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Synthetic and structural studies on new vinylcyclopentadienyl derivatives of titanium, iron and thallium

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Abstract

An improved procedure for the preparation of vinylcyclopentadienyllithium (1) from 6-methylfulvene and lithium diisopropylamide in THF solution has been developed. Reaction of 1 with thallium ethoxide in THF has produced vinylcyclopentadienylthallium (3). Compounds 1 and 3 have been used in the synthesis of vinyl- (4) and 1,1′-divinyltitanocene dichloride (5). Treatment of 1,2,3,4,6-pentamethylfulvene with lithium diisopropylamide in THF solution has afforded vinyltetramethylcyclopentadienyllithium (2) in high yield. Reactions of 2 with $FeCl_2$ or $TiCl_4$ have led to bis(η^5-vinyltetramethylcyclopentadienyl)iron (7) and (η^5-vinyltetramethylcyclopentadienyl)titanium trichloride (8), respectively. Compound 8 reacts with (η^5-C_5H_5)Tl to produce 1-vinyl-2,3,4,5-tetramethyltitanocene dichloride (9) in high yield. The crystal structure of 5 has been determined. 5 is monoclinic, $C2/c$, with $a = 14.420(3)$, $b = 6.610(2)$, $c = 14.111(3)$ Å, $\beta = 102.18(2)°$ and $D_{calc} = 1.52$ g cm^{-3} for $Z = 4$. The Ti atom resides on a crystallographic two-fold axis. The η^5-vinylcyclopentadienyl groups are slightly staggered with the carbons bonded to the vinyl groups next to one another and between the Cl–Ti–Cl bond. The Ti–C(η^5) separations range from 2.343(4) to 2.450(3) Å, the latter values for the carbon atoms bonded to the vinyl group.

Introduction

η^5-Vinylcyclopentadienyl derivatives of the transition metals have been of considerable interest in recent years, since they can undergo addition homo- and copolymerizations to produce organometallic polymers [1]. η^5-Vinylcyclopentadienyl derivatives of iron [2–5], ruthenium [3,6], osmium [3,6], manganese [7,8] and chromium [9,10] are most conveniently prepared by the classic acetylation, reduction and dehydration route starting from the corresponding metallo-aromatic η^5-

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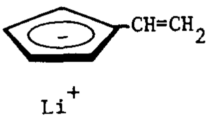
cyclopentadienyl analogs. (η^5-Vinylcyclopentadienyl)tricarbonylmethyltungsten [11,12] and (η^5-vinylcyclopentadienyl)dicarbonylcobalt [13,14] can be obtained from the respective η^5-formylcyclopentadienyl derivatives by means of Wittig reactions. We subsequently developed a convenient, general route to η^5-vinylcyclopentadienylmetal compounds by treatment of 6-methylfulvene with lithium diisopropylamide (LDA) in THF solution to form vinylcyclopentadienyllithium (**1**) [15]. This organolithium reagent, which can be isolated and characterized, serves as a useful precursor to η^5-vinylcyclopentadienyl derivatives of molybdenum, tungsten, cobalt, rhodium, iridium and copper [15,16].



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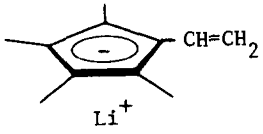

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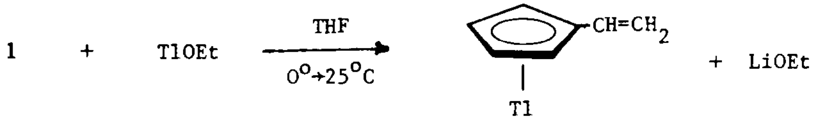
We now report on extensions of these studies to include several new η^5-vinylcyclopentadienyl compounds of thallium and titanium. We have also extended this synthetic approach to the formation of vinyltetramethylcyclopentadienyllithium (**2**), and illustrate its utility in the formation of the first (η^5-vinyltetramethylcyclopentadienyl) derivatives of the transition metals, namely, iron and titanium. An improved procedure for the preparation of **1** is also described. Results of X-ray crystallographic studies on several of these new vinyl organometallic compounds are likewise discussed.

