LOW-VALENT TITANOCENE PRODUCTS FROM ATTEMPTED SYNTHESES OF TITANOCENE BEARING DIMETHYL(3,3,3-TRIFLUOROPROPYL)SILYL GROUPS

Lenka LUKEŠOVÁ[a1], Michal HORÁČEK[a2], Róbert GYEPES[b1], Ivana CÍSAŘOVÁ[b2], Petr ŠTĚPNIČKA[b3], Jiří KUBIŠTA[a3] and Karel MACH[a4],*

[a] J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, 182 23 Prague 8, Czech Republic; e-mail: [1] lukesova@jh-inst.cas.cz, [2] horacek@jh-inst.cas.cz, [3] kubista@jh-inst.cas.cz, [4] mach@jh-inst.cas.cz

[b] Department of Inorganic Chemistry, Charles University, Hlavova 2030, 128 40 Prague 2, Czech Republic; e-mail: [1] gyepes@natur.cuni.cz, [2] cisarova@natur.cuni.cz, [3] stepnic@natur.cuni.cz

Reduction of silyl-substituted titanocene dichloride [TiCl$_2${η^5-C$_5$Me$_4$(SiMe$_2$CH$_2$CH$_2$CF$_3$)}$_2$] (**1**) with one molar equivalent of magnesium afforded a mixture of products, thus precluding the isolation of the possibly formed titanocene [Ti{(η^5-C$_5$Me$_4$(SiMe$_2$CH$_2$CH$_2$CF$_3$)}$_2$]. The presence of isolable monochloride [TiCl{η^5-C$_5$Me$_4$(SiMe$_2$CH$_2$CH$_2$CF$_3$)}$_2$] (**2**) in the mixture indicates that the mangnesium is consumed in concurrent reactions, that produce various titanocene compounds of which some were obtained by the reduction of **1** with excess magnesium. Those include the trinuclear Ti^{III}–Mg^{II}–Ti^{III} hydride-bridged complex [Ti{η^5-C$_5$Me$_4$-(SiMe$_2$CH$_2$CH$_2$CF$_3$)}$_2$(μ-H)$_2$]$_2$Mg (**3**) and a dimeric dinuclear Ti–Mg complex **4** containing the [Ti^{III}(μ-H)$_2$Mg(μ-X)]$_2$ core where, however, the nature of the bridging moiety X remains unknown. The reduction of **1** with excess magnesium in the presence of bis(trimethylsilyl)ethyne afforded the product of C–H activation [Ti{η^5-C$_5$Me$_4$(SiMe$_2$CH$_2$CH$_2$CF$_3$)}-{η^5:η^1-C$_5$Me$_3$(CH$_2$)(SiMe$_2$CH$_2$CH$_2$CF$_3$)}] (**5**) in 47% yield. This compound reacted rapidly with *tert*-butylethyne to give the Ti^{III}–acetylide complex [Ti(η^1-C≡CCMe$_3$){η^5-C$_5$Me$_4$-(SiMe$_2$CH$_2$CH$_2$CF$_3$)}$_2$] (**6**). All the reductions of **1** at molar ratios Mg:Ti ≥ 1 gave mixtures, where a good deal of the reduction products remained in the mother liquors unidentified. The structures of **1**, **2**, **3**, **5**, and **6** were determined by X-ray diffraction analysis and, for **2**, **3**, **4**, **5**, and **6**, further corroborated by ESR spectra.

Keywords: Metallocenes; Sandwich complexes; Titanium; Titanocenes; Magnesium; Silyl derivatives; (3,3,3-Trifluoropropyl)silyl group; Hydrides; ESR spectroscopy; X-ray diffraction; Crystal structure.

It is well recognized that electron-donating methyl substituents at cyclopentadienyl rings increase the stability of titanocenes[1] but do not prevent subsequent hydrogen abstraction reactions induced by the electron-poor

titanium(II) atom for tetramethylated[2] and even pentamethylated cyclopentadienyl rings[3]. Well-defined, thermally stable monomeric titanocenes have been known since 1998 when Lawless et al.[4] reported the preparation of silyl-substituted titanocene, $[Ti\{\eta^5\text{-}C_5Me_4(SiMe_2t\text{-}Bu)\}_2]$, by the reduction of the monochloride $[TiCl\{\eta^5\text{-}C_5Me_4(SiMe_2t\text{-}Bu)\}_2]$ with sodium amalgam. The other well-defined titanocene, $[Ti\{\eta^5\text{-}C_5Me_4(SiMe_3)\}_2]$ was obtained by thermolysis at 70 °C of its bis(trimethylsilyl)ethyne (BTMSE) complex[5] $[Ti\{\eta^5\text{-}C_5Me_4(SiMe_3)\}_2(\eta^2\text{-}btmse)]$ because the reduction of $[TiCl_2\{\eta^5\text{-}C_5Me_4(SiMe_3)\}_2]$ with magnesium metal led to products arising from C–H activation of the $SiMe_3$ group[6]. In contrast, the reduction of titanocene dichlorides $[TiCl_2(\eta^5\text{-}C_5Me_4R)_2]$, where $R = SiMe_2CH_2CH_2Ph$, $SiMe_2Ph$, and $SiMePh_2$, with magnesium in tetrahydrofuran gave thermally stable silyl-substituted titanocenes[7].

The rennaisance of titanocene investigations connected with the recent discoveries in the mechanism of nitrogen complexation by this type of complexes[8a,8b] has re-opened the question of stable alkyl-substituted titanocenes[8c]. In all crystallographically characterized titanocenes, the presence of the triorganosilyl group in addition to four methyl groups on each cyclopentadienyl ligand was decisive in stabilization of the electron-poor titanocenes. The nature of this effect is not yet clear but it is apparent that the stabilization relates to electronic and steric effects of the substituents at the silicon atom. For instance, the (diphenylmethyl)silyl-substituted titanocene displayed a very low affinity to BTMSE[7] when compared with the trimethylsilyl-substituted titanocene[5].

The choice of reducing agent used for the preparation of titanocenes is also crucial. The use of sodium amalgam to reduce titanocene monochlorides in toluene seems to afford the titanocenes in a clean way[4,8b,8c]. The use of magnesium, a safe and environmentally friendly reagent, for the reduction of titanocene dihalides to transiently formed titanocenes is highly effective if the titanocenes are stabilized by soft π-ligands, e.g., by BTMSE[9] or if they rapidly react with intramolecular functional group to give a single product, e.g., pendant double bonds to give cyclopentadienyl ring-tethered titanacyclopentanes[10]. On the other hand, in the absence of such reagents, transiently formed titanocenes undergo various hydrogen abstraction and hydrogen transfer reactions in which magnesium plays an active role and participates in the formation of final products. This is the case of the reduction of $[TiCl_2(\eta^5\text{-}C_5Me_4R)_2]$ compounds for R = H (lit.[11]), $SiMe_3$ (lit.[6]), $SiMe_2CH_2CH_2CH=CH_2$ (lit.[12]) or Ph (lit.[13]). However, the above mentioned smooth formation of thermally stable titanocenes $[Ti(\eta^5\text{-}$

$C_5Me_4R)_2]$ for R = $SiMe_2CH_2CH_2Ph$, $SiMe_2Ph$, and $SiMePh_2$ (lit.[7]) makes the magnesium reduction method a good alternative to the reduction of titanocene monochlorides with alkali metal amalgams[4,8c].

Here we report our attempt to prepare new thermally stable titanocene bearing the dimethyl(3,3,3-trifluoropropyl)silyl substituent in the tetramethylcyclopentadienyl ligands by the reduction of the corresponding titanocene dichloride with magnesium in tetrahydrofuran.

