Unexpected Substitution Reactions of Alkoxy-, Acyloxy-, and Chlorobis(η^5-cyclopentadienyl)methyltitanium(IV) Complexes with Acids

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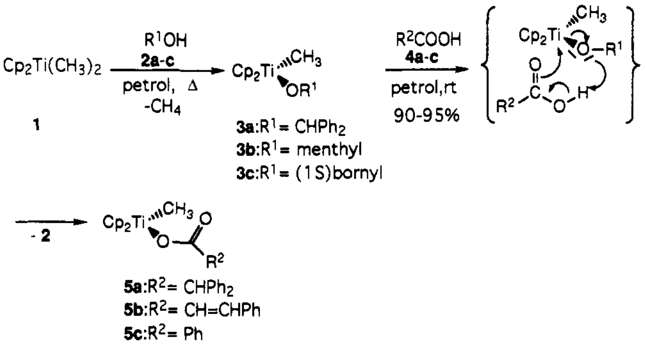
Summary: **The title compounds undergo some unexpected substitution reactions when they are treated with different carboxylic acids. Bis(η^5-cyclopentadienyl)methylalkoxytitanium(IV) complexes exclusively react by substitution of the alkoxy ligand in preference to the metal-bound methyl group. Bis(η^5-cyclopentadienyl)methylchlorotitanium(IV) yields a 1:1 mixture of titanocene dichloride and bis(carboxylato)titanocene. The "nonnucleophilic" tetrafluoroboric acid gives rise to substitution of both the acyloxy and methyl ligands in bis(η^5-cyclopentadienyl)methyl(acyloxy)titanium(IV) complexes with fluoride, thus forming titanocene difluoride and methyldifluoroborane.**

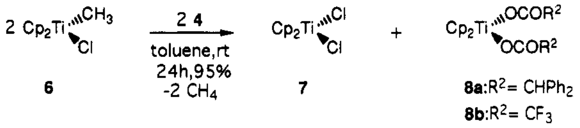
We are currently investigating the effect of the bis(η^5-cyclopentadienyl)titanium(IV) moiety on alkoxy ligands attached to it. As we have reported previously,[1] dimethyltitanocene **1** reacts readily and smoothly with alcohols **2** to furnish bis(η^5-cyclopentadienyl)alkoxymethyltitanium(IV) complexes **3** along with evolution of methane. Bearing in mind Caulton's findings[2] of alkoxy ligands acting as strong π-donors when bound to the Cp$_2$Ti^{IV} moiety, one should expect the complexes **3** to react with carboxylic acids **4** even more readily than **1** itself to yield the corresponding alkoxy–acyloxy derivatives of **1**. On the contrary, we found that upon stirring mixtures of **3**, **4**, and petroleum ether at room temperature for a few hours bis(η^5-cyclopentadienyl)(acyloxy)methyltitanium(IV) complexes **5** are formed in lieu of the expected alkoxy–acyloxy derivatives, which means displacement of the alkoxy ligand occurs in preference to that of the methyl group by the carboxylic acid **4**.

If it is carried out in THF or toluene at room temperature, the reaction leads to quite the same mixture of products **2** and **5** which are then soluble and more difficult to separate. However, the complexes **5** do react with alcohols **2** under more vigorous conditions (toluene, reflux, 24 h) to give the alkoxy–acyloxy derivatives of **1**, albeit in just moderate yield. Despite the fact that the acyloxy ligand is a better σ-acceptor and a less effective π-donor compared to an alkoxy residue, the methy group is substituted in this case. Given that the proton transfer from the acid **4** onto the oxygen atom of the alkoxy ligand of **3** is the initial step of the substitution reaction shown in Scheme I, it becomes clear that the alkoxy ligand cannot be that much of a three-electron donor, bearing even a positive charge on its oxygen atom, as suggested by Caulton to explain the X-ray data of similar complexes. It is obviously the mere availability of the "lone pair" electrons at the oxygen atom next to titanium in the complexes **3** and **5** that determines the site of protonation by weak acids such as **4** or **2**. As to the reaction of Scheme I, proton transfer and displacement of the alcohol **2** from the metal center are likely to proceed simultaneously via a six-membered ring in the pivotal step. Any chiral information at the α or any more remote C atom in the alkoxy ligand is undisturbed, in any event; for instance, optically pure (–)-menthol (**2b**) and (1*S*)-borneol (**2c**) are obtained from the reaction of acids **4** with the corresponding complexes **3b** and **3c**, respectively.