Results and discussion

Our original preparation of **1** from LDA and 6-methylfulvene in THF solution has been reported to proceed in high yield [15,16]. In a number of runs, however, the yields of **1** were variable and the desired product was often obtained as an oily solid. For these reasons, the synthesis of **1** has been further investigated. We find that the deprotonation of diisopropylamine is more satisfactorily initiated at −78 °C rather than at 25 °C, and that the reaction proceeds much more favorably using n-butyllithium rather than methyllithium as described previously. Using the more reactive n-butyllithium, a reflux period is not necessary to complete the reaction, and LDA is obtained as a light amber solution.

In the subsequent step, we have found that freshly prepared 6-methylfulvene leads to purer product in higher yields than 6-methylfulvene that has been stored at −20 °C under nitrogen in the dark for extended periods of time. Compound **1** can be routinely prepared in ca. 80% yield as an air-sensitive yellow-white powder under the above conditions, and a detailed procedure is described in the Experimental section.

In the synthesis of functionally substituted cyclopentadienyl-transition metal compounds, organothallium precursors are frequently more convenient and versatile reagents than their organosodium or -lithium analogs [17–24]. It was therefore of interest to attempt the preparation of vinylcyclopentadienylthallium (**3**). We have found that this new organothallium compound can be readily synthesized from a reaction between **1** and thallium ethoxide in THF solution. Concentration of the reaction mixture and addition of diethyl ether precipitates **3** as a yellow-orange solid in 80% yield. The product is air-sensitive and decomposes slowly in air. Like the lithium analog **1**, however, it can be stored for extended periods of time under argon at −20 ° C. On the other hand, a sample of **3** stored in a glove box under nitrogen at 25 ° C for several weeks apparently decomposed and was unsuitable for further synthetic purposes.



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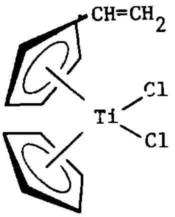
The synthetic utility of **3** has been demonstrated by its reaction with (η^5-C_5H_5)$TiCl_3$ in THF solution to form vinyltitanocene dichloride (**4**) in 44% yield. Compound **4** can also be obtained in lower yield from a reaction between (η^5-C_5H_5)$TiCl_3$ and **1** [13]. 1,1′-Divinyltitanocene dichloride (**5**) can likewise be prepared in 75% yield from a reaction between 2 equivalents of **1** and $TiCl_4 \cdot 2THF$ in THF solution. Both **4** and **5** are dark red-green, air and thermally stable solids.

The ^1H NMR spectra of **1**, **3**–**5** are in agreement with their proposed structures, and proton assignments are illustrated in structure **6**. Typically, a pair of apparent



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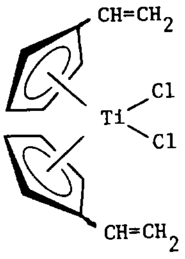

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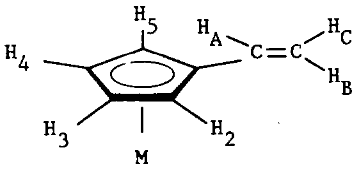

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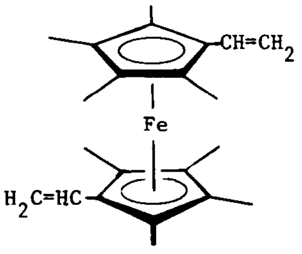

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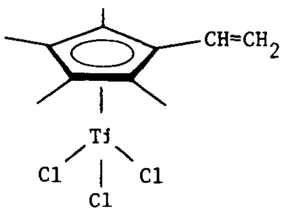
triplets (AA′BB′ pattern) are observed for protons H(3,4) and H(2,5) of the monosubstituted cyclopentadienyl ring. The vinylic proton region is generally well resolved, and occurs as an ABX pattern similar to vinylferrocene [3]. The *trans* [*J*(AB)], *cis* [*J*(AC)] and *geminal* [*J*(BC)] coupling constants associated with the vinylic protons of both **1** and **3** are 17.4, 10.7 and 2.4 Hz, respectively. For **5**, the respective values are 17.6, 10.8 and 1.3 Hz. The ^1H NMR data for these vinylcyclopentadienyl-metal compounds is therefore consistent with data for similar vinyl analogs described by us previously [16].