RESULTS AND DISCUSSION

Synthesis of $[TiCl_2\{\eta^5-C_5Me_4(SiMe_2CH_2CH_2CF_3)\}_2]$ (1) and Its Reductions with Magnesium

The silyl-substituted cyclopentadiene $C_5HMe_4(SiMe_2CH_2CH_2CF_3)$ and the respective titanocene dichloride $[TiCl_2\{\eta^5-C_5Me_4(SiMe_2CH_2CH_2CF_3)\}_2]$ (**1**) were obtained by the standard procedures used previously for the synthesis of $[TiCl_2\{\eta^5-C_5Me_4(SiMe_3)\}_2]$ (lit.[14]) (Scheme 1). The reaction of $[TiCl_3(thf)_3]$ with 2 molar equivalents of lithium cyclopentadienide $Li[C_5Me_4-(SiMe_2CH_2CH_2CF_3)]$ in tetrahydrofuran (THF) followed by oxidation of the Ti^{III} product with one half molar equivalent of $PbCl_2$ (lit.[15]) gave **1** in 35% yield. The reduction of **1** with a half molar equivalent of magnesium metal in THF afforded the blue monochloride $[TiCl\{\eta^5-C_5Me_4(SiMe_2CH_2CH_2CF_3)\}_2]$ (**2**) in 70% isolated yield.
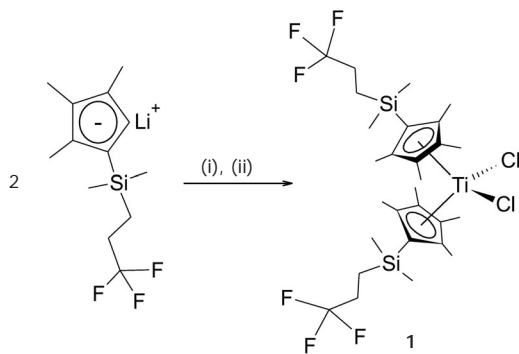

(i) $[TiCl_3(thf)_3]$, THF, 30 h reflux; (ii) AgCl (1 equiv.), workup

SCHEME 1

Compound **1** was identified by EI-MS and ^1H, ^{13}C, and ^{19}F NMR spectra, and paramagnetic compound **2** by EI-MS, ESR, and UV-VIS spectra. The ESR and UV-VIS spectra for **2** are very similar to those of trialkylsilyl-substituted titanocene chlorides $[TiCl(\eta^5-C_5Me_4R)_2]$, where R = $SiMe_3$

(lit.[14]), SiMe$_2$CH$_2$CH$_2$Ph (lit.[7]), and SiMe$_2$CH$_2$CH$_2$CH=CH$_2$ (lit.[12]), and their features fit to other highly methyl-substituted titanocene monochlorides (ESR spectra[16], for ESR and UV-VIS spectra[17]). The EI-MS spectra of **1** and **2** display many similar features. Molecular ions of the both compounds show eliminations of HCl, subsequently 2 molecules of HF or the fragment CH$_2$CH$_2$CF$_3$ while among low-molecular fragments in MS spectra the [SiMe$_2$F]$^+$ and [SiMe$_2$H]$^+$ ions dominate. On the other hand, the low-abundant M$^{\bullet+}$ of **1** eliminates one complete cyclopentadienyl ligand (Cp′), and the formed [Cp′TiCl$_2$]$^+$ ion then eliminates HCl or HF. This fragmentation pathway is absent in the EI-MS spectrum of **2**. The M$^{\bullet+}$ ion of **2** (base peak) gives rise to a fragment ion at *m/z* 280 which can be attributed to [Cp″TiCl]$^+$, where Cp″ has the C$_5$Me$_4$SiMe$_2$F composition. The crystal structures of both the compounds **1** and **2** were determined by X-ray single crystal diffraction analysis (see below).

When the reduction of **1** with one molar equivalent of magnesium in THF was carried out until all the magnesium was consumed (32 h at 60 °C), the workup of the reaction mixture gave surprisingly compound **2**, which was isolated by crystallization, in yield as high as 40%. The ESR spectra of the mother liquor showed still the presence of **2** in addition to other products which were later identified as complex hydrides **3** and **4**. The hydrides were isolated from the reduction of **1** using a 10-fold molar excess of magnesium. This reduction was monitored by measuring ESR spectra, and was stopped by separation of the unreacted magnesium from the reaction solution when the ESR signal of **2** completely disappeared. The workup of the reaction solution afforded the trinuclear Ti–Mg–Ti hydride-bridged complex [Ti{η^5-C$_5$Me$_4$(SiMe$_2$CH$_2$CH$_2$CF$_3$)}$_2$(μ-H)$_2$]$_2$Mg (**3**) as a less soluble in hexane minor product and complex **4** containing the dinuclear hydride-bridged Ti–Mg moiety as the major product (Scheme 2). The yields of com-
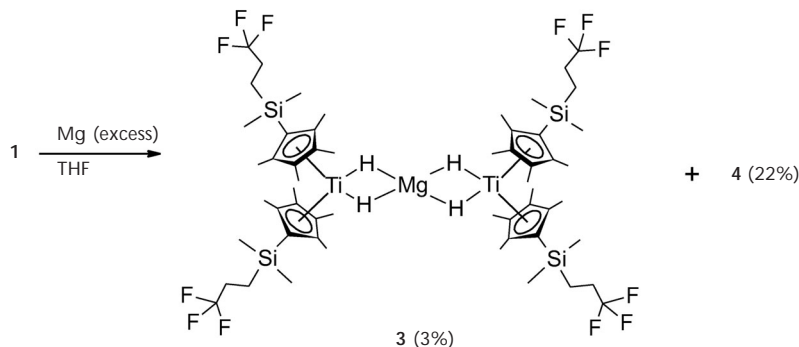
SCHEME 2

pounds **3** and **4** were rather low (ca. 3 and 22%, respectively). This implies that some more soluble products were formed in the extensive reduction of **1**; however, they were reluctant to crystallize out from the mother liquor. The presence of eventually formed titanocene in a mixture of paramagnetic and diamagnetic products in the mother liquor could not be established.

The X-ray crystal structure of **3** was corroborated by ESR spectra in toluene solution and frozen glass. The ESR spectrum of the solution showed a broad single line at $g = 1.990$. When the solution was cooled to –140 °C, a typical ESR spectrum of an electronic triplet state of axial symmetry at the same g-value was obtained in the toluene glass. The value of zero-field splitting $D = 0.01161$ cm^{-1} determined from outer features of the spectrum is smaller than in $[Ti(\eta^5-C_5Me_4Ph)_2(\mu-H)_2]_2Mg$ ($D = 0.01240$ cm^{-1})[18] and in the $[\{(\eta^5-C_5H_{5-n}Me_n)_2Ti(\mu-H)_2\}_2Mg]$ ($n = 3$–5) complexes ($n = 3$, $D = 0.0132$ cm^{-1}; $n = 4$, 0.01327 cm^{-1}; $n = 5$, 0.01217 cm^{-1})[19]. The value of D is inversely proportional to the distance between the titanium(III) atoms bearing d^1 electrons with unpaired spins[20,21] and, provided the crystal structures were known, the Ti–Ti distances calculated from the D values reasonably fitted to the crystallographic d(Ti–Ti) distances[19–21]. For **3**, the smallest value of D corresponds to the crystallographic d(Ti–Ti) distance of 5.919(2) Å (vide infra), which is the longest of all known titanocene complexes of this type. The presence of the hydride bridges was also demonstrated by a broad IR absorption band at 1200 cm^{-1} which was observed in IR spectra of all the so far obtained Ti–Mg–Ti complexes[18,19,21]. The EI-MS spectra of **3** showed the $[Cp'_2Ti – H]^+$ fragment ion as a base peak. A similar fragmentation was observed for $[Ti(\eta^5-C_5Me_4Ph)_2(\mu-H)_2]_2Mg$: the M$^{•+}$ was absent and $[Cp'_2Ti – H]^+$ formed a base peak[18]. On the other hand, the $[\{(\eta^5-C_5H_{5-n}Me_n)_2Ti(\mu-H)_2\}_2Mg]$ ($n = 3$–5) compounds displayed low-abundant M$^{•+}$ peaks and the $[Cp'_2Ti]^+$ fragments as base peaks[19]. The $[Cp'_2Ti – H]^+$ ions of **3** eliminated subsequently 2 HF molecules or the trifluoropropyl fragment with very low efficiency. The $[Cp'Ti]^+$ or $[Cp']^+$ ions were not observed, and the fragments of Cp' (m/z 275) were of lower intensity than in the spectra of **1** or **2**.

