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Dialkyl- and Chloroalkyltitanium *ansa*-Metallocene Complexes: Synthesis and Characterization. Crystal Structure of $[\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2Si(CH_3)_2]TiClCH_3$

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Summary: Dialkyl and chloroalkyl *ansa*-titanocene complexes $[\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2Si(CH_3)_2]TiR_2$ [R = CH_3 (**1**), Bz (**2**), *o*-xylidene (**3**)] and $[\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2Si(CH_3)_2]TiClR$ [R = CH_3 (**4**), $CH_2Si(CH_3)_3$ (**5**), $Si(CH_3)_3$ (**6**)] were prepared by reacting the *ansa*-metallocene dihalide $[\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2Si(CH_3)_2]TiCl_2$ with the adequate alkyl reagent. $[\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2Si(CH_3)_2]TiClCH_3$ (**4**) crystallizes from toluene/hexane in the monoclinic space group $P2_1/m$ with unit cell dimensions a = 7.270 (7) Å, b = 8.751 (9) Å, c = 10.66 (1) Å, β = 90.78 (6)°, V = 678 (2) Å^3, and D_{calcd} = 1.392 g cm^{-3}. The structure was refined to R = 0.048 and R_w = 0.046 for 7887 reflections having $I > 3\sigma(I)$.

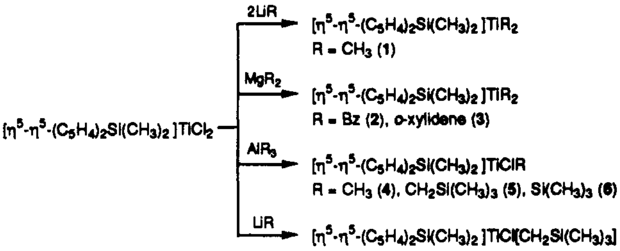
The chemistry of alkyl and aryl derivatives of group 4 metallocenes with two η^5-cyclopentadienyl rings [C_5H_5, $C_5(CH_3)_5$] is widely known, and this kind of compound plays an important role in a variety of attractive reactions (activation of small molecules, reduction processes, organic synthesis, and other catalytic processes).[1] More recently, new types of similar alkyl and aryl complexes have been published in which the two cyclopentadienyl rings are linked by a bridging group.[2] This strategy modifies substantially the mobility of the cyclopentadienyl groups with the subsequent effect in the chemical behavior of these compounds.[2a] We are interested in the study of the properties of these *ansa*-metallocene derivatives in order to compare their behavior with that of the compounds containing the two separated rings.

In this paper we describe the synthesis of new dialkyl- and chloroalkyltitanium complexes of the type $[\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2Si(CH_3)_2]TiR_2$ and $[\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2Si(CH_3)_2]TiClR$ and the X-ray structure of $[\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2Si(CH_3)_2]TiClCH_3$.

Results and Discussion

The reaction of $[\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2Si(CH_3)_2]TiCl_2$ with the appropriate reagent (LiR, MgR_2, AlR_3) proceeds with the formation of the corresponding dialkyl or chloroalkyl derivative, as shown in Scheme I. The alkylation with AlR_3 is the most convenient method to obtain monoalkylated compounds, as reactions with 1 equiv of LiR or MgRX always lead to mixtures of mono- and dialkyls involving an additional separation and subsequent lower yields.

Scheme I



Compound **5** was always contaminated by the dialkyl, as observed by NMR spectroscopy, even when the aluminum reagent was used.

All these compounds were characterized by elemental analysis, EI-MS, IR, and NMR spectroscopy, and the crystal structure analysis of compound **4** has been carried out.

The complexes are solids readily soluble in aromatic hydrocarbons and ethers, and particularly, compound **1** is very soluble in aliphatic hydrocarbons. They can be stored under nitrogen or argon without decomposition, and compounds **1**, **4**, and **5** do not change in the air for weeks, whereas compounds **2**, **3**, and **6** decompose in the air in 2-3 h.