Peralkylated cyclopentadienyl-metal compounds have played an important role in the development of organometallic chemistry in recent years, since such compounds often exhibit enhanced solubility and stability features compared to their η^5-cyclopentadienyl counterparts. In an effort to combine these desirable characteristics with ring functionality, we have developed a convenient synthetic route to vinyltetramethylcyclopentadienyllithium (**2**). By slow addition of 1,2,3,4,6-pentamethylfulvene [25,26] to a THF solution of LDA at −20 °C followed by warming and stirring overnight, **2** has been obtained as a pyrophoric light yellow powder in 88% yield, based on starting fulvene. Compound **2** has been characterized by its ^1H NMR spectrum in THF-d_8. The spectrum shows two sharp singlets at δ 1.80 and 1.94 ppm, each integrating to six protons and assignable to the C(3,4) and C(2,5) methyl groups, respectively. The vinylic region appears as an ABX pattern (see structure **6**), with one-proton resonances at δ 4.28 [H(C)], 4.68 [H(B)] and 6.58 [H(A)] ppm, and *J*(AB), *J*(AC) and *J*(BC) coupling constants of 17.6, 11.5 and 2.9 Hz, respectively.

The synthetic utility of **2** is illustrated by its conversion into several transition metal analogs. Bis-(η^5-vinyltetramethylcyclopentadienyl)iron (**7**) has been prepared in 51% yield by a reaction of 2 equivalents of **2** with anhydrous $FeCl_2$ in refluxing THF. Compound **7** was characterized by its ^1H NMR, ^{13}C NMR, and EI mass spectra, and by elemental analysis. The ^1H NMR spectrum shows two sharp singlets at δ 1.70 and 1.80 ppm, assignable to the C(3,4) and C(2,5) methyl substituents bonded to each cyclopentadienyl ring, respectively. The vinyl groups give signals at δ 6.36 for H(A), δ 5.23 for H(B), and δ 5.21 ppm for H(A), with $J(AB) = 18.4$ Hz, $J(AC) = 10.8$ Hz, and $J(BC) = 2.1$ Hz. The ^{13}C NMR spectrum shows signals at δ 9.13 and 10.22 ppm for the methyl groups, whereas the ring carbons give rise to the expected three signals at δ 78.56, 78.60 and 79.30 ppm. The vinylic carbons occur as two signals at δ 112.43 and 133.46 ppm, assignable to the CH_2 and CH carbons, respectively. These assignments are confirmed by use of the DEPT pulse sequence which reverses CH and CH_3 carbon signals from CH_2 and quaternary carbon signals. The EI mass spectrum of **7** exhibits peaks for the molecular ion (*m/e* 350) as well as fragmentation peaks due to losses of 1–3 methyl groups.

A reaction between **2** and $TiCl_4$ in refluxing toluene has afforded (η^5-vinyltetramethylcyclopentadienyl)titanium trichloride (**8**) as a moderately air-stable red solid in 82% yield. A subsequent reaction between **8** and η^5-cyclopentadienylthallium in refluxing toluene, following a procedure developed for the preparation of $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)TiCl_2$ [27], produced (η^5-cyclopentadienyl)(η^5-vinyltetramethylcyclopentadienyl)titanium dichloride (**9**) as an air-stable red-purple crystalline solid in 89% yield. As in the case of **7**, these new organotitanium compounds **8** and **9** have been characterized by their ^1H NMR, ^{13}C NMR and EI mass spectra as well as by microanalyses (see Experimental section).



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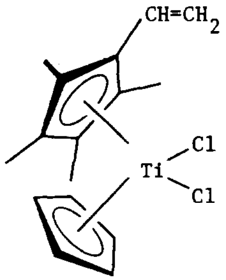

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Chemical reactivity studies on these new vinylcyclopentadienyl-metal compounds, including polymerization activity, are currently under investigation.

X-Ray crystallographic studies

Crystallographic examination of crystals of **7** revealed serious disorder similar to that observed for Cp_2V [28]. The Fe atom apparently resides on a center of inversion with all five ring carbon positions disordered orientationally and disordered with respect to their substituents. Satisfactory resolution of the disorder was inadequate for any meaningful discussion of the structure.

The molecular structure of **5** is depicted in Fig. 1, while bond distances and angles are given in Table 1. The molecule resides on a crystallographic two-fold axis. The Cp rings are slightly staggered with the vinyl substituents on carbon atoms nearly over one another and in between the Cl–Ti–Cl bond. This orientation minimizes the steric interaction of the vinyl groups with each other and with the Cl atoms. The orientation is similar to that observed for $(\eta^5\text{-}C_5H_4Me)_2TiCl_2$ [29].