With no crystallographic data available for blue powdery **4** the only information on its structure was obtained from its solution ESR spectra. They showed a triplet 1:2:1 at $g = 1.991$ with superhyperfine splitting $a_H = 7.7$ G accompanied by ca. twenty times weaker wings due to coupling of the unpaired electron with ^{47}Ti and ^{49}Ti isotopes. From the low-field wing the coupling constant $a_{Ti} = 6.4$ G was determined. The ESR spectra with similar parameters were first observed by Brintzinger[22] and tentatively ascribed to

species $[Cp_2TiH_2]^-$. Later on, Symons et al.[23] on the basis of ESR indices suggested the presence of alkali metal or magnesium cations in monomeric Ti–metal dihydride complexes. More recently, the crystal structures of some complexes displaying such ESR spectra proved that they form dimers of the type $[Ti(Cp')_2(\mu\text{-}H)_2Mg(OR_2)(\mu\text{-}X)]_2$, where X is a bridging halogen atom (X = Cl or Br) and OR_2 is either diethyl ether[24] or THF [11] (Chart 1, A). In the very similar silyl-substituted titanocene systems $[TiCl_2\{\eta^5\text{-}C_5Me_4(SiMe_3)\}_2]$/ Mg/THF the dimeric hydride complexes were bridged through magnesium–methylene–magnesium three-centric electron-defficient bonds (Chart 1, B), and the magnesium atom further coordinated one THF molecule[6]. The ESR data for **4** are virtually identical with those for B, and it is therefore reasonable to suggest a similar structural arrangement in **4**. Just because the IR spectra of **3** and **4** are nearly identical one can suggest that compound **4** does not coordinate THF. No THF (*m/z* 72) was also found in the first EI-MS scans of **4**. The EI-MS spectra of **4** showed similarly to **3** the fragment ion $[Cp'_2Ti - H]^+$ as a base peak, no molecular ion, and its fragmentation pattern was undistinguishable from that of **3**.
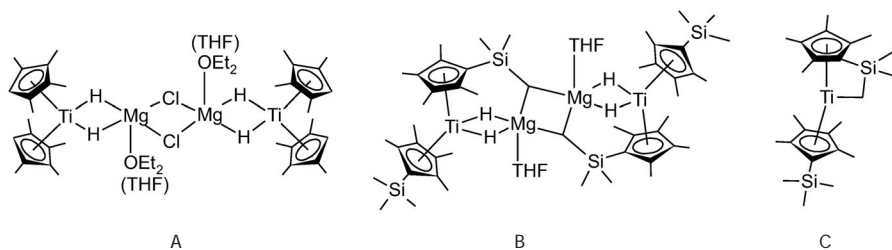

Chart 1

The reduction of **1** with excess magnesium in the presence of bis(trimethylsilyl)ethyne (BTMSE) did not afford the titanocene–BTMSE complex $[Ti(\eta^2\text{-}btmse)\{\eta^5\text{-}C_5Me_4(SiMe_2CH_2CH_2CF_3)\}_2]$ similarly to analogous reduction of $[TiCl_2\{\eta^5\text{-}C_5Me_4(SiMe_3)\}_2]$ at ambient temperature[6]. Instead, the single tucked-in complex $[Ti\{\eta^5\text{-}C_5Me_4(SiMe_2CH_2CH_2CF_3)\}\{\eta^5\text{:}\eta^1\text{-}C_5Me_3(CH_2)\text{-}(SiMe_2CH_2CH_2CF_3)\}]$ (**5**) was obtained as the only isolated product in 27% yield (Scheme 3). Its structure as a single tucked-in titanocene possessing the methylene group in the vicinity of the silicon-bearing carbon atom was determined by X-ray diffraction analysis (see below). The structure is fully compatible with the IR spectrum which shows an absorption band at 3047 cm^{-1} which is typical for the presence of *exo*-methylene group in such compounds[25]. Missing from the spectra is a broad absorption band centered at 1200 cm^{-1} in **3** and **4**. The EI-MS spectra showed the molecular ion as a base peak, the low abundant $[M - HF]^+$ and $[M - 2 HF]^+$ fragments and low-

molecular-weight fragments of the ligand in intensities closely resembling those found for **3** or **4**. This allows us to consider that the $[Cp'_2Ti - H]^+$ ions in EI-MS spectra of **3** or **4** are generated by a subsequent ionization of **5** liberated by their thermolysis in a direct inlet. Like the parent single tucked-in $[Ti(\eta^5\text{-}C_5Me_5)\{\eta^5\text{:}\eta^1\text{-}C_5Me_4(CH_2)\}]$ complex[26], compound **5** is paramagnetic and displays very similar highly anisotropic ESR features. It is of interest that the reduction of $[TiCl_2\{\eta^5\text{-}C_5Me_4(SiMe_3)\}_2]$ under similar conditions affords the titanocene derivative with intramolecular bridge Si–CH_2–Ti (see Chart 1, C) in a high yield[6]. The preferred activation of the trimethylsilyl group was also observed in zirconocene compounds[27]. The reason for this variation in the reaction pathway is to be tentatively sought in different involvement of magnesium, compound **5** being formed with little aid of Mg. The formation of **5** probably proceeds via intramolecular abstraction of hydrogen by Ti(II) followed by its transfer to BTMSE which acts as a hydrogen acceptor. Such process is known from the formation of the double tucked-in titanocene $[Ti(\eta^5\text{-}C_5Me_5)\{\eta^3\text{:}\eta^4\text{-}C_5Me_3\text{-}(CH_2)_2\}]$ by thermolysis of $[Ti(\eta^2\text{-btmse})(\eta^5\text{-}C_5Me_5)_2]$ (lit.[9]). Thus, the isolation of **5** indicates at least the formation of a Ti(II) titanocene intermediate. Since the yield of **5** in this experiment was rather low the presence of other reduction products has to be anticipated. However, none of them could be isolated from the mother liquor due to their very high solubility.

5 (27%)   6 (100%)
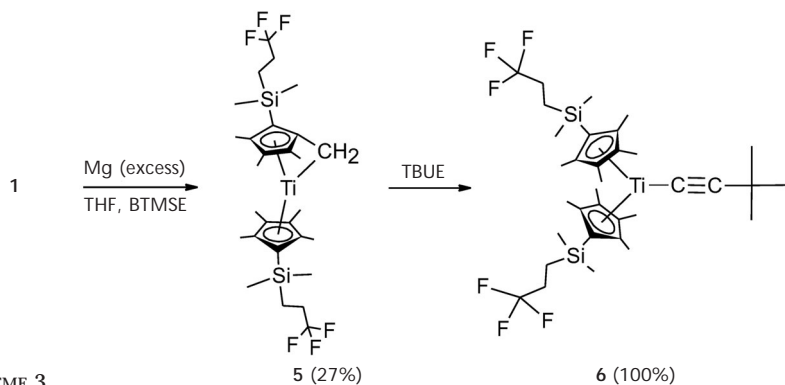
The Reaction of 5 with tert-Butylethyne

Since compound **5** is the first case of a single tucked-in complex formed from silyl-substituted tetramethylcyclopentadienyl ligands its reactivity is the matter of interest. It reacted instantly in hexane with *tert*-butylethyne (TBUE) to give titanocene acetylide $[Ti(\eta^1\text{-}C\equiv CCMe_3)\{\eta^5\text{-}C_5Me_4\text{-}(SiMe_2CH_2CH_2CF_3)\}_2]$ (**6**) as the only isolated product. In this respect it

behaved similarly to the parent tucked-in complex [Ti(η^5-C$_5$Me$_5$){η^5:η^1-C$_5$Me$_4$(CH$_2$)}] whose σ-Ti–C bond is highly reactive[28]. The structure of **6** was deduced from EI-MS and ESR spectra. The mass spectra showed the molecular peak, the fragment ion arising from the loss of TBUE as a base peak, and fragment ions appropriate for the cyclopentadienyl ligand as observed in the spectra of **3**–**5**. The loss of TBUE was observed in EI-MS spectra of all the three titanocene *tert*-butylacetylides known[18,29,30]. The ESR spectrum giving a broad signal at low *g*-factor and very anisotropic spectrum in toluene glass is very similar to titanocene acetylide spectra of [Ti(η^1-C≡CCMe$_3$)(η^5-C$_5$Me$_4$Ph)$_2$] (lit.[18]) and *ansa*-[Ti(III)(η^1-C≡CCMe$_3$){η^5:η^5-C$_5$Me$_4$SiMe$_2$CH=CHCH$_2$CH$_2$SiMe$_2$C$_5$Me$_4$}] (lit.[29]). Likewise, the electronic absorption bands of $1a_1 \rightarrow 2a_1$ and $1a_1 \rightarrow b_1$ transitions and ν(C≡C) vibration (2070 cm^{-1}) also closely agree with data for the reference compounds[18,29]. The structure of **6** was unequivocally confirmed by X-ray diffraction analysis (vide infra).