The ^1H and the ^{13}C NMR spectra for the dialkyl derivatives show the same features already reported for the complex $[\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2Si(CH_3)_2]M[CH_2Si(CH_3)_3]_2$[3] (M = Ti, Zr). The ^1H NMR spectra show the typical two pseudotriplets for the protons of the C_5H_4 group corresponding to a AA'BB' spin system and a singlet for both equivalent methyls of the Me_2Si bridging group, as expected for compounds containing identical groups in the other pseudotetrahedral positions around the titanium center. Similarly, the ^{13}C NMR data are consistent with this equivalency. On the other hand the resonance due to the bridgehead carbon atom is displaced to higher fields with respect to the corresponding dichloro precursor compound $[\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2Si(CH_3)_2]TiCl_2$, this displacement being more pronounced in relation to the similar compound containing the unsubstituted rings $(\eta^5\text{-}C_5H_5)_2TiCl_2$. This behavior seems to be characteristic for this type of *ansa*-metallocene.[2b,3]

As expected, the chloroalkyl derivatives show a significantly different NMR behavior. For them the protons of the C_5H_4 groups are observed as four multiplets indicative of an ABCD spin system. In the same way the protons of the two nonequivalent methyls of the Me_2Si group appear as two singlets. This situation is caused by the presence of two different ligands occupying the other pseudotetrahedral positions around the titanium center. Furthermore, NMR spectra show the characteristic signals

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Table I. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for 4

	x	y	z	U(eq)
Ti	1869 (2)	2500	3178 (2)	38 (1)
Si	4023 (4)	2500	510 (3)	43 (1)
Cl	8786 (3)	2500	3801 (3)	62 (1)
C(1)	3189 (9)	969 (8)	1568 (6)	40 (2)
C(2)	1326 (1)	542 (9)	1714 (8)	57 (3)
C(3)	1131 (13)	−206 (10)	2866 (10)	72 (4)
C(4)	2797 (14)	−148 (11)	3484 (9)	76 (4)
C(5)	4071 (10)	578 (9)	2714 (7)	53 (3)
C(6)	2936 (15)	2500	5124 (10)	66 (5)
C(7)	2778 (17)	2500	−1012 (10)	73 (5)
C(8)	6563 (13)	2500	386 (10)	57 (4)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

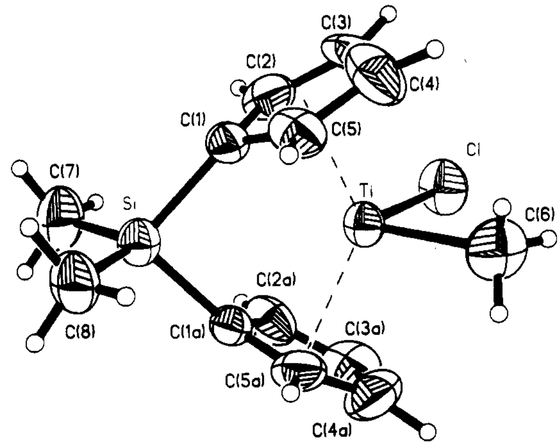

Figure 1. X-ray crystal structure of $[\eta^5$-η^5-$(C_5H_4)_2Si(CH_3)_2]TiClCH_3$ (4) with molecular geometry and atom-numbering scheme.

for the alkyl groups. The same spectroscopic features are observed in the ^{13}C NMR spectrum for these chloro alkyl complexes.

Table II. Bond Lengths (Å) and Angles (deg) for 4

Ti–C(1)	2.390 (6)	Ti–C(2)	2.348 (8)
Ti–C(3)	2.449 (8)	Ti–C(4)	2.435 (10)
Ti–C(5)	2.378 (7)	Ti–C(6)	2.197 (11)
Ti–centroid	2.084	Ti–Cl	2.346 (4)
Si–C(1)	1.859 (7)	Si–C(7)	1.846 (12)
Si–C(8)	1.854 (10)	C(1)–C(2)	1.415 (10)
C(1)–C(5)	1.414 (10)	C(2)–C(3)	1.401 (13)
C(3)–C(4)	1.373 (14)	C(4)–C(5)	1.399 (12)

C(6)–Ti–centroid	105.2	centroid–Ti–Cl	108.6
centroid–Ti–centroid a	129.4	Cl–Ti–centroid a	108.7
C(1)–Si–C(7)	111.9 (3)	C(1)–Si–C(8)	112.1 (3)
C(7)–Si–C(8)	114.5 (5)	C(1)–Si–C(1a)	92.3 (4)
C(7)–Si–C(1a)	111.9 (3)	C(8)–Si–C(1a)	112.1 (3)
Si–C(1)–C(2)	125.3 (5)	Si–C(1)–C(5)	123.4 (5)
C(2)–C(1)–C(5)	105.3 (6)	C(1)–C(2)–C(3)	109.2 (7)
C(2)–C(3)–C(4)	107.7 (8)	C(3)–C(4)–C(5)	108.8 (8)
C(1)–C(5)–C(4)	108.8 (7)		