The cyclopentadienyl groups are asymmetrically bonded to Ti, tilted such that the vinyl-carrying carbon atoms are farthest away. There are two short (Ti–C(2),C(3) = 2.350(7) Å average), two medium (Ti–C(1),C(4) = 2.409(1) Å average) and one long (Ti–C(5) = 2.450(3) Å) separations with a 0.107 Å range. The Ti–centroid distance is 2.07 Å.

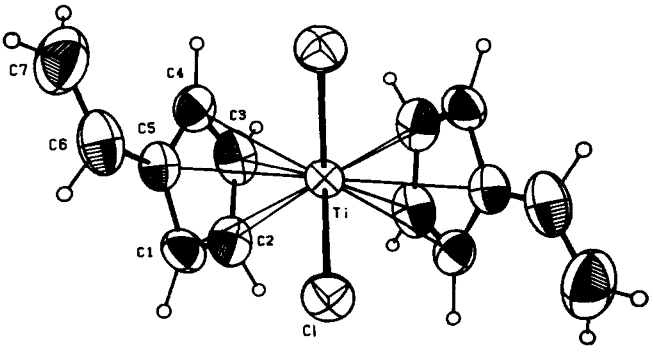

Fig. 1. Molecular structure and atom-labeling scheme for **5**.

Table 1

Bond distances (Å) and angles (deg) for $(\eta^5\text{-}C_5H_4C_2H_3)_2TiCl_2$ (5)

Atoms	Distance	Atoms	Distance
Ti–Cl	2.363(1)	Ti–C(1)	2.409(3)
Ti–C(2)	2.343(4)	Ti–C(3)	2.357(4)
Ti–C(4)	2.409(4)	Ti–C(5)	2.450(3)
C(1)–C(2)	1.390(6)	C(1)–C(5)	1.405(5)
C(2)–C(3)	1.401(5)	C(3)–C(4)	1.396(5)
C(4)–C(5)	1.415(5)	C(5)–C(6)	1.456(5)
C(6)–C(7)	1.282(6)	Ti–Cent	2.07
Atoms	**Angle**	**Atoms**	**Angle**
Cl–Ti–Cla	95.56(6)	C(2)–C(1)–C(5)	108.8(4)
C(1)–C(2)–C(3)	108.0(4)	C(2)–C(3)–C(4)	108.1(4)
C(3)–C(4)–C(5)	108.1(3)	C(1)–C(5)–C(4)	106.9(3)
C(1)–C(5)–C(6)	125.5(4)	C(4)–C(5)–C(6)	127.5(4)
C(5)–C(6)–C(7)	124.9(5)	Cent–Ti–Cent [a]	131.9
Cent–Ti–Cl	105.7	Cent–Ti–Cl [a]	106.1

[a] The Cl atom and Cent (centroid of the five membered ring) are related to the others by the crystallographic two-fold axis.

The Cp ring is planar to within 0.007 Å with C(6) 0.033 Å and C(7) 0.279 Å out of the plane away from the metal. The two shortest internal C–C bonds (C(1)–C(2) and C(3)–C(4)) are each one carbon removed from the vinyl substituent and average 1.393(3) Å. The remaining three distances average 1.407(6) Å; the difference is only 2.3σ.

The average bonding parameters for 5, Ti-C(η^5) = 2.39(4) Å, Ti–centroid = 2.07 Å, Ti–Cl = 2.363 Å, centroid–Ti–centroid = 131.9°, centroid–Ti–Cl = 105.9°, Cl–Ti–Cl = 95.56(6)°, are within the ranges established by $(\eta^5\text{-}C_5H_5)_2TiCl_2$ [30], $(\eta^5\text{-}C_5Me_5)_2TiCl_2$ [31], $(\eta^5\text{-}C_5H_4Me)_2TiCl_2$ [29], and $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)TiCl_2$ [27]. The values observed for 5 most closely resemble those observed for $(\eta^5\text{-}C_5H_5)_2TiCl_2$.

Experimental

All operations were carried out under an argon atmosphere using Schlenk or glovebox techniques except where specified. Argon was deoxygenated with activated BTS catalyst and dried with molecular sieves and phosphorus pentoxide. Pentane, hexane, toluene, diethyl ether and tetrahydrofuran were distilled under argon from sodium–potassium alloy, while dichloromethane was distilled under argon from calcium hydride. Diisopropylamine, obtained from Aldrich Chemical Co., was dried over BaO and distilled under argon before use. Thallium ethoxide was obtained from Aldrich. $(\eta^5\text{-}C_5H_5)TiCl_3$ [32], $(\eta^5\text{-}C_5H_5)Tl$ [33], $TiCl_4 \cdot 2THF$ [34], 6-methylfulvene [16,35] and 1,2,3,4,6-pentamethylfulvene [25] were prepared by literature methods. ^1H and ^{13}C NMR spectra were obtained on a Varian XL-200 spectrometer; whereas IR spectra were recorded on Beckmann IR-10 or Perkin-Elmer 1310 spectrometers. Electron impact mass spectra were obtained at 70 eV on a Varian CH7 mass spectrometer. Microanalyses were performed by the Microanalytical Laboratory, University of Massachusetts, Amherst, MA.