Crystal Structures of Compounds 1, 2, and 6

The molecules of compounds **1**, **2**, and **6** are unsymmetric although situated in monoclinic unit cells. Compound **2** contains one molecule of THF of crystallization per one molecule of the complex. The unit cell of **6** contains 2 independent molecules which do not differ within three-fold esd's; therefore the drawing and data for molecule 1 of **6** will be given only. The PLATON representations of compounds **1**, **2**, and **6** are depicted in Figs 1, 2,
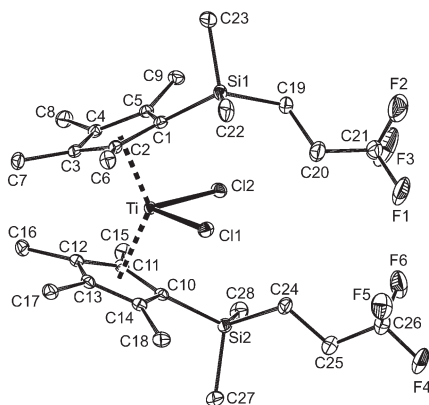

Fig. 1
PLATON drawing of compound **1** at the 30% probability level with atom labeling scheme. Hydrogens are omitted for clarity
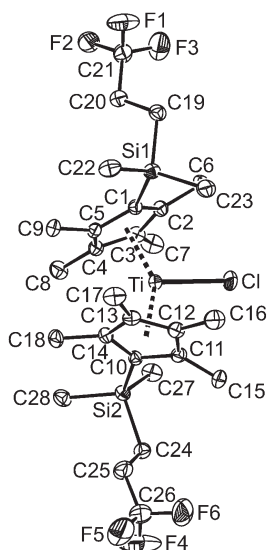
FIG. 2
PLATON drawing of compound **2** at the 30% probability level with atom labeling scheme. Hydrogens are omitted for clarity
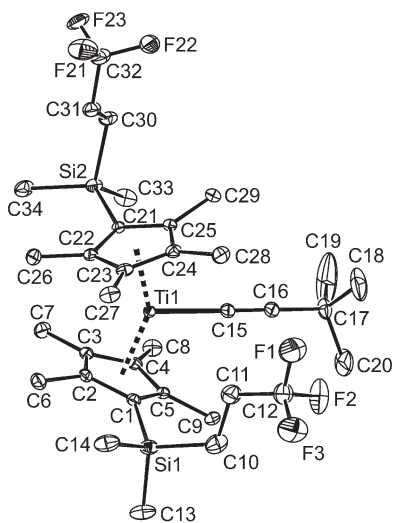

FIG. 3
PLATON drawing of compound **6** at the 30% probability level with atom labeling scheme. Hydrogens are omitted for clarity

and 3, respectively, and essential common geometric parameters are listed in Table I. The differences in the structures of titanocene moieties follow from the pseudotetrahedral coordination of the central titanium atom in **1** and the trigonal coordination in **2** and **6**. A higher coordination number of **1** is reflected in slightly longer Ti–Cg distances with respect to those of **2** and **6**. Cg denotes a centroid (in detail see note to Table I). Some steric repulsion between the chlorine atoms and cyclopentadienyl rings in **1** induces a smaller Cg1–Ti–Cg2 angle (larger φ) than in **2** and **6** (Table I). Compared with the crystal structure of $[TiCl_2\{\eta^5\text{-}C_5Me_4(SiMe_3)\}_2]$ (lit.[14]) the Ti–Cg distances are virtually the same, the bite angle φ is larger (42.8(1)° vs 39.8(2)°), the Cl1–Ti–Cl2 angle is larger (95.35(4)° vs 89.5(1)°), and the Ti–Cl bonds are shorter (av. 2.352(1) Å vs 2.365(1) Å). A comparison of the structure of **2** with that of $[TiCl\{\eta^5\text{-}C_5Me_4(SiMe_3)\}_2]$ (lit.[14]) gives no difference in angles Cg1–Ti–Cg2 and φ but somewhat longer Ti–Cl bond length (2.354(2) Å vs 2.340(1) Å).

The cyclopentadienyl rings in all the compounds are staggered, with methyl groups in hinge positions declined from the cyclopentadienyl ring plane away from the metal more than the other methyl groups of the

TABLE I
Selected bond lengths (in Å) and bond angles (in °) for **1**, **2**, and **6**[a]

	1	**2**	**6**
Bond dinstances			
Ti–Cg1 [b]	2.125(1)	2.073(3)	2.065(1)
Ti–Cg2 [b]	2.127(1)	2.069(3)	2.070(1)
Ti–Cl1	2.357(1)	2.354(2)	–
Ti–Cl2	2.347(1)	–	2.105(2) [c]
Bond angles			
Cg1–Ti–Cg2	134.91(5)	144.1(1)	147.56(4)
Cl1–Ti–Cl2	95.35(4)	–	–
φ [d]	42.8(1)	35.7(2)	33.0(1)
τ [e]	26.3(2)	41.4(4)	35.6(2)

[a] Molecule 1 of the two independent molecules of **6**. [b] Cg1 denotes the centroid of the C(1–5) cyclopentadienyl ring atoms; Cg2 is the centroid of the other cyclopentadienyl ring. [c] The bond length Ti–C15. [d] Dihedral angle between the least-squares planes of cyclopentadienyl rings. [e] Dihedral angle between the planes defined by atoms Ti,C1,Si1 and Ti,C10,Si2 for **1** and **2**, or Ti,C21,Si2 for molecule 1 of **6**.

ligand. The orientation of dimethyl(3,3,3-trifluoropropyl)silyl groups seems to be controlled by crystal packing requirements. Whereas in **2** and **6** these groups are placed on opposite sides with respect to the Cg1,Ti,Cg2 plane in **1**, they are directed roughly in the direction of Ti–Cl vectors. In the molecular structure of **1** they fill the space around the chlorine atoms (Fig. 1), and in **2**, they are directed in opposite directions to reach the maximum distance between their trifluoromethyl groups. Their interconnection is roughly in the Cg1,Ti,Cg2 plane and perpendicular to the Ti–Cl vector (Fig. 2). In **6**, molecule 2 has the silyl substituents directed like in **2** and molecule 1 has one group directed like in molecule 2 and the other roughly perpendicularly to the first one filling the space aside the acetylide group (Fig. 3). The trifluoromethyl group geometry is rather regular with C–F bond lengths in the range 1.295(4)–1.345(4) Å and angles F–C–F spanning extremes 102.6(4)–107.1(3)°. The acetylide group geometry (molecule 1) – Ti–C15 2.105(2) Å, C15–C16 1.215(3) Å, C16–C17 1.480(3) Å, Ti–C15–C16 175.7(2)°, and C15–C16–C17 177.6(3)° – does not differ from parameters of this group in $[Ti(\eta^1\text{-C}\equiv\text{CCMe}_3)(\eta^5\text{-C}_5\text{Me}_4\text{Ph})_2]$ (lit.[18]) and $[Ti(\eta^1\text{-C}\equiv\text{CCMe}_3)(\eta^5\text{-C}_5\text{Me}_5)_2]$ (lit.[30]).

Crystal Structure of Compound **3**

The monoclinic unit cell of **3** contains 4 equivalent molecules of compound **3** and 2 molecules of hexane of crystallization which are partially disordered. The solvate molecules are loosely bound; the crystals were disintegrating into a pale blue powder during their filling into Lindemann glass capillaries under nitrogen atmosphere. The molecules of hexane and magnesium atoms of complex **3** lie in special positions on a two-fold axis. This axis is perpendicular to the Ti–Ti′ vector and intersects the planes defined by Mg, H1, H2 and Mg, H1′, H2′ atoms under the same angle, close to 45°. Because of the imposed symmetry only one half of the molecule is crystallographically independent (Fig. 4). Important geometric parameters are listed in Table II. The titanium atom is pseudotetrahedrally coordinated and the magnesium is tetrahedrally coordinated by four bridging hydrogen atoms. The titanocene moiety is very similar to that of the monochloride **2** both by the magnitude of the bite angle and by the arrangement of the dimethyl(3,3,3-trifuoropropyl)silyl groups. The hydrogen bridges between the titanium and magnesium atoms form almost a perfect plane and do not impose any steric strain on the cyclopentadienyl ligands. The both bridging planes are almost perpendicular (88.4(4)°). The Ti–H bonds are equal within esd's and are considerably longer than the Mg–H bonds (av. 1.97(1) Å vs

1.87(1) Å). This is remarkable in comparison with the structures of the $[\{(\eta^5\text{-}C_5H_{5-n}Me_n)_2Ti(\mu\text{-}H)_2\}_2Mg]$ (n = 3–5) complexes where for n = 5 the Ti–H bonds were much shorter than the Mg–H bonds (av. 1.70 Å vs 1.90 Å), and for n = 4 and n = 3 both types of the bonds were roughly equal but for n = 3 they were longer (av. 1.95(5) Å) than for n = 4 (av. 1.78(4) Å)[19b]. A comparison of Ti–H bond lengths for the persubstituted complexes indicates that the silyl group in **3** is responsible for weakening of Ti–H bonds through its electronic rather than steric effect. This would be in line with the opinions that the $SiMe_3$ group is less electron-donating than the Me group[8,31].

