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Synthetic and Structural Studies on Carboxy, Carbomethoxy, and Trimethylsilyl Derivatives of (η^5-Cyclopentadienyl)(η^7-cycloheptatrienyl)titanium

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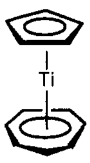
Summary: The mono- or dilithiation of (η^5-C_5H_5)(η^7-C_7H_7)Ti followed by carbonation or reaction with Me_3SiCl has produced the following new derivatives in high yields: (η^5-C_5H_5)(η^7-$C_7H_6CO_2H$)Ti, (η^5-$C_5H_4CO_2H$)(η^7-$C_7H_6CO_2H$)Ti, and (η^5-$C_5H_4SiMe_3$)(η^7-$C_7H_6SiMe_3$)Ti. Both carboxylic acids are readily converted into ester derivatives by reactions with diazomethane. Preliminary crystallographic data on (η^5-$C_5H_4CO_2CH_3$)(η^7-$C_7H_6CO_2CH_3$)Ti reveal the aromatic rings to be parallel, with the carbons carrying the CO_2CH_3 substituents very nearly eclipsed.

The ability of various (η^5-cyclopentadienyl)–metal compounds to undergo the hydrogen–lithium interchange (metalation) reaction has played an important role in the development of the chemistry of these systems.[1-4] The metalation of ferrocene by *n*-butyllithium was reported independently by two research groups in 1954, and the monolithio- and 1,1′-dilithioferrocenes so produced were readily converted into carboxylic acid, triphenylsilyl, and trimethylsilyl derivatives.[5-7] In subsequent studies, the metalation reaction using alkyllithium reagents has been extended to a variety of other (η^5-cyclopentadienyl)–metal compounds, including ruthenocene,[8] osmocene,[8] cymantrene,[9-11] (η^5-C_5H_5)(η^7-C_7H_7)V,[12] (η^5-C_5H_5)$(CO)_2$FeR (R = Et, Ph, Bz),[11,13] [(η^5-C_5H_5)$Fe(CO)_2]_2$,[13] (η^5-C_5H_5)$(CO)_3$WR (R = Me, Bz),[11] and (η^5-C_5H_5)(PPh_3)(NO)ReX (X = Cl, Br, I).[14]

Previous investigations have demonstrated that the mixed sandwich complex (η^5-C_5H_5)(η^7-C_7H_7)Ti (1) is readily monometalated by 1 equiv of *n*-butyllithium in ethyl ether solution at 0 °C, and that the metalation of 1 takes place preferentially on the seven-membered ring.[15] We have subsequently found that treatment of 1 with 2.4 equiv of *n*-BuLi/TMEDA produces the dimetalated product (η^5-C_5H_4Li)(η^7-C_7H_6Li)Ti·2TMEDA in high yield. The latter reacts readily with Ph_2PCl or Me_2PCl to form bis(phosphino) complexes, which on further reaction with metal carbonyls, $Ni(1,5\text{-}C_8H_{12})_2$, etc., provide convenient high-yield routes to new heterobimetallic compounds.[16,17] In this note we report the results of synthetic and structural studies on carboxy and trimethylsilyl derivatives of 1.

Results and Discussion

Metalation of 1 with 1 equiv of *n*-butyllithium in ethyl ether solution at 0 °C followed by carbonation of the monolithium intermediate at −78 °C produced the lithium salt of the desired acid as a green-white solid. Dissolution of this salt in deoxygenated water followed by acidification with acetic acid afforded (η^5-C_5H_5)(η^7-$C_7H_6CO_2H$)Ti (2) in 89% yield as a light green solid. The ^{1}H NMR spectrum of 2 contained a singlet for the η^5-cyclopentadienyl protons at δ 5.29 ppm, a multiplet for the two deshielded protons flanking the carboxy group on the η^7-cycloheptatrienyl ring at δ 6.58 ppm, and a multiplet for the remaining four η^7-cycloheptatrienyl protons at δ 5.75 ppm.



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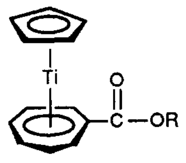
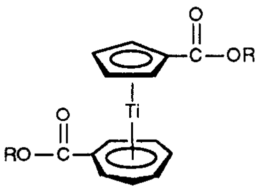
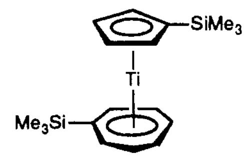


R = H (2), CH_3 (4)