Vinylcyclopentadienyllithium (1)

Into a 300-ml, round-bottom Schlenk flask was placed 150 ml of THF and 3.46 ml (24.7 mmol) of diisopropylamine. The flask was cooled to −78°C and the solution was stirred for 20 min. n-Butyllithium in hexane (9.88 ml, 24.7 mmol) was subsequently added via a syringe over a 5 min period. The solution was stirred for 1 h at −78°C and allowed to warm to room temperature, affording lithium diisopropylamide as a light amber-yellow solution. The solution was cooled to −20°C and a mixture of freshly distilled 6-methylfulvene (3.03 ml, 32.9 mmol) and 10 ml of THF was added via a small addition funnel over a 30 min period. The reaction mixture was stirred at −20°C for 5 h and the solvent was then removed under vacuum. Pentane (160 ml) was added to the flask and the mixture was stirred for 10 min. A small amount of diethyl ether was subsequently added, producing a fine precipitate, followed by another 50 ml of pentane. The mixture was stirred for 1 h at room temperature and the resulting precipitate was collected on a frit under argon. The precipitate was washed with pentane (2 × 100 ml) to afford vinylcyclopentadienyllithium (3.00 g, 81%) as an air-sensitive, yellow-white powder. ^{1}H NMR (THF-d_8) δ 4.28 (dd, 1H, H(C)), 4.90 (dd, 1H, H(B)), 5.62 (t, 2H, H(3,4)), 5.83 (t, 2H, H(2,5)), 6.54 (dd, 1H, H(A)).

Vinylcyclopentadienylthallium (3)

A solution of vinylcyclopentadienyllithium (1.12 g, 11.4 mmol) in 100 ml of THF, prepared in an argon-flushed Schlenk flask, was cooled to 0°C and stirred for 30 min. To the flask was added dropwise via an addition funnel a solution of thallium ethoxide (0.81 ml, 11.4 mmol) in 15 ml of THF over a period of 40 min at 0°C. Approximately one-half way through the addition, a yellow precipitate began to form. After completion of the addition, the suspension was allowed to warm to room temperature and stirring was continued for 16 h. Addition of diethyl ether (50 ml) produced a small amount of additional precipitate. The mixture was filtered on a frit under argon, and the solid was washed thoroughly with cold THF, diethyl ether, pentane, and dried under reduced pressure. The solid was transferred to a small Schlenk tube to afford 2.70 g (80%) of vinylcyclopentadienylthallium as a yellow-orange solid (Anal. Found: C, 28.68; H, 2.56. C_7H_7Tl calc.: 28.45; H, 2.39%.) ^{1}H NMR (DMSO-d_6) δ 4.38 (dd, 1H, H(C)), 4.90 (dd, 1H, H(B)), 5.51 (t, 2H, H(3,4)), 5.83 (t, 2H, H(2,5)), 6.42 (dd, 1H, H(A)).

(η^5-Vinylcyclopentadienyl)(η^5-cyclopentadienyl)dichlorotitanium (Vinyltitanocene dichloride) (4)