Scheme I



Scheme II



We also wish to report that bis(η^5-cyclopentadienyl)methylchlorotitanium(IV) (**6**),[3] when it is treated with 1 equiv of the carboxylic acid **4**, furnishes an exact 1:1 mixture of titanocene dichloride (**7**) and bis(η^5-cyclopentadienyl)bis(carboxylato)titanium(IV) complexes **8**. No complexes with a mixed-ligand distribution could be detected by NMR and TLC monitoring of the toluene solution at any stage of reaction progress. We surmise a reaction pathway quite analogous to the one depicted above with the difference that the continuously formed small amounts of hydrochloric acid are sufficient to cause evolution of methane and subsequent formation of the thermodynamically favored couple of products by exhaustive scrambling of ligands.

Another intriguing reaction is the formation of titanocene difluoride (**10**) upon addition of the strong nonnucleophilic tetrafluoroboric acid (**9**) to a well-stirred solution of **5** in dichloromethane at –30 °C. This swift reaction, which proceeds with vigorous effervescence due to the evolution of methyldifluoroborane (trapped and identified according to ref 4) is particularly remarkable when one remembers the exclusive formation of the stable salt Cp$_2$Ti(BF$_4$)$_2$ (**11**) once **1** is treated with 2 equiv or even more of tetrafluoroboric acid (**9**) under otherwise similar conditions. However, the transfer of fluoride becomes reasonable when the reaction is once more considered to proceed concertedly via a six-membered ring by simultaneous attack of the carboxylic oxygen on the proton, thus pushing electron density via fluorine and the adjoining boron atom onto the fluorine next to the central metal. The more the Ti–O bond is weakened, the more the electron density is shifted toward this fluorine atom. Finally the acid **4** is regained whereas the adduct of boron

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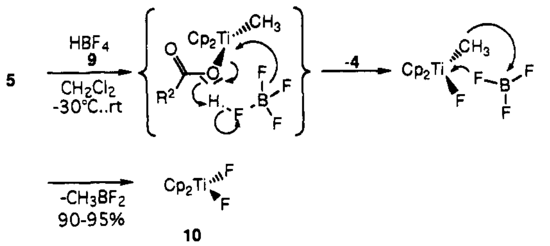
Scheme III



trifluoride and bis(η^5-cyclopentadienyl)fluoromethyltitanium(IV) readily reacts with formation of methyldifluoroborane and the difluoro complex **10**, as is well-known from the reaction of other methylated organometallic compounds with boron trifluoride.[5]

Whereas alcohols **2** react with complexes **5** as mentioned above, oxygen rather than the methyl group in **5** is the more basic site provided for the prime attack of strong acids such as tetrafluoroboric acid; otherwise salts such as **11** plus evolution of methane would be anticipated. We emphasize that there might even be some conceivable synthetic applications of these new reactions shown above, such as the use of complex **3**, bearing chiral alkoxy ligands, as a means for resolution of racemic acids **4** according to Scheme I.