In a similar manner, a slurry of the dilithium derivative (η^5-C_5H_4Li)(η^7-C_7H_6Li)Ti·2TMEDA in ethyl ether was carbonated at −78 °C to form the dilithium salt (η^5-$C_5H_4CO_2Li$)(η^7-$C_7H_6CO_2Li$)Ti. Subsequent acidification with acetic acid produced (η^5-$C_5H_4CO_2H$)(η^7-$C_7H_6CO_2H$)Ti (3) as a green solid in 81% yield. The ^{1}H NMR spectrum of diacid 3 was similar to that of monoacid 2 except that the η^5-cyclopentadienyl ring protons appeared as two apparent triplets at δ 5.31 and 5.71 ppm, as anticipated for



R = H (3), CH_3 (5)



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a monosubstituted η^5-cyclopentadienyl ring containing an electron-withdrawing substituent.[18-20]

In order to examine the reactivities of 2 and 3, we briefly investigated their conversions into ester derivatives. Both 2 and 3 were readily converted into their respective carbomethoxy analogues $(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_6CO_2CH_3)Ti$ (4) and $(\eta^5\text{-}C_5H_4CO_2CH_3)(\eta^7\text{-}C_7H_6CO_2CH_3)Ti$ (5) by reactions with diazomethane in THF–ethyl ether solution. Both ester derivatives 4 and 5 were characterized by elemental analyses and by their ^1H NMR, ^{13}C NMR, and IR spectra.[21] They were easily purified as green crystalline solids by recrystallization from hot hexane solution.

Crystallographic data on the diester 5 indicate that there are two unique molecules in the asymmetric unit. These are packed such that the centroid–Ti–centroid angles are at right angles to one another. The major feature of interest is the nearly eclipsed nature of the ester substituents. The $(H_3CO_2C)\text{–}C_5\text{–}C_7\text{–}(CO_2CH_3)$ torsion angles are very small, averaging 12°. Interestingly, in $(\eta^5\text{-}C_5H_4PPh_2)(\eta^7\text{-}C_7H_6PPh_2)Ti$, the phosphine substituents are trans.[16]

A reaction of $(\eta^5\text{-}C_5H_4Li)(\eta^7\text{-}C_7H_6Li)Ti\cdot 2TMEDA$ with 2 equiv of trimethylchlorosilane in hexane solution likewise afforded $(\eta^5\text{-}C_5H_4SiMe_3)(\eta^7\text{-}C_7H_6SiMe_3)Ti$ (6) as a blue crystalline solid in 83% yield. In addition to resonances for the nonequivalent trimethylsilyl groups at δ 0.14 and 0.35 ppm, the ^1H NMR spectrum of 6 exhibited two sets of apparent triplets for the η^5-cyclopentadienyl protons and a multiplet resonance for the η^7-cycloheptatrienyl protons.

In contrast to analogous ferrocene compounds, all the above derivatives of 1 are air-sensitive. However, they can be easily manipulated by using standard Schlenk and glovebox techniques and can be stored at room temperature under an inert atmosphere for long periods of time.

The facile formation of phosphino, silyl, and carboxy derivatives of 1 suggests that the intermediate lithium reagents should be useful in the formation of other organic and organometallic analogues of 1. Further, ester derivatives such as 4 and 5 could serve as potential intermediates in titanium-containing addition and condensation polymers. Studies in these areas are currently in progress in our laboratory.

Experimental Section

All operations were carried out under an argon atmosphere with Schlenk or glovebox techniques. Argon was deoxygenated with activated BTS catalyst and dried with molecular sieves and phosphorus pentoxide. Hexane, toluene, ethyl ether, and tetrahydrofuran (THF) were distilled under argon from sodium–potassium alloy. Trimethylchlorosilane was purchased from Strem Chemicals and was freshly distilled before use. Diazomethane was generated by using a Diazald Kit obtained from Aldrich Chemical Co. NMR spectra and IR spectra were recorded on Varian XL-200 and Perkin-Elmer 1310 spectrometers, respectively. (η^5-Cyclopentadienyl)(η^7-cycloheptatrienyl)titanium[22,23] and (η^5-lithiocyclopentadienyl)(η^7-lithiocycloheptatrienyl)titanium·2TMEDA[17] were prepared by literature procedures. Microanalyses were performed by the Microanalytical Laboratory, University of Massachusetts, Amherst, MA.