Method A. Into a 250-ml three-neck round-bottom flask were placed (η^5-cyclopentadienyl)trichlorotitanium (1.11 g, 5.1 mmol) and ca. 50 ml of diethyl ether. The flask was cooled to 0°C and a slurry of vinylcyclopentadienyllithium (0.51 g, 5.2 mmol) in 20 ml of diethyl ether was added dropwise. After the addition was complete, the mixture was refluxed for 1.5 h. The solution was cooled to 25°C, 5 ml of water was added, and the mixture stirred vigorously. The solution was filtered, dried over anhydrous magnesium sulfate, and filtered again. The solvent was removed under vacuum to give 0.22 g (16%) of vinyltitanocene dichloride. An analytical sample was obtained by recrystallization from toluene/hexane as dark red crystals, m.p. 154.5–157°C (Anal. Found: C, 52.39; H, 4.48. $C_{12}H_{12}Cl_2Ti$ calc.: C, 52.40; H, 4.40%.) ^{1}H NMR (CDCl$_3$) δ 5.51 (m, 1H, H(B)), 5.78 (m, 1H, H(C)), 6.38–6.66 (10 H, C_5H_5 + C_5H_4 + H(A)). IR (KBr) 3110 (s), 1430 (s), 1340 (w), 960 (m), 840 (m), 780 (s) cm^{-1}. MS *m/e* 274 (M^+), 239 $(M - Cl)^+$, 209 $(C_5H_4CHCH_2TiCl_2)^+$, 183 $(C_5H_5TiCl_2)^+$, 174 $(C_5H_4CHCH_2TiCl)^+$, 148 $(C_5H_5TiCl)^+$, 91 $(C_7H_7)^+$.

Method B. Into a 100-ml Schlenk flask were placed vinylcyclopentadienylthallium (0.600 g, 2.03 mmol) and (η^5-cyclopentadienyl)trichlorotitanium (0.445 g, 2.03 mmol) followed by 70 ml of THF. The resulting milky yellow-orange suspension was stirred at room temperature for 24 h. The mixture was filtered through a Celite plug on a frit under argon and the solvent was removed under vacuum. The resulting residue was dissolved in dichloromethane, and the solution concentrated and cooled to −20 ° C to afford 0.24 g (44%) of vinyltitanocene dichloride. The MS, IR and NMR spectral data were identical to those described in Method A.

Bis-(η^5-vinylcyclopentadienyl)dichlorotitanium (1,1′-Divinyltitanocene dichloride) (5)

Into a 100-ml Schlenk flask were placed vinylcyclopentadienyllithium (0.53 g, 5.40 mmol) and $TiCl_4 \cdot 2THF$ (0.90 g, 2.73 mmol). The flask was cooled to 0 ° C under argon, THF (65 ml) was added, and the solution was stirred for 20 min. The solution was then allowed to warm to room temperature and stirred for 72 h, during which time the color of the solution changed from black to dark red. The solvent was removed under vacuum and the resulting residue was washed with a large amount of pentane and redissolved in benzene to give a dark red solution. The solution was filtered through a Celite plug on a frit under argon, and the solvent was removed to produce a dark-red crystalline solid. The solid was dissolved in a minimum amount of dichloromethane, layered with hexane, and cooled to −20 ° C to afford 0.81 g (75%) of 1,1′-divinyltitanocene dichloride as red-black needles. An analytical sample was prepared by recrystallization from dichloromethane/hexane. (Anal. Found: C, 55.76; H, 4.70; Cl, 23.81. $C_{14}H_{14}Cl_2Ti$ calc.: C, 55.85; H, 4.69; Cl, 23.55%.) ^1H NMR (toluene-d_8) δ 5.07 (dd, 2H, H(C)), 5.31 (dd, 2H, H(B)), 5.91 (t, 4H, H(3,4)), 6.78 (t, 4H, H(2,5)), 6.33 (dd, 2H, H(A)). ^{13}C NMR (C_6D_6) δ 117.7, 118.1, 120.3, 129.8, 130.2.

Vinyltetramethylcyclopentadienyllithium (2)

Into a 250 ml Schlenk flask under argon was added 5.0 g (50 mmol) of diisopropylamine and 100 ml of THF. The solution was cooled to −78 ° C and one equivalent (19.8 ml) of n-butyllithium (2.5 *M* in hexane) was added dropwise with stirring over a period of 30 min. The solution was allowed to warm to room temperature and stirred for 3 h. The mixture was cooled to −20 ° C, and 1,2,3,4,6-pentamethylfulvene (8.79 g, one equivalent, 80% pure as a mixture with vinylcyclopentadiene isomers) [26] in 10 ml of THF was added dropwise over a period of 1 h. After stirring the reaction mixture overnight, the solution was concentrated to ca. 15 ml. Small amounts of diethyl ether and pentane were added, resulting in a light-colored precipitate. The solid was collected on a frit under argon, washed with pentane and dried under vacuum to produce vinyltetramethylcyclopentadienyllithium (6.3 g, 88%) as a pyrophoric light yellow solid. ^1H NMR (THF-d_8) δ 1.80 (s, 6H, CH_3), 1.94 (s, 6H, CH_3), 4.28 (dd, 1H, H(C)), 4.68 (dd, 1H, H(B)), 6.58 (dd, 1H, H(A)).