Experimental Section

General Comments. All manipulations were carried out under a dry and oxygen-free atmosphere of argon. Dimethyltitanocene (**1**),[6] bis(η^5-cyclopentadienyl)alkoxymethyltitanium(IV) (**3**),[1] and bis(η^5-cyclopentadienyl)chloromethyltitanium(IV) (**6**)[7] were prepared according to the literature. Solutions were dried over anhydrous sodium sulfate or anhydrous magnesium sulfate. Diethyl ether was distilled from sodium–benzophenone ketyl, dichloromethane from phosphorus pentoxide, and toluene from sodium. Petrol refers to petroleum ether (bp 40–60 °C). Melting points were determined on a Reichert hot stage apparatus and are uncorrected. IR spectra were recorded on a Beckman Acculab A8 spectrophotometer. Mass spectra were recorded under EI conditions using a Varian CH4 instrument. Microanalyses were performed in our organic chemistry microanalytical laboratory. ^{1}H NMR spectra were recorded in C_6D_6 or $CDCl_3$ using a JEOL JNM-GX 400 spectrometer. ^{13}C NMR spectra were recorded in C_6D_6 at 100.4 MHz on the same instrument. Chemical shifts are measured in ppm downfield from TMS, and coupling constants are measured in Hz.

Preparation of Bis(η^5-cyclopentadienyl)(acyloxy)methyltitanium(IV) (5) from 3 and 4: Typical Procedure. A 10-mmol amount of the carboxylic acid **4** was added as a solid into a well-stirred solution of 10 mmol of bis(η^5-cyclopentadienyl)alkoxymethyltitanium(IV) (**3**) in about 80 mL of petrol. The resulting mixture was stirred at room temperature for 2 h. Subsequently, the yellow to orange precipitate of **5** was gathered by filtration and purified by recrystallization from ether/petrol (1:3), whereas the soluble alcohol **2** could be isolated by evaporation of the mother liquor, which proved to be void of any residual product **5**. **5a** ($R^2 = CHPh_2$): 3.84 g (9.5 mmol, 95%) from 10 mmol of **3a**, **3b**, or **3c** and 2.12 g (10 mmol) of diphenylacetic acid (**4a**); mp 99 °C dec; IR (KBr) ν 3100, 3050, 3015, 2960, 2900, 1640 st, 1490 m, 1450 m, 1310 st, 1220 m, 1120, 1080, 1040, 970, 825 st, 750, 710 st, 650 m cm^{-1}; ^{1}H NMR (C_6D_6) δ 0.83 (3 H, s, Me), 4.91 (1 H, s, CH), 5.65 (10 H, s, Cp), 7.04–7.43 (10 H, m, Ph); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 45.0, 60.4, 114.4, 126.8, 127.8, 128.5, 141.0, 174.9; MS m/z 389, 278, 193, 178 (100%), 167, 152, 129, 113. Anal. Calcd for $C_{25}H_{24}O_2Ti$: C, 74.26; H, 5.98. Found: C, 74.42; H, 5.92. **5b** ($R^2 = CH{=}CHPh$): 3.23 g (9.5 mmol, 95%) from 10 mmol of **3a**, **3b**, or **3c** and 1.48 g (10 mmol) of cinnamoic acid **4b**; mp 98 °C dec; IR (KBr) ν 3120, 3040, 2980, 1655 st, 1620 m, 1455 m, 1335 m, 1310 st, 1215 w, 1030, 1020, 990 w, 825 st, 775 m, 700 m cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.00 (3 H, s, Me), 5.91 (10 H, s, Cp), 6.55 (1H$^\alpha$, d, $J_{H^\alpha H^\beta} = 16$), 7.00–7.45 (5 H, m, Ph), 7.60 (1 H$^\beta$, d, $J_{H^\alpha H^\beta} = 16$); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 43.4, 114.4, 118.3, 123.3, 128.9, 129.4, 135.8, 142.2, 171.0; MS m/z 340, 325 (100%), 260, 193, 178, 167, 131, 103, 77. Anal. Calcd for $C_{20}H_{20}O_2Ti$: C, 70.59; H, 5.92. Found: C, 70.67; H, 6.23. **5c** ($R^2 = Ph$): 2.86 g (9.1 mmol, 91%) from 10 mmol of **3a**, **3b**, or **3c** and 1.22 g (10 mmol) of benzoic acid **4c** (for data see ref 1).