Crystal Structure of Compound 5

The molecule of **5** is symmetric with respect to a two-fold axis which bisects the Cg1–Ti–Cg′ angle. The molecule is disordered because the methylene group that is linked to the metal is equally abundant at the both cyclopentadienyl ligands. The PLATON drawing of **5** (Fig. 5) shows the carbon atom C6A of unreacted methyl group and the carbon atom C6B′ of the
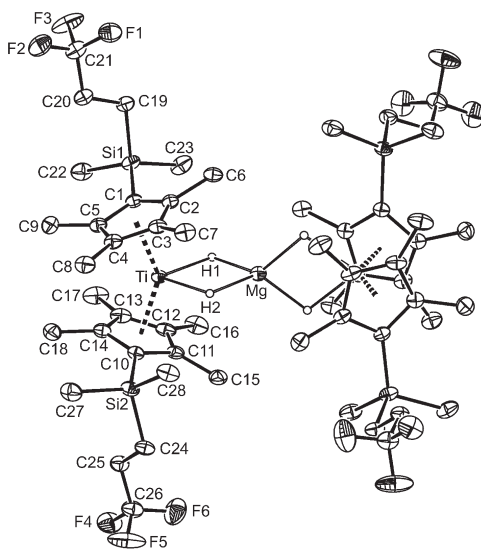

Fig. 4

Molecular structure of compound **3** (30% probability ellipsoids) with atom labeling scheme. Hydrogen atoms except bridging hydrides are omitted; the prime-labeled atoms are generated by symmetry operation ($-x$, y, $1/2 - z$)

methylene group; both the carbon atoms were refined with isotropic thermal motion parameters. The structure of **5** is only the second crystal structure of a single tucked-in complex and the precision of the diffraction data is better than that of the data reported for $[Ti(\eta^5-C_5Me_5)\{\eta^5:\eta^1-C_5Me_4(CH_2)\}]$ **(7)**[26a]. Hence, the geometric parameters of **5** are listed in Table III in more detail. The cyclopentadienyl rings are staggered, and canted away by the Ti–C6B–C2 bridges. Due to this canting, the Cg–Ti–Cg′ angle is equal to 155.7(1)° and the bite angle ϕ to 13.5(1)°. The difference of the sum of these angles from 180° can be ascribed to slippage of the cyclopetandienyl ring, i.e., to a shift of the Cg point from the position where the vector perpendicular to the least-squares cyclopentadienyl plane laid from the Ti atom

TABLE II
Selected bond lengths (in Å) and bond angles (in °) for **3**

Bond distances			
Ti–Cg1 [a]	2.094(2)	Ti–Cg2 [a]	2.097(2)
Ti–H1	1.98(1)	Ti–H2	1.96(1)
Mg–H1	1.87(1)	Mg–H2	1.88(1)
C1–Si1	1.868(4)	C10–Si2	1.871(4)
Si1–C19	1.879(5)	Si2–C24	1.886(5)
C19–C20	1.531(7)	C24–C25	1.527(6)
C20–C21	1.480(7)	C25–C26	1.478(7)
Ti–C	2.382–2.451(4)	C_{Cp}–C_{Cp}	1.398–1.441(6)
C–C_{Me}	1.496–1.514(7)	C–F	1.314–1.338(7)
Ti–Ti′ [b]	5.919(2) [c]		
Bond angles			
Cg–Ti–Cg′ [b]	143.77(9)	Ti–Mg–Ti′ [b,c]	179.14(8)
H1–Ti–H2	76.9(5)	H1–Mg–H2	81.8(5)
Ti–H1–Mg	100.3(5)	Ti–H2–Mg	100.9(5)
H1–Mg–H1′ [b]	124.8(7)	H2–Mg–H2 [b]	123.1(7)
H1–Mg–H2′ [b]	125.7(5)	ϕ [d]	35.8(2)
τ [e]	40.1(3)		

[a] Cg1 denotes the centroid of the C(1–5) cyclopentadienyl ring atoms; Cg2 is the centroid of the C(10–14) cyclopentadienyl ring. [b] Prime-labeled equivalent positions are generated by the symmetry operation (–x, y, 1/2 – z). [c] Nonbonding distance or angle. [d] Dihedral angle between the least-squares cyclopentadienyl planes. [e] Dihedral angle between the planes defined by atoms Ti,C1,Si1 and Ti,C10,Si2 for **3**.

Selected bond lengths (in Å) and bond angles (in °) for **5**

Bond distances			
Ti–C1	2.278(3)	Ti–C2	2.228(3)
Ti–C3	2.342(3)	Ti–C4	2.413(3)
Ti–C5	2.377(3)	Ti–C6B	2.330(8)
C1–C2	1.447(5)	C2–C3	1.423(5)
C3–C4	1.415(5)	C4–C5	1.420(5)
C1–C5	1.433(5)	C2–C6A	1.525(9)
C2–C6B	1.471(8)	Ti–Cg [a]	1.987(1)
C1–Si	1.876(3)	C10–Si	1.889(4)
C–C$_{Me}$	1.500–1.505(5)		

Bond angles			
Cg–Ti–Cg′ [b]	155.7(1)	Cg–Ti–C6B	70.4(1)
Ti–C6B–C2	67.4(3)	φ [c]	13.5(1)

[a] Cg denotes the centroid of the cyclopentadienyl ring. [b] Prime-labeled equivalent positions are generated by the symmetry operation (–x, y, 1/2 – z). [c] Dihedral angle between the least-squares cyclopentadienyl planes.
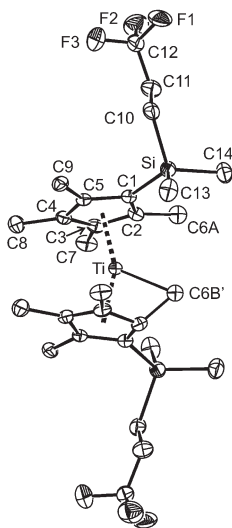

F$_{IG}$. 5
Molecular structure of compound **5** (30% probability ellipsoids) with atom labeling scheme. Hydrogen atoms are omitted for clarity; the prime-labeled atoms are generated by symmetry operation (–x, y, 1/2 – z)

passes the ring plane. As a result, the distance of Ti atom from the plane (1.978(1) Å) is shorter than the Ti–Cg distance 1.987(1) Å (Table III). The geometry at the tucked-in methylene group resembles that of the parent complex **7** (lit.[26a]), however, the C2–C6B bond length 1.471(8) Å is longer than 1.437(14) Å in **7** and the Ti–C6B–C2 angle 67.4(3)° is larger than 63.9(5)° in **7**. The silicon atoms are declined from the least-squares cyclopentadienyl plane by about 0.195(5) Å farther away from titanium, and the 3,3,3-trifluoropropyl group is directed above the cyclopentadienyl ligands. The silicon and carbon chain lie close to the plane: the torsion angle Si1,C10,C11, and C12 is 176.7(3)° (see Fig. 6).