X-ray Structure of $[\eta^5$-η^5-$(C_5H_4)_2Si(CH_3)_2]TiClCH_3$ (4). Final atomic positional and displacement parameters can be taken from Table I. A perspective view of the complex with the labeling scheme is shown in Figure 1. Bond lengths and selected angles are represented in Table II. The molecule consists of two identical C_5H_4 (Cp) rings related to each other by a mirror plane and connected to a common Si atom on the mirror plane. The environment of Si is pseudotetrahedral, with very regular average Si–C distances of 1.85 Å and C(7)–Si–C(1) and C(8)–Si–C(1) angles being 112.0°. The two rings are however strongly attracted by Ti, giving rise to an angle of only 92° for C(1)–Si–C(1a), which results in a relaxation of the C(7)–Si–C(8) angle to 114.5°. Even more, the C(1)–Si bond is not equatorial but is inclined by 18.4° to the plane of the Cp ring. The rings themselves are flat with a mean deviation to their least-squares plane of less than 0.02 Å, and the nonequatorial C(1)–Si bond and the C(1)–Si–C(1a) angle are normal to this plane. The Ti–centroid distance of 2.08 Å is that found for titanocenes containing unbridged cyclopentadienyl ligands,[4] but the distances from Ti to the carbon atoms of the ring vary between 2.35 and 2.45 Å, the shortest distances being those to C(2) and C(5) and the largest those to C(3) and C(4) (opposite to the C(1)–Si bond), which show the shortest C–C distance in the ring (1.37 Å). This structural disposition is a common feature for this type of *ansa*-metallocene[3] and different from that observed for unbridged metallocenes. Like Si, Ti is also pseudotetrahedrally surrounded, i.e. by two equivalent rings, a chlorine atom, and a methyl group. Since the rings cannot approach the Ti atom any more (they are already closer than the sum of the individual van der Waals radii) the angle centroid–Ti–centroid remains at 129°. The centroid–Ti–methyl (105°) and the centroid–Ti–Cl (109°) angles are very close to the ideal tetrahedral angles. C(6) and Cl are both strongly repulsed by the rings, C(6) having a contact distance to C(4) of only 2.9, to C(5) of 3.2, and to Cl of 3.3 Å. The Cl atom is only 3.1 Å away from C(3) and 3.3 Å from C(4). This results in a very tight angle of 93° for C(6)–Ti–Cl. The structure is packed with the molecules arranged around a 2_1 axis and their internal symmetry corresponding to the space groups mirror planes. There are no short intramolecular distances, due to a lack of strong interaction between the molecules, resulting in loose packing and also the occurrence of twinning. The majority of crystals were built of two domains with a common *c* axis, the *ab* planes having an angle of 1.6° between their normals. A very small crystal (0.075 × 0.150 × 0.225 mm) proved however by axial photographs along all three axes to be of a single domain.

Experimental Section

All experiments were performed under argon or N_2 using Schlenk-type glassware. Solvents were destilled under N_2, dried by standard methods, and degassed before use. The starting complex $[\eta^5$-η^5-$(C_5H_4)_2Si(CH_3)_2]TiCl_2$ was synthesized as described elsewhere.[3] MeLi (Ventron) and Me_3Al (Ethyl Corp.) were obtained commercially and used without purification. $Mg(CH_2Ph)_2(THF)_2$,[5] $Mg[CH_2(C_6H_4)CH_2$-$o](THF)_{1.5}$,[6] $LiCH_2Si(CH_3)_3$,[7a] $Al[CH_2Si(CH_3)_3]_3$,[7b] and $Al[Si(CH_3)_3]_3(OEt_2)$[8] were prepared via the literature routes.

The C and H analyses were carried out for all complexes except 5 on a Perkin-Elmer 240B microanalyzer. Infrared spectra between 4000 and 200 cm^{-1} were recorded as Nujol mulls on a 505 or 883 Perkin-Elmer spectrophotometers. ^1H and ^{13}C NMR spectra were recorded on a Varian FT-80 A or a JEOL FT-270 instrument, and mass spectra were obtained by using a Varian MAT A-300 instrument with inlet/sample chamber conditions (10^{-7} Torr, 250 °C).