Bis-(η^5-vinyltetramethylcyclopentadienyl)iron (7)

Vinyltetramethylcyclopentadienyllithium (1.0 g, 6.5 mmol) and anhydrous $FeCl_2$ (0.411 g, 3.25 mmol) were weighed in a glove box under nitrogen into a 100 ml

Schlenk flask. The flask was removed, 100 ml of THF was added, a condenser was attached, and the mixture heated at reflux for 20 h. The solvent was removed under vacuum, the residue was dissolved in dichloromethane, and the solution filtered through Celite. The dichloromethane was removed, and the residue was extracted with pentane, filtered again through Celite, and concentrated. After cooling the solution to −20 °C, 0.58 g (51%) of bis(η^5-vinyltetramethylcyclopentadienyl)iron crystallized as air-stable orange needles. The product was collected by filtration. (Anal. Found: C, 75.16; H, 8.67. $C_{22}H_{30}Fe$ calc.: C, 75.43; H, 8.63%.) ^1H NMR ($CDCl_3$) δ 1.70 (s, 12H, CH_3), 1.80 (s, 12H, CH_3), 5.21 (dd, 2H, H(B)), 5.23 (dd, 2H, H(C)), 6.36 (dd, 2H, H(A)). ^{13}C NMR ($CDCl_3$) δ 9.13, 10.22, 78.56, 79.30, 112.43, 133.46. MS *m/e* 350 (M^+), 335 $(M-CH_3)^+$, 320 $(M-2CH_3)^+$, 305 $(M-3CH_3)^+$, 147 $(C_{11}H_{16})^+$, 131 $(C_{11}H_{16}-CH_3)^+$, 115 $(C_{11}H_{16}-2CH_3)^+$.

Trichloro-(η^5-vinyltetramethylcyclopentadienyl)titanium (8)

Vinyltetramethylcyclopentadienyllithium (0.75 g, 4.8 mmol) was weighed into a 100 ml Schlenk flask. After the addition of ca. 40 ml of toluene, $TiCl_4$ (0.53 ml, 4.8 mmol) was added slowly via a syringe, resulting in a deep red solution. The reaction mixture was heated at reflux for 2 h, filtered through Celite, and the solvent was removed under vacuum to yield 1.2 g (82%) of trichloro-(η^5-vinyltetramethylcyclopentadienyl)titanium as a deep red solid. An analytical sample was obtained by double sublimation at 130–140 °C/0.01 torr. (Anal. Found: C, 44.29; H, 4.99. $C_{11}H_{15}Cl_3Ti$ calc.: C, 43.82; H, 5.01%.) ^1H NMR ($CDCl_3$) δ 2.40 (s, 6H, CH_3), 2.50 (s, 6H, CH_3), 5.61 (dd, 1H, H(C)), 5.74 (dd, 1H, H(B)), 6.85 (1H, H(A)). ^{13}C NMR ($CDCl_3$) δ 14.31, 15.30, 121.31, 129.61, 135.61, 136.49, 138.31. MS *m/e* 301 (M^+), 266 $(M-Cl)^+$, 147 $(C_{11}H_{16})^+$.

Dichloro-(η^5-cyclopentadienyl)(η^5-vinyltetramethylcyclopentadienyl)titanium (1-vinyl-2,3,4,5-tetramethyltitanocene dichloride) (9)

Trichloro-(η^5-vinyltetramethylcyclopentadienyl)titanium (0.272 g, 0.90 mmol) and cyclopentadienylthallium (0.243 g, 0.90 mmol) were weighed into a 50 ml Schlenk flask. Toluene (20 ml) was added and the reaction mixture was heated at reflux for 18 h. After cooling to room temperature, the solution was filtered through Celite and the solvent was removed under vacuum to yield 0.265 g (89%) of 1-vinyl-2,3,4,5-tetramethyltitanocene dichloride as red-purple crystals. An analytical sample was obtained by recrystallization from dichloromethane/hexane. (Anal. Found: C, 58.43; H, 5.94. $C_{16}H_{20}Cl_2Ti$ calc.: C, 58.03; H, 6.09%.) ^1H NMR ($CDCl_3$) δ 2.10 (s, 6H, CH_3), 2.15 (s, 6H, CH_3), 5.49 (dd, 1H, H(C)), 5.51 (dd, 1H, H(B)), 6.30 (s, 5H, C_5H_5), 6.57 (dd, 1H, H(A)). ^{13}C NMR ($CDCl_3$) δ 13.7, 14.3, 118.3, 120.8, 123.7, 127.8, 130.1, 134.6. MS *m/e* 330 (M^+), 295 $(M-Cl)^+$, 260 $(M-2Cl)^+$, 147 $(C_{11}H_{16})^+$.