Conclusions

The reduction of novel titanocene dichloride **1** bearing pendant dimethyl-(3,3,3-trifluoropropyl)silyl groups with magnesium in THF revealed that abstraction of chlorine with magnesium is accompanied by concurrent hydrogen abstraction reactions also involving magnesium. The isolation of compounds **3** and **4** gives evidence of these processes; however, the hydrogen source for these minor products remains unknown. In this system the hydrogen can come from the cyclopentadienyl ligands or from THF; however, gas chromatography analysis of volatiles evaporated in vacuum from the reaction mixture and trapped at liquid nitrogen temperature did not reveal any impurity, and no further titanium products could be isolated due to their high solubility in hexane. In none of the previous studies any evidence of such processes was obtained either[6,11,13,18].
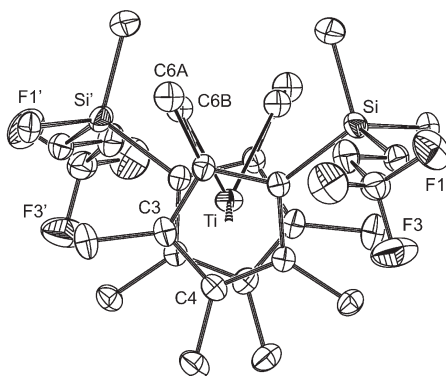

FIG. 6
View of **5** in the Cg–Cg′ direction

In the presence of BTMSE, the formation of **5** was not accompanied by products **3** and **4**, and though the alkene or alkane arising from hydrogenation of BTMSE was not detected by GC-MS of a sample of BTMSE distilled from the reaction mixture, the hydrogen transfer from a transient titanocene to BTMSE can rationalize the experimental result. All the isolated products contained the unchanged trifluoromethyl group in spite of the fact that the length of the pendant dimethyl(3,3,3-trifluoropropyl)silyl group is suitable for an interaction of the Ti(II) center with the C–F bonds. At least, comparable in length pendant allyldimethylsilyl[32] or (but-3-enyl)-dimethylsilyl[12] groups reacted by their double bonds with transiently formed titanocenes. In the presence of magnesium in excess, defluorination of the 3,3,3-trifluoropropyl group can be considered, with the formation of Mg–F moieties and unsaturated C–C bonds which would then react with the Ti(II) center. The missing evidence of the formation of such products is either due to their presence in untreatable mother liquors or their absence due to mild conditions.

EXPERIMENTAL

General Comments and Methods

Synthesis of titanocene dichloride **1** was carried out under argon atmosphere but the product was worked up and handled in air. The reductions of **1** and all subsequent manipulations with solutions of the reduction products were performed on a vacuum line in all-glass devices equipped with magnetically breakable seals. A combined device equipped with a pair of quartz cuvettes (10.0 mm and 1.0 mm, Hellma) and a quartz tube was used for UV-VIS and ESR measurements. Crystals for EI-MS measurements and melting point determinations were placed in glass capillaries in a glovebox Labmaster 130 (mBraun) under purified nitrogen (concentrations of oxygen and water were lower than 2.0 ppm). ^{1}H (399.95 MHz), ^{13}C (100.58 MHz), and ^{19}F (376.3 MHz) NMR spectra were recorded on a Varian Unity Inova 400 spectrometer in C_6D_6 solutions at 25 °C. Chemical shifts (δ, ppm) are given relative to the solvent signal (δ_H 7.15, δ_C 128.0) or to external neat $CFCl_3$ (δ_F 0), coupling constants (J) are given in Hz. EI-MS spectra were obtained on a VG-7070E mass spectrometer at 70 eV. Crystalline samples from sealed capillaries were inserted into the direct inlet under argon. The spectra are represented by the peaks of relative abundances higher than 6% and by important peaks of lower intensity. EPR spectra were recorded on an ERS-220 spectrometer (Center for Production of Scientific Instruments, Academy of Sciences of GDR, Berlin, Germany) operated by a CU-1 unit (Magnettech, Berlin, Germany) in the X-band. g-Values were determined by using an Mn^{2+} standard at g = 1.9860 (M_I = –1/2 line). A variable temperature unit STT-3 was used for measurements in the range from –140 to +25 °C. UV-VIS measurements were performed on a Varian Cary 17 D spectrometer in the range 340–2000 nm. IR spectra (ν, cm^{-1}) were recorded in an air-protecting cuvette on a Nicolet Avatar FT IR spectrometer in the range 400–4000 cm^{-1}. Samples in KBr pellets were prepared in a glovebox Labmaster 130 (mBraun).

As low-valent titanium complexes are extremely sensitive to air and moisture, classical elemental analyses were not carried out. The EI-MS samples of **1**, **2**, **5**, and **6** were completely evaporated without changing the fragmentation pattern; this proves the uniformity of the compounds. Furthermore, crystal structures of **1**, **2**, **3**, **5**, and **6** were determined by X-ray diffraction analysis.

Chemicals

Solvents THF, hexane, and toluene were dried by refluxing over $LiAlH_4$ and stored as solutions of dimeric titanocene $[(\mu-\eta^5:\eta^5-C_{10}H_8)(\mu-H)_2\{Ti(\eta^5-C_5H_5)\}_2]$ (lit.[33]). Butyllithium (BuLi) in hexanes, magnesium turnings (Aldrich, purum for Grignard reactions) and chlorodimethyl-(3,3,3-trifluoropropyl)silane (Fluorochem Ltd.) were used as obtained. 1,2,3,4-Tetramethyl-cyclopentadiene (Aldrich) was distilled in vacuum before use. Bis(trimethylsilyl)ethyne (Aldrich) was degassed, stored as a solution of dimeric titanocene for 4 h, and finally sealed in ampoules by distillation on a vacuum line.

Synthesis of 1,2,3,4-Tetramethyl-5-[(3,3,3-trifluoropropyl)dimethylsilyl]-cyclopenta-1,3-diene and Titanocene Dichloride (**1**)

Butyllithium in hexane (2.5 M solution, 41.0 ml) was added to 1,2,3,4-tetramethylcyclo-pentadiene (12.2 g, 100 mol) in dry THF (200 ml), and the obtained yellowish suspension was stirred until it turned white (after 2 h). Then, chlorodimethyl(3,3,3-trifluoropropyl)-silane (20.0 g, 105 mmol) was added with syringe, and the mixture was refluxed under stirring for 8 h. Solvents were partially distilled off to reduce the volume to ca. 40 ml, and hexane (20 ml) was added. The solution was decanted from a white precipitate of LiCl, the solvent was evaporated under vacuum and the product distilled under the vacuum of oil rotary pump. The nearly colorless fraction boiling at 70–80 °C was collected. Yield 22.2 g (80%).

$HC_5Me_4(SiMe_2CH_2CH_2CF_3)$. ^1H NMR (C_6D_6): –0.18 (s, 6 H, $SiMe_2$); 0.50–0.56 (m, 2 H, $SiCH_2$); ca. 1.67–1.80 (m, 2 H, CH_2CF_3; obscured by strong methyl resonances); 1.74, 1.79 (2 × s, 6 H, C_5Me_4); 2.54 (s, 1 H, $C_5Me_4\mathbf{H}$). $^{13}C\{^1H\}$ NMR (C_6D_6): –3.4 ($SiMe_2$); 6.0 ($SiCH_2$); 11.1, 14.5 ($C_5\mathbf{Me_4}$); 29.1 (q, $^2J_{FC}$ = 29, $\mathbf{C}H_2CF_3$); 53.9 (C_5Me_4, $\mathbf{C}H$); 128.4 (q, $^1J_{FC}$ = 276, CF_3); 132.6, 136.2 (C_5Me_4, $\mathbf{C}_{ipso}$). IR (neat): 2966 (s), 2917 (vs), 2861 (s), 2741 (vw), 1634 (w), 1446 (s), 1375 (m), 1363 (s), 1315 (m), 1263 (vs), 1212 (vs), 1125 (vs), 1068 (s), 1029 (m), 986 (m), 953 (w), 899 (s), 841 (s), 822 (m), 773 (m), 726 (w), 697 (vw), 667 (vw), 646 (vw), 618 (m), 549 (w), 486 (m).

Titanocene dichloride $[TiCl_2\{\eta^5-C_5Me_4(SiMe_2CH_2CH_2CF_3)\}_2]$ (**1**) was prepared by reacting $[TiCl_3(thf)_3]$, which was generated in situ by adding BuLi in hexanes (22.5 ml of 1.6 M solution, 36.0 mmol) to $TiCl_4$ (4.0 ml, 36.0 mmol) in THF (50 ml) followed by short reflux, with lithium cyclopentadienide obtained by reacting BuLi (30 ml of 2.5 M solution in hexanes, 75.0 mmol) with the above cyclopentadiene (20.1 g, 73.0 mmol) in THF (500 ml) at room temperature for 24 h under stirring. After refluxing this mixture for 30 h and subsequent stirring with AgCl (5.16 g, 36.0 mmol) at 40 °C for 5 h, the product was worked up as described for $[TiCl_2\{\eta^5-C_5Me_4(SiMe_3)\}_2]$ (lit.[14]). Yield of dark red crystals of **1** was 8.3 g (34.5%).