Preparation of $[\eta^5$-η^5-$(C_5H_4)_2Si(CH_3)_2]Ti(CH_3)_2$ (1). $[\eta^5$-η^5-$(C_5H_4)_2Si(CH_3)_2]TiCl_2$ (0.5 g, 1.64 mmol) was suspended in 50 mL of dry diethyl ether and cooled to −30 °C. A 2.05-mL (3.28 mmol) aliquot of a 1.6 M solution of methyllithium in diethyl ether was added. Upon warming to room temperature, the reaction mixture was stirred for 12 h. The solvent was removed and an

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equal volume of hexane was transferred to the residue. After filtration, the solution was concentrated in vacuo. The storage of the hexane solution at −78 °C yielded red-orange crystals of **1** (0.28 g, 65% yield). Anal. Calcd for $C_{14}H_{20}SiTi$: C, 63.60; H, 7.50. Found: C, 63.50; H, 7.69. ^1H NMR (270 MHz, C_6D_6, 28 °C): δ 0.00 [s, 6 H, $Si(CH_3)_2$], 0.17 (s, 6 H, Ti–CH_3), 5.21 [t, J = 2.4 Hz, 4 H (distal), C_5H_4], 7.08 [t, J = 2.4 Hz, 4 H (proximal), C_5H_4]. ^{13}C NMR (67.8 MHz, C_6D_6, 28 °C): δ −5.63 [$Si(CH_3)_2$], 45.33 (Ti–CH_3), 101.3 [$C_1(C_5H_4)$], 115.3 [$C_{3,4}(C_5H_4)$], 125.4 [$C_{2,5}(C_5H_4)$]. EI-MS (70 eV): m/z = 234 ($[M - 2CH_3]^+$, 100%).

Preparation of $[\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2Si(CH_3)_2]Ti(CH_2Ph)_2$ (2). $[\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2Si(CH_3)_2]TiCl_2$ (0.5 g, 1.64 mmol) was dissolved in 50 mL of dry THF and cooled to −30 °C. $Mg(CH_2Ph)_2(THF)_2$ (0.57 g, 1.64 mmol) was dissolved in 20 mL of THF and added to the solution of the starting material. Upon warming to room temperature, the mixture was stirred for 12 h. The solvent was removed, and the residue was extracted with hexane. After filtration and evaporation of the solvent, the residue was recrystallized from hexane to −20 °C to give complex **2** as violet crystals (0.52 g, 76% yield). Anal. Calcd for $C_{26}H_{28}SiTi$: C, 75.00; H, 6.70. Found: C, 74.92; H, 6.65. ^1H NMR (270 MHz, C_6D_6, 28 °C): δ −0.15 [s, 6 H, $Si(CH_3)_2$], 2.09 (s, 4 H, Ti–CH_2–), 5.01 [t, J = 2.4 Hz, 4 H (distal), C_5H_4], 7.04 [t, J = 2.4 Hz, 4 H (proximal), C_5H_4], 6.89 (m), 7.19 m, Ph. ^{13}C NMR (67.8 MHz, THF-d_8, 28 °C): δ −5.80 [$Si(CH_3)_2$], 73.5 (Ti–CH_2–), 103.3 [$C_1(C_5H_4)$], 118.2 [$C_{3,4}(C_5H_4)$], 126.4 [$C_{2,5}(C_5H_4)$], 121.7, 127.7, 128.3, 154.5 [C_4, $C_{3,5}$, $C_{2,6}$, C_1 (Ph)].

Preparation of $[\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2Si(CH_3)_2]Ti[CH_2(C_6H_4)CH_2\text{-}o]$ (3). $[\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2Si(CH_3)_2]TiCl_2$ (0.5 g, 1.64 mmol) was dissolved in 50 mL of dry THF and cooled to −30 °C. $Mg[CH_2(C_6H_4)\text{-}CH_2\text{-}o](THF)_{1.5}$ (0.39 g, 1.64 mmol) was dissolved in 20 mL of THF and added to the solution of the starting material. The mixture gradually became blue-violet as it warmed to room temperature and was stirred for 12 h. The solvent was removed, and the residue was extracted with hexane. Recrystallization in hexane at −30 °C gave **3** as dark green crystals (0.25 g, 44% yield). Anal. Calcd for $C_{20}H_{22}SiTi$: C, 71.00; H, 6.50; Found: C, 70.83; H, 6.25. ^1H NMR (80 MHz, C_6D_6, 28 °C): δ 0.12 [s, 6 H, $Si(CH_3)_2$], 2.06 (s, 4 H, Ti–CH_2–), 5.06 [t, J = 2.2 Hz, 4 H (distal), C_5H_4], 6.20 [t, J = 2.2 Hz, 4 H (proximal), C_5H_4], 6.86 (m), 7.29 (m, Ph). ^{13}C NMR (67.8 MHz, C_6D_6, 28 °C): δ −5.5 [$Si(CH_3)_2$], 62.0 (Ti–CH_2–), 98.8 [$C_1(C_5H_4)$], 113.9 [$C_{3,4}(C_5H_4)$], 122.3 [$C_{2,5}(C_5H_4)$], 125.1, 126.5, 142.2 [$C_{3,4}$; $C_{2,5}$; $C_{1,6}$ (C_6H_4)]. EI-MS (70 eV): m/z = 338 (M^+), 234 ($[M - CH_2C_6H_4CH_2]^+$, 100%).