(η^5-Cyclopentadienyl)(η^7-carboxycycloheptatrienyl)titanium (2). A slurry of (η^5-cyclopentadienyl)(η^7-cycloheptatrienyl)titanium (2.00 g, 9.81 mmol) in 180 mL of ethyl ether was cooled to 0 °C in an argon-purged Schlenk flask. *n*-Butyllithium in hexane (3.69 mL, 9.90 mmol) was then added very slowly dropwise via an addition funnel over a period of 90 min. The reaction mixture was stirred at 0 °C for 5 h, during which time the blue color of the starting material disappeared to give a dark brown slurry containing (η^5-cyclopentadienyl)(η^7-lithiocycloheptatrienyl)titanium. The reaction mixture was subsequently cooled to −78 °C. A large amount of dry ice was freshly cracked, added to an argon-purged 500-mL Schlenk flask, and covered with ethyl ether. The dark brown slurry was transferred via cannula over a 30-min period. The mixture was stirred and allowed to warm very slowly to room temperature. Stirring was continued for a total of 5 h. After the carbonation reaction, the solvent was removed under vacuum to yield a light green-white powder. The latter was dissolved in ca. 200 mL of deoxygenated water to form a dark green solution. Acetic acid was slowly added via a pipet to the solution with vigorous stirring until the solution was acidic. The resulting precipitate was filtered, washed with deoxygenated water until the washings were neutral, then washed with a small amount of cold methanol, which had previously been deoxygenated and dried. The remaining light green precipitate amounted to 2.15 g (89%) of 2 as an air-sensitive solid. An analytically pure sample was prepared by crystallization from toluene. Anal. Calcd for $C_{13}H_{12}O_2Ti$: C, 62.93; H, 4.87. Found: C, 62.61; H, 4.91. ^1H NMR (methanol-d_4): δ 5.29 (s, 5 H, C_5H_5), 5.75 (m, 4 H, $H_{3,4,5,6}$), 6.58 (m, 2 H, $H_{2,7}$).

(η^5-Carboxycyclopentadienyl)(η^7-carboxycycloheptatrienyl)titanium (3). An argon-purged 300-mL Schlenk flask was charged with (η^5-lithiocyclopentadienyl)(η^7-lithiocycloheptatrienyl)titanium·2TMEDA (4.53 g, 10.1 mmol) followed by 160 mL of ethyl ether, and the mixture was stirred and cooled to −78 °C. A large amount of freshly crushed dry ice was placed in an argon-flushed 500-mL Schlenk flask and was covered with 200 mL of ethyl ether. To this mixture was transferred the brown-black slurry of the dilithium intermediate slowly via a cannula over a 1-h period. The mixture was allowed to warm slowly to room temperature, and stirring and continued for a 5-h period. The solvent was subsequently removed under reduced pressure to yield the lithium salt of 3 as a light green powder. This solid was dissolved in deoxygenated water and the solution stirred for 20 min to produce a dark green solution. Acetic acid was slowly added until the solution was acidic, resulting in a light-green precipitate. The latter was washed with a large amount of deoxygenated water until the washings were neutral and then washed with a small amount of cold methanol. After drying under vacuum, 3 was obtained as a green solid (2.40 g, 81%). An analytical sample was prepared by redissolving the product in deoxygenated aqueous $NaHCO_3$, filtering through Celite, acidifying of the clear dark green solution with acetic acid, washing, and drying. Anal. Calcd for $C_{14}H_{12}O_4Ti$: C, 57.56; H, 4.14. Found: C, 57.11; H. 4.05. ^1H NMR (methanol-d_4): δ 5.31 (t, 2 H, $C_{3,4}$), 5.71 (t, 2 H, $C_{2,5}$), 5.78 (m, 4 H, $C_{3,4,5,6}$), 6.65 (m, 2 H, $H_{2,7}$).

(η^5-Cyclopentadienyl)(η^7-(carbomethoxy)cycloheptatrienyl)titanium (4). Into an argon-purged 300-mL Schlenk flask was added (η^5-cyclopentadienyl)(η^7-carboxycycloheptatrienyl)titanium (1.22 g, 4.92 mmol) and 100 mL of THF. The mixture was cooled to −78 °C and stirred for 20 min. To this solution was added 22 mL of an ethyl ether solution of diazomethane (0.23 g, 5.47 mmol) over a period of 40 min, during which time N_2 was evolved. The solution was then allowed to slowly warm to room temperature. Stirring was continued overnight, resulting in a green solution and a yellow-white precipitate. The solvent was removed under vacuum, and the resulting solid was extracted with hot toluene to give a clear green solution. The toluene was subsequently removed under vacuum to produce a blue-green solid. The latter was crystallized from hot hexane to yield 1.09 g (85%) of 4 as blue-green crystals. Anal. Calcd. for $C_{14}H_{14}O_2Ti$: C, 64.15; H, 5.38; Ti, 18.26. Found: C, 64.22; H, 5.28; Ti, 18.30. ^1H NMR (toluene-d_8): δ 3.64 (s, 3 H, CO_2CH_3), 4.92 (s, 5 H, C_5H_5), 5.35–5.52 (m, 4 H, $C_{3,4,5,6}$), 6.70–6.84 (m, 2 H, $C_{2,7}$). ^{13}C NMR (toluene-d_8): δ 51.79 (CH_3), 87.76, 88.34, 90.19 (C_7 carbons), 99.52 (C_5 carbons), 168.4 (C=O). IR (CH_2Cl_2): 1682 cm^{-1} (s).