Compound **1**. ^1H NMR (C_6D_6): 0.37 (s, 6 H, $SiMe_2$); 0.98–1.04 (m, CH_2Si); 1.55 (s, 6 H, C_5Me_4); 1.79–1.92 (m, 2 H, CH_2CF_3); 2.00 (s, 6 H, C_5Me_4). $^{13}C\{^1H\}$ NMR (C_6D_6): 0.0 ($SiMe_2$);

9.3 (q, $^3J_{CF} \approx 1.5$, CH$_2$Si); 11.9, 16.8 (C$_5$**Me**$_4$H); 29.2 (q, $^2J_{CF} = 29$, **C**H$_2$CF$_3$); 127.3 (2 C, C$_5$Me$_4$, **C**$_{ipso}$); 128.6 (q, $^1J_{CF} = 277$, CF$_3$); 134.0 (1 C); 138.4 (2 C; C$_5$Me$_4$, **C**$_{ipso}$). ^{19}F NMR (C$_6$D$_6$): –68.3 (t, $^3J_{FH} = 10$). EI-MS (150 °C), m/z (relative abundance): 668 (M$^{\bullet+}$; 5), 653 ([M – Me]$^+$; 5), 636 (9), 635 (21), 634 (18), 633 ([M – Cl]$^+$; 38), 613 ([M – Cl – HF]$^+$; 11), 597 ([M – Cl – HCl]$^+$; 14), 573 (13), 571 ([M – CH$_2$CH$_2$CF$_3$]$^+$; 16), 395 (8), 393 ([Cp′TiCl$_2$]$^+$; 13), 377 (18), 376 (18), 375 (71), 374 (32), 373 ([Cp′TiCl$_2$ – HF]$^+$; 100), 372 (13), 371 (11), 359 (19), 358 (13), 357 ([Cp′TiCl$_2$ – HCl]$^+$; 39), 301 (18), 300 (14), 299 (36), 283 (10), 282 (26), 275 ([Cp′]$^+$; 15), 256 ([Cp′ – HF]$^+$; 30), 197 (22), 179 (31), 178 (31), 177 ([Cp′ – CH$_2$CH$_2$CF$_3$]$^+$; 22), 164 (14), 160 (8), 136 (12), 135 (41), 133 (27), 121 (9), 120 (8), 119 (32), 105 (16), 91 (8), 81 (16), 77 ([SiMe$_2$F]$^+$; 58), 59 ([SiMe$_2$H]$^+$; 51), 58 (14), 56 (9). IR (KBr): 2999 (sh), 2983 (sh), 2965 (sh), 2954 (s), 2899 (vs), 2728 (vw), 1476 (m), 1445 (m), 1423 (w), 1391 (w), 1378 (m), 1362 (s), 1343 (m), 1315 (m), 1265 (vs), 1246 (s), 1209 (vs), 1113 (vs), 1069 (s), 1023 (m), 951 (vw), 902 (s), 844 (vs), 813 (m), 770 (s), 736 (w), 687 (w), 623 (w), 549 (vw), 425 (m), 416 (m).

Synthesis of [TiCl{η^5-C$_5$Me$_4$(SiMe$_2$CH$_2$CH$_2$CF$_3$)}$_2$] (**2**)

[TiCl$_2${η^5-C$_5$Me$_4$(SiMe$_2$CH$_2$CH$_2$CF$_3$)}$_2$] (**1**) (0.334 g, 0.50 mmol) and Mg turnings (0.006 g, 0.25 mmol) in an ampule were degassed and THF (15 ml) was distilled in on a vacuum line. After stirring at 60 °C for 11 h the metallic magnesium disappeared. THF was distilled off under vacuum, and the residue was extracted with hexane (20 ml). The obtained solution was reduced to 10 ml, and then left standing overnight in a refrigerator. A brownish green solution was separated from a white precipitate on ampule walls. The volume of the solution was further reduced by evaporation in vacuum to 5 ml, and then it was cooled in a freezer to –18 °C. A crop of blue crystals was obtained, which were identified by X-ray diffraction analysis to be [TiCl{η^5-C$_5$Me$_4$(SiMe$_2$CH$_2$CH$_2$CF$_3$)}$_2$] (**2**). Yield 0.22 g (70%).

Compound **2**. M.p. 96 °C. EI-MS (120 °C), m/z (relative abundance): 637 (14), 636 (31), 635 (77), 634 (71), 633 (M$^{\bullet+}$; 100), 632 (20), 631 (14), 618 (12), 617 ([M – CH$_4$]$^+$; 17), 616 (7), 615 (11), 614 (9), 613 ([M – HF]$^+$; 17), 599 (8), 598 (15), 597 ([M – HCl]$^+$; 30), 577 ([M – HCl – HF]$^+$; 9), 536 ([M – CH$_2$CH$_2$CF$_3$]$^+$; 10), 283 (8), 282 (13), 281 (11), 280 ([(C$_5$Me$_4$SiMe$_2$F)TiCl]$^+$; 22), 279 (11), 237 ([C$_5$Me$_4$SiMe$_2$CH$_2$CH=CHF]$^+$; 16), 217 ([C$_5$Me$_4$SiMe$_2$CH=C=CH$_2$]$^+$; 16), 201 (16), 179 (18), 178 (16), 177 (25), 160 (12), 133 (11), 119 (20), 105 (15), 81 (12), 77 ([SiMe$_2$F]$^+$; 79), 59 ([SiMe$_2$H]$^+$; 64). IR (KBr): 2961 (s), 2941 (m), 2911 (s), 1479 (w), 1446 (m), 1380 (m), 1363 (m), 1330 (s), 1263 (vs), 1211 (vs), 1198 (s), 1119 (vs), 1065 (s), 1026 (m), 898 (vs), 839 (s), 812 (m), 777 (m), 749 (vw), 686 (w), 622 (w), 574 (vw), 550 (w), 425 (m), 417 (m). ESR (hexane, 22 °C): $g = 1.952$, $\Delta H = 16.0$ G; (toluene, –140 °C): $g_1 = 2.000$, $g_2 = 1.981$, $g_3 = 1.875$, $g_{av} = 1.952$. UV-VIS (hexane, 22 °C): 365 (sh) >> 560 > 665 (sh).

Reduction of **1** with Magnesium at Molar Ratio Ti/Mg = 1:1

Compound **1** (0.334 g, 0.50 mmol) and Mg turnings (0.012 g, 0.50 mmol) were mixed with THF (15 ml) and reacted at 60 °C until Mg disappeared (after ca. 40 h). The dirty green solution was evaporated in vacuum and the residue was extracted with hexane (20 ml). The obtained solution was reduced to about a half, and then left standing overnight in a refrigerator. A clear turquoise solution was separated from a white precipitate on ampule walls. After reducing its volume to 5 ml the solution was cooled in a freezer. A crop of blue crystals was

obtained, which were identified by EI-MS, ESR, and UV-VIS spectra to be [TiCl{η^5-C$_5$Me$_4$-(SiMe$_2$CH$_2$CH$_2$CF$_3$)}$_2$] (**2**). Yield 0.13 g (40%). Attempted crystallization of the green mother liquor gave no defined product.

Reduction of **1** with Excess Magnesium

The reduction of **1** (0.67 g, 1.0 mmol) in THF was performed as above with magnesium in excess (0.24 g, 10 mmol). The course of the reduction was followed by ESR spectroscopy using an ESR sample tube attached to the ampule. The reaction was stopped by separation of the solution from excess magnesium when ESR signal due to **2** was no longer detectable. THF was distilled back onto magnesium, and the solid residue was extracted with hexane. The extract was concentrated and cooled to –5 °C overnight. A clear dirty blue solution was separated from a white precipitate of MgCl$_2$, concentrated to 5 ml, and cooled with dry ice overnight. A blue solid was separated from a brownish mother liquor, washed with a condensing vapor of hexane, and finally dissolved in hexane (15 ml; when separated from the mother liquor, the solid was much less soluble in hexane). After cooling to –5 °C for several days, fine pale blue crystals (ca. 20 mg, 0.016 mmol) crystallized out, and were separated. They were used for X-ray single-crystal diffraction analysis which revealed that the compound is a hexane solvate of trinuclear complex Mg[(μ-H)$_2$Ti{η^5-C$_5$Me$_4$(SiMe$_2$CH$_2$CH$_2$CF$_3$)}$_2$]$_2$ (**3**). The hexane of crystallization is held very loosely because the crystals decomposed already during their filling into Lidemann glass capillaries in a glovebox. The yield of **3** after evaporation of hexane was 20 mg (3.2% relative to **1**). The volume of the mother liquor was reduced to ca. 5 ml and cooled to –18 °C to afford a blue powdery solid (ca. 60 mg). Attempts to obtain a crystalline material suitable for X-ray diffraction investigation failed and thus the nature of the product as a dinuclear Ti–Mg hydride complex **4** was established from solution ESR spectra.