Preparation of $[\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2Si(CH_3)_2]TiClCH_3$ (4). $[\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2Si(CH_3)_2]TiCl_2$ (0.5 g, 1.64 mmol) was suspended in 50 mL of dry toluene and cooled to −60 °C. A 1-mL (1.71 mmol) aliquot of 1.71 M solution of trimethylaluminum in toluene was added and the solution stirred for 12 h. Then 0.64 g (1.71 mmol) of tetraphenylphosphonium chloride were added, the solution was filtered, and the solvent was removed in vacuo. Recrystallization in toluene at −30 °C gave **4** as red crystals (0.25 g, 54% yield). Anal. Calcd for $C_{13}H_{17}ClSiTi$: C, 54.83; H, 5.97. Found: C, 54.65; H, 6.02. ^1H NMR (80 MHz, C_6D_6, 28 °C): δ −0.06 [s, 3 H, $Si(CH_3)_2$], 0.09 (s, 3 H, $Si(CH_3)_2$], 0.98 (s, 3 H, Ti–CH_3), 5.28 [m, 2 H (distal), C_5H_4], 5.54 [m, 2 H (distal), C_5H_4], 6.90 [m, 2 H (proximal), C_5H_4], 7.06 [m, 2 H (proximal), C_5H_4]. ^{13}C NMR (67.8 MHz, C_6D_6, 28 °C): δ −5.00, −6.31 [$Si(CH_3)_2$], 48.89 (Ti–CH_3), 104.65 [$C_1(C_5H_4)$], 114.46, 119.37, 126.62, 131.44 [C_2, C_3, C_4, C_5 (C_5H_4)]. ^{13}C NMR (67.8 MHz, $CDCl_3$, 28 °C): δ −4.8, −6.2 [$Si(CH_3)_2$], 50.8 (Ti–CH_3), 103.4 [$C_1(C_5H_4)$], 113.7, 118.8, 126.0, 130.9 [C_2, C_3, C_4, C_5 (C_5H_4)].

Preparation of $[\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2Si(CH_3)_2]TiCl[CH_2Si(CH_3)_3]$ (5). Method A. A 0.5-g (1.64 mmol) sample of $[\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2Si(CH_3)_2]TiCl_2$ was suspended in 50 mL of toluene and cooled to −30 °C. $Al[CH_2Si(CH_3)_3]_3(OEt_2)$ (0.59 g, 1.64 mmol) dissolved in toluene was added to the suspension. The mixture was warmed to room temperature and stirred for 12 h. Then 0.64 g (1.71 mmol) of tetraphenylphosphonium chloride was added, and the solution was filtered, concentrated to 10 mL, and cooled at −30 °C to give compound **5** as a microcrystalline dark red compound (0.19 g, 33% yield), always contaminated with traces of the dialkyl.

Method B. A 0.5-g (1.64 mmol) sample of $[\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2Si(CH_3)_2]TiCl_2$ was dissolved in 50 mL of THF and cooled to −30 °C, and then a solution of 0.15 g (1.64 mmol) of $LiCH_2Si(CH_3)_3$ in THF was added. The mixture was warmed to room temperature and stirred for 2 h. After removal of the solvent, the residue was extracted with 50 mL of toluene. The solution was filtered, concentrated to 10 mL, and cooled at −30 °C to give compound **5** as an microcrystalline dark red compound (0.10 g, 17% yield), always contaminated with traces of dialkyl. ^1H NMR (80 MHz, C_6D_6, 28 °C): δ 0.00 [s, 3 H, $Si(CH_3)_2$], 0.04 [s, 3 H, $Si(CH_3)_2$], 0.09 [s, 9 H, $Si(CH_3)_3$], 2.22 (s, 2 H, Ti–CH_2–), 5.19 [m, 2 H (distal), C_5H_4], 5.69 [m, 2 H (distal), C_5H_4], 7.06 [m, 2 H (proximal), C_5H_4], 7.36 [m, 2 H (proximal), C_5H_4]. ^{13}C NMR (67.8 MHz, $CDCl_3$, 28 °C): δ −4.6, −6.3 [$Si(CH_3)_2$], 2.7 [$Si(CH_3)_3$], 79.7 (Ti–CH_2–), 103.5 [C_1 (C_5H_4)], 113.5, 120.1, 128.4, 128.5 [C_2, C_3, C_4, C_5 (C_5H_4)].