X-Ray data collection, structure determination and refinement for 5

A single crystal of the title compound was mounted on a pin and transferred to the goniometer. The space group was determined to be either the centric *C*2/*c* or acentric *Cc* from the systematic absences. The subsequent solution and successful refinement of the structure was carried out in the space group *C*2/*c*. A summary of data collection parameters is given in Table 2.

Table 2

Crystal data and summary of intensity data collection and structure refinement

Compound	5
Color/Shape	dark green/parallelepiped
Form. wt.	301.1
Space group	$C2/c$
Temp., °C	20
Cell Constants [a]	
a, Å	14.420(3)
b, Å	6.610(2)
c, Å	14.111(3)
β, deg	102.18(2)
Cell vol, Å^3	1315
Formula units/unit cell	4
D_{calc}, g cm^{-3}	1.52
μ_{calc}, cm^{-1}	10.5
Diffractometer/scan	Enraf-Nonius CAD-4/$\omega-2\theta$
Radiation, graphite monochromator	Mo-K_α ($\lambda = 0.70173$)
Max crystal dimensions, mm	$0.35 \times 0.35 \times 0.40$
Scan width	$0.80 + 0.35 \tan \theta$
Standard reflections	200;040;004
Decay of standards	±2%
Reflections measured	2614
2θ range, deg	$2 \leqslant 2\theta \leqslant 50$
Range of h,k,l	$\pm 17, +7, +16$
Reflections observed [$F_o \geq 5\sigma(F_o)$] [b]	854
Computer programs [c]	SHELX [36]
Structure solution	heavy atom techniques
No. of parameters varied	78
Weights	$[\sigma(F_o)^2]^{-1}$
GOF	1.13
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.038
R_w	0.039
Largest feature final diff. map	0.3 e Å^{-3}

[a] Least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 25 reflections $\theta > 20°$. [b] Corrections: Lorentz polarization. [c] Neutral scattering factors and anomalous dispersion corrections from ref. 37.

Table 3

Final fractional coordinates for $(\eta^5\text{-}C_5H_4C_2H_3)_2TiCl_2$ (5)

Atom	x/a	y/b	z/c	B(eq) [a]
Ti	0.5000	0.2343(1)	0.2500	1.77
Cl	0.41185(7)	−0.0059(2)	0.31836(7)	2.74
C(1)	0.5552(3)	0.2817(7)	0.4220(3)	2.86
C(2)	0.5305(3)	0.4677(7)	0.3778(3)	3.13
C(3)	0.5944(3)	0.5104(7)	0.3182(3)	3.11
C(4)	0.6573(3)	0.3481(7)	0.3240(3)	2.76
C(5)	0.6335(3)	0.2041(6)	0.3891(3)	2.43
C(6)	0.6814(4)	0.0139(8)	0.4199(3)	3.60
C(7)	0.7625(4)	−0.0379(9)	0.4041(4)	4.65
H(1)[C(1)]	0.524	0.221	0.474	(iso)
H(1)[C(2)]	0.470	0.532	0.384	(iso)
H(1)[C(3)]	0.607	0.643	0.277	(iso)
H(1)[C(4)]	0.706	0.344	0.281	(iso)
H(1)[C(6)]	0.667	−0.056	0.476	(iso)
H(1)[C(7)]	0.798	−0.155	0.429	(iso)
H(2)[C(7)]	0.805	0.066	0.378	(iso)

[a] $B(\text{eq}) = 4/3[(aa)b11 + (bb)b22 + (cc)b33 + (ab)(\cos\gamma)(b12) + (ac)(\cos\beta)(b13) + (bc)(\cos\alpha)(b23)]$.

Least-squares refinement with isotropic thermal parameters led to $R = 0.092$. The hydrogen atoms were located from a difference Fourier map and included with fixed contribution ($B = 5.5$ Å^2). Refinement of nonhydrogen atoms with anisotropic temperature factors led to the final values of $R = 0.038$ and $R_w = 0.039$. The final values of the positional parameters are given in Table 3.

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