H(CHO)$ with Aqueous HCl

$Ta_2Cp'_2Cl_4H(CHO)$ (0.09 g, 0.108 mmol) was added to a vial along with 0.2 ml of pentanediol. The solution was cooled to 0°. Aqueous HCl (12N, 60 μl, 0.72 mmol) and ethanol (6.2 μl, 0.106 mmol) were added. The solution was slowly warmed to 25°. Methanol was measured by GLC on Carbowax 20M using ethanol as the internal standard (0.088 mmol, 82%).

In a separate experiment $Ta_2Cp'_2Cl_4H(CHO)$ (0.083 g, 0.1 mmol) in n-propanol was treated with 0.5 ml 12N HCl(aq) (6 mmol). After 0.5 hour a 1 μl sample was withdrawn for GLC analysis. Methanol (4.1 μl, 0.1 mmol) was added to the reaction mixture and another 1 μl sample was withdrawn for GLC analysis. Comparison of peak areas indicated a 79% yield of methanol.

Reaction of $Ta_2Cp'_2Cl_4H(CHO)$ with Anhydrous HCl

A solution of $Ta_2Cp'_2Cl_4H(CHO)$ (0.42 g, 0.5 mmol) in 100 ml toluene was cooled to -78°. HCl (25 ml, 1.1 mmol) was added to the flask by syringe. The reaction was slowly warmed to 22° with stirring. The color changed from orange-red to red and, after several hours at room temperature, to orange. The volume was reduced to approximately 80 ml under vacuum. The solution was transferred to another flask by cannula. Pentane (100 ml) was added. The solution was cooled to 0° for 12 hours. The reaction mixture was filtered and the solvent was removed from the filtrate in vacuo. An orange solid formed as the solution was concentrated; yield 0.3 g.

^1H NMR (C_6D_6): ppm 4.381 (s, OCH_3), 2.68 (m, $C_5\underline{CH_2}CH_3$), 2.338, 2.234, 2.213, 2.136, 2.098 (s, C_5CH_3), 0.763 (t, $C_5CH_2\underline{CH_3}$). $^{13}C\{^1H\}$ NMR (C_6D_6): ppm 133.7, 131.3, 130.1, 128.6, 128.3 (ring carbons), 21.2, 20.4 ($C_5\underline{CH_2}CH_3$ carbons), 15.2 ($C_5CH_2\underline{CH_3}$ carbons), 13.0, 12.7, 12.5, 12.0 ($C_5\underline{CH_3}$ carbons).