Preparation of $[\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2Si(CH_3)_2]TiCl[Si(CH_3)_3]$ (6). $[\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2Si(CH_3)_2]TiCl_2$ (0.5 g, 1.64 mmol) was suspended in 50 mL of dry hexane and cooled to −30 °C. $Al[Si(CH_3)_3]_3(OEt_2)$ (0.52 g, 1.64 mmol) dissolved in hexane was added to the suspension. The mixture was warmed to room temperature and stirred for 8 h until the solution became light green. Then 0.64 g (1.71 mmol) of tetraphenylphosphonium chloride were added, and the solution was filtered, concentrated to 10 mL, and cooled at −78 °C to give light green crystals of compound **6** (0.24 g, 43% yield). Anal. Calcd for $C_{15}H_{23}ClSi_2Ti$: C, 52.55; H, 6.71. Found: C, 52.83; H, 6.88. ^1H NMR (80 MHz, C_6D_6, 28 °C): δ −0.20 [s, 3 H, $Si(CH_3)_2$], −0.05 [s, 3 H, $Si(CH_3)_2$], 0.35 [s, 9 H, Ti–$Si(CH_3)_3$], 5.32 [m, 2 H (distal), C_5H_4], 5.60 [m, 2 H (distal), C_5H_4], 6.86 [m, 2 H (proximal), C_5H_4], 7.57 [m, 2 H (proximal), C_5H_4]. ^{13}C NMR (67.8 MHz, $CDCl_3$, 28 °C): δ −5.0, −5.5 [$Si(CH_3)_2$], 8.5 [$Si(CH_3)_3$], 101.7 [C_1 (C_5H_4)], 114.3, 115.9, 120.3, 125.8 [C_2, C_3, C_4, C_5 (C_5H_4)].

X-ray Data Collection. $[\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2Si(CH_3)_2]TiClCH_3$, M = 285, monoclinic, space group $P2_1/m$, a = 7.270 (7) Å, b = 8.751 (9) Å, c = 10.66 (1) Å, β = 90.78 (6)°, V = 678 (2) Å^3, and D_{calc} = 1.392 g cm^{-3} for Z = 2, $F(000)$ = 295, Mo Kσ radiation (=0.7107 Å), μ(Mo Kσ) = 0.88 mm^{-1}.

A colorless crystal of irregular shape and dimensions 0.075 × 0.150 × 0.225 mm was mounted on a Siemens P3 automatic single-crystal diffractometer. The cell parameters were determined by least-squares refinement of the accurately determined diffraction angles of 24 reflections. Mo Kσ radiation with a graphite monochromator was used to make intensity measurements in an optimised ω-scan mode out to $2\theta = 60°$ ($-10 \le h \le 10$, $-12 \le k \le 12$, $-15 \le l \le 15$) yielding 7887 reflections of which 2093 were unique (R_{int} = 0.046) and 735 were considered to be observed (due to bad profiles, many reflections were estimated uncorrectly and had to be removed by a general cutoff $I > 4\sigma(I)$).

Three standard reflections, measured every 150 reflections, showed no significant change. Normal Lorentz and polarization corrections were applied. An absorption correction was considered unnecessary. The structure was solved by direct methods and subsequent difference Fourier syntheses. Full-matrix least-squares refinement on F converged to an R value of 0.048. Variables to be refined included, apart from the scale factor, atomic positional and anisotropic displacement parameters. Unit weights were used, and the hydrogen atoms were taken into account at their calculated positions. The largest Δ/σ was negligable (<0.001), and the remaining electron density was 0.4 e Å^{-3}. Final atom coordinates and bond lengths are shown in Tables I and II, respectively.

Anomalous dispersion corrections and atomic scattering factors were taken from ref 9. All calculations were performed with SHELXTL-PLUS[10] on a MicroVAX 2000 computer.

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Supplementary Material Available: Tables of bond lengths and angles, anisotropic displacement parameters, and H atom coordinates (2 pages); a listing of structure factors (8 pages). Ordering information is given on any current masthead page.

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