Preparation of Bis(η^5-cyclopentadienyl)bis(carboxylato)titanium(IV) (8) from 6 and 4: Typical Procedure. A solution of 2.28 g (10 mmol) of bis(η^5-cyclopentadienyl)chloromethyltitanium(IV) (**6**) and 10 mmol of carboxylic acid **4** in 100 mL of toluene was stirred at room temperature for 24 h, at which time an orange precipitate had formed. After concentration and chilling to −20 °C, the mixture was filtered through a sintered-glass funnel and the solid thus obtained extracted several times with hot petrol/ether (1:1) to redissolve complexes **8**, which formed orange crystals upon cooling of the combined extracts in a freezer. The red residue insoluble in hot petrol/ether consisted of almost analytically pure titanocene dichloride (**7**). **8a** ($R^2 = CHPh_2$): 2.80 g (4.7 mmol, 47%) from **6** and 2.12 g (10 mmol) of diphenylacetic acid (**4a**); mp 169 °C dec; IR (KBr) ν 3110, 3020, 2940, 1635 st, 1600 m, 1490 m, 1450 m, 1340 m, 1300 m, 1225 m, 1210 m, 820 st, 700 st, 645 st cm^{-1}; ^{1}H NMR (C_6D_6) δ 5.20 (2 H, s, $HCPh_2$), 5.88 (10 H, s, Cp), 7.10–7.21 (16 H, m, arom), 7.55–7.60 (4 H, m, arom); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 60.9, 118.3, 127.7, 128.7, 129.3, 140.8, 176.0; MS m/z 535, 389, 194, 178 (100%). Anal. Calcd for $C_{38}H_{32}O_4Ti$: C, 75.99; H, 5.37. Found: C, 75.90; H, 5.34. **8b** ($R^2 = CF_3$): 1.85 g (4.6 mmol, 46%) from **6** and 1.14 g (10 mmol) of trifluoroacetic acid **4d**; mp 159–162 °C dec; IR (KBr) ν 3120 w, 1700 st (sh at 1685 st), 1550 m, 1400 st, 1200, 1190 st, 1140 st, 1020 w, 830 st, 780 w, 720 m, 610 w cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.65 (s); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 115.4 (quartet, $^1J_{CF} = 290$), 120.2, 161.3 (quartet, $^2J_{CF} = 40$); MS m/z 404, 339, 291, 151 (100%), 132. Anal. Calcd for $C_{14}H_{10}F_6O_4Ti$: C, 41.62; H, 2.47. Found: C, 41.86; H, 2.67.

Preparation of Bis(η^5-cyclopentadienyl)difluorotitanium(IV) (10) from 5 and 9. A 250-mL round-bottomed flask connected with three successive cooling traps which were terminated by a mercury valve was chilled to −20 °C and charged with 10 mmol of complex **5** and 100 mL of dichloromethane. With vigorous stirring 1.37 mL of a 7.3 M ethereal solution of tetrafluoroboric acid (**9**) in ether was slowly syringed into the solution, whereupon effervescence due to evolution of methyldifluoroborane occurred. After addition of the acid the second trap (cooled to −78 °C) contained 0.60 g (93%) of this substance. The first trap was chilled to −20 °C to retain traces of dichloromethane. The last trap held at room temperature was found empty. After an additional trap-to-trap condensation methyldifluoroborane was characterized according to the literature.[4] The contents of the reaction flask were diluted with about 20 mL of ether and subsequently filtered through a sintered-glass funnel to yield 2.11 g (9.8 mmol, 98%) of **10** as a bright yellow flaky solid that was characterized according to refs 8 and 9. The concurrently formed carboxylic acid **4** could be isolated almost quantitatively by evaporation of the filtrate and repeated recrystallization from petrol/ether (1:1).

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