(η^5-(Carbomethoxy)cyclopentadienyl)(η^7-(carbomethoxy)cycloheptatrienyl)titanium (5). A slurry of (η^5-carboxy-

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cyclopentadienyl)(η^7-carboxycycloheptatrienyl)titanium (1.20 g, 4.11 mmol) in 150 mL of THF was cooled to −78 °C and stirred for 20 min. To the slurry was added 34 mL of an ethyl ether solution of diazomethane (0.40 g, 9.44 mmol) very slowly over 40 min, during which time N_2 was evolved. The mixture was allowed to warm to room temperature, and stirring was continued overnight to produce a dark green solution and a brown precipitate. The solvent was removed under vacuum, and the residue was extracted with hot hexane. The resulting extract was filtered through Celite on a glass frit under argon, and the filtrate was concentrated and cooled to afford **5** as green crystals (0.49 g, 37%). Anal. Calcd for $C_{16}H_{16}O_4Ti$: C, 60.02; H, 5.04. Found: C, 60.14; H, 5.03. ^{1}H NMR (toluene-d_8): δ 3.54 (s, 3 H, C_5–CO_2CH_3), 3.69 (s, 3 H, C_7–CO_2CH_3), 4.78 (t, 2 H, $C_{3,4}$), 5.34–5.54 (m, 4 H, $C_{3,4,5,6}$), 5.60 (t, 2 H, $C_{2,5}$), 6.69–6.85 (m, 2 H, $C_{2,7}$). ^{13}C NMR (toluene-d_8): δ 51.18, 51.99 (CH_3), 89.39, 89.54, 92.01 (C_7 carbons), 100.9, 101.6 (C_5 carbons), 167.6 (C=O). IR (CH_2Cl_2): 1690–1720 cm^{-1} (s, br).

(η^5-(Trimethylsilyl)cyclopentadienyl)(η^7-(trimethylsilyl)cycloheptatrienyl)titanium (6). A slurry of (η^5-lithiocyclopentadienyl)(η^7-lithiocycloheptatrienyl)titanium·2TMEDA (4.40 g, 9.81 mmol) in 100 mL of hexane was cooled with stirring to −78 °C, and stirring was continued for 20 min. To the mixture was then added very slowly via a cannula trimethylchlorosilane (2.54 mL, 20.0 mmol) over a period of 45 min. Hexane (80 mL) and ethyl ether (20 mL) were subsequently added, and the mixture was allowed to warm slowly to room temperature and stirred overnight. The solvent was removed under vacuum to give a blue solid. The solid was dissolved in 70 mL of hexane, and the solution was concentrated to ca. half the original volume. Cooling to −20 °C yielded **6** as a blue crystalline solid (2.84 g, 83%). An analytically pure sample was obtained by an additional recrystallization from hexane. Anal. Calcd for $C_{18}H_{28}Si_2Ti$: C, 61.04; H, 8.10. Found: C, 61.45; H, 8.18. ^{1}H NMR ($CDCl_3$): δ 0.14 (s, 9 H, C_5–$SiMe_3$), 0.35 (s, 9 H, C_7–$SiMe_3$), 5.08 (t, 2 H, $C_{3,4}$), 5.17 (t, 2 H, $C_{2,5}$), 5.45–5.67 (m, 6 H, C_7 protons), MS: *m/e* 348 (M^+).

X-ray Structural Studies on (η^5-$C_5H_4CO_2CH_3$)(η^7-$C_7H_6CO_2CH_3$)Ti (5). Crystallographic analysis on single cystals of (η^5-$C_5H_4CO_2Me$)(η^7-$C_7H_6CO_2CH_3$)Ti did not provide satisfactory refinements. The crystals are triclinic, $P\bar{1}$, with a = 11.371 (8) Å, b = 11.59 (1) Å, c = 12.47 (1) Å, α = 80.7 (1)°, β = 81.02 (9)°, and γ = 65.50 (9)°. The positions of two unique titanium atoms and all ring carbons were achieved, leading to an R factor of 0.151. The ester groups on each C_7 ring were severely disordered, which affected the refinement of all carbon atoms. Although an R factor of 0.078 based on 2891 observed [$F_o \geq 5\sigma(F_o)$] reflections and 397 variable parameters was achieved, the carbon atom refinement was very poor. However, the most salient feature of the structure, the eclipsed nature of the substituents, is unequivocal. A complete investigation of the acentric space group $P1$ did not solve the refinement difficulties or the disorder problem.

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