Compound **3**. EI-MS (230 °C), *m/z* (relative abundance): 600 (8), 599 (26), 598 (51), 597 ([Cp$'_2$Ti – H]$^+$; 100), 596 (16), 595 (10), 578 (7), 577 ([Cp$'_2$Ti – H – HF]$^+$; 13), 557 ([Cp$'_2$Ti – H – 2 HF]$^+$; 5), 500 ([Cp$'_2$Ti – H – CH$_2$CH$_2$CF$_3$]$^+$; 5), 201 (11), 187 (22), 177 (15), 159 (13), 157 (9), 119 (11), 105 (10), 77 (62), 59 (49). IR (KBr): 2955 (s), 2909 (vs), 2870 (m), 1484 (w), 1446 (m), 1381 (m), 1361 (s), 1328 (s), 1313 (m), 1264 (vs), 1210 (vs), 1196 (vs), 1120 (vs), 1064 (s), 1023 (m), 897 (s), 840 (vs), 812 (s), 772 (m), 687 (w), 662 (w), 550 (w), 409 (m). A broad band centered at about 1200 cm^{-1} is overlapped by sharp bands in the region 1300–1100 cm^{-1}. ESR (hexane, 22 °C): g = 1.990, ΔH = 15.0 G; (toluene, –140 °C): electronic triplet state, g = 1.990, D = 0.01161 cm^{-1}, E = 0. UV-VIS (hexane, 22 °C): 354 > 410 (sh) > 560 nm.

Compound **4**. EI-MS (220 °C): *m/z* (relative abundance) 600 (7), 599 (24), 598 (51), 597 ([Cp$'_2$Ti – H]$^+$; 100), 596 (14), 595 (11), 578 (6), 577 ([Cp$'_2$Ti – H – HF]$^+$; 12), 201 (11), 187 (23), 177 (16), 159 (13), 157 (12), 119 (12), 105 (11), 77 (53), 59 (49). ESR (hexane, 22 °C): g = 1.991, triplet 1:2:1, a_H = 7.3 G, a_{Ti} = 6.8 G; (toluene, –140 °C): g_1 = 2.002, g_2 = 1.992, g_3 = 1.977, g_{av} = 1.990, $A_2(H)$ = 11.7 G. UV-VIS (hexane, 22 °C): 370 (sh) >> 580 nm (extending to 900 nm).

Synthesis of [Ti{η^5-C$_5$Me$_4$(SiMe$_2$CH$_2$CH$_2$CF$_3$)}{η^5:η^1-C$_5$Me$_3$(CH$_2$)(SiMe$_2$CH$_2$CH$_2$CF$_3$)}] (**5**)

Compound **1** (0.67 g, 1.0 mmol) and magnesium (0.24 g, 10 mmol) in an ampule attached to a vacuum line were degassed and THF (20 ml) and BTMSE (1.0 ml, 4.5 mmol) were added by vacuum distillation. The ampule was sealed off and heated to 60 °C for 25 h. The dark

brown solution was separated from unreacted magnesium, all volatiles were evaporated in vacuum to dryness, and the residue was extracted with 20 ml of hexane. The volume of the solution was reduced to ca. 5 ml, and the solution was cooled in a freezer to –18 °C for 2 days. A dark blue solid in large blocks crystallized out. The solid was separated from the mother liquor, washed with condensing hexane vapor, and recrystallized from 10 ml of hexane. The yield of crystalline **5** was 0.16 g (27%).

Compound **5**. M.p. 69 °C. EI-MS (80 °C), *m/z* (relative abundance): 600 (8), 599 (26), 598 (51), 597 (M$^{\bullet+}$; 100), 596 (15), 595 (11), 577 ([M – HF]$^+$; 9), 217 (9), 201 (12), 187 (25), 177 (14), 167 (8), 159 (12), 157 (11), 119 (11), 105 (10), 77 (75), 73 (9), 71 (9), 59 (74), 57 (15). IR (KBr): 3047 (w), 2961 (s), 2936 (m), 2911 (s), 2864 (m), 1445 (m), 1381 (w), 1360 (m), 1331 (m), 1314 (m), 1264 (vs), 1210 (s), 1197 (s), 1120 (vs), 1061 (s), 1027 (m), 898 (s), 839 (s), 816 (s), 775 (m), 688 (w), 655 (vw), 621 (w), 549 (w), 521 (w), 445 (w), 406 (m). ESR (hexane, 22 °C): g = 1.946, ΔH = 19 G; (toluene, –140 °C): g_1 = 2.000, g_2 = 1.981, g_3 = 1.857, g_{av} = 1.946. UV-VIS (hexane, 22 °C): 587 nm.

Synthesis of [Ti(η^1-C≡CCMe$_3$){η^5-C$_5$Me$_4$(SiMe$_2$CH$_2$CH$_2$CF$_3$)}$_2$] (**6**)

Compound **5** (0.20 g, 0.33 mmol) was dissolved in 10 ml of hexane in an all-glass device for measurement of UV-near-IR and ESR spectra and TBUE (1.0 ml, 8.0 mmol) was added by vacuum distillation. The blue color of the solution turned immediately brown. The concentration of TBUE then did not change even after heating the mixture to 60 °C for 3 h (the absorption band of TBUE at 1534 nm did not change its intensity[11]). Then, all volatiles were evaporated in vacuum, and the brown residue was extracted with hexane (10 ml). The solution was concentrated and compound **6** crystallized out at –18 °C. Yield of brown crystals 0.15 g (67%).

Compound **6**. EI-MS (140 °C), *m/z* (relative abundance): 680 (9), 679 (M$^{\bullet+}$; 15), 600 (8), 599 (25), 598 (46), 597 ([M – Me$_3$CC≡CH]$^+$; 100), 596 (15), 595 (12), 268 (20), 267 (10), 237 (13), 201 (9), 187 (15), 177 (10), 167 (8), 159 (16), 157 (8), 119 (10), 77 (73), 73 (9), 59 (64). IR (KBr): 2964 (vs), 2912 (s), 2868 (m), 2070 (w), 1446 (m), 1361 (m), 1330 (w), 1314 (w), 1263 (vs), 1210 (s), 1121 (s), 1065 (s), 1027 (m), 898 (s), 840 (s), 812 (m), 773 (m), 727 (w), 687 (w), 622 (w), 550 (w), 441 (w), 408 (m). ESR (hexane, 22 °C): g = 1.944, ΔH = 40 G; (toluene, –140 °C): g_1 = 2.998, g_2 = 1.979, g_3 = 1.852, g_{av} = 1.943. UV-VIS (hexane, 22 °C): 483 > 617 nm.

X-ray Crystal Structure Determination

A dark red fragment of **1**, black block of **2**, blue prism of **3**, dark blue plate of **5** or brown block of **6** were inserted into a Lindenmann glass capillaries under purified nitrogen in a glovebox (mBraun) and the capillaries were sealed with flame. Diffraction data were collected on a Nonius KappaCCD diffractometer and analyzed with HKL program package[34]. The structures were solved by direct methods (SIR97 [35]), followed by consecutive Fourier syntheses and refined by full-matrix least-squares on F^2 (SHELX97 [36]). The non-hydrogen atoms were refined anisotropically except the disordered carbon atoms C6A and C6B in **5** which were refined isotropically. Hydrogen atoms were placed in ideal positions and refined as riding atoms except H1 and H2 in **3** which were located on the difference Fourier map and refined isotropically. Compound **2** contained one molecule of THF of crystallization per one molecule of the complex. The quality of crystal of **3** was hampered by 2 molecules of *n*-hexane of crystallization in the unit cell whose position was highly disordered. However,

TABLE IV
Crystal and structure refinement data for **1**, **2**, **3**, **5**, and **6**

Parameter	1	2	3	5	6
Formula	$C_{28}H_{44}Cl_2F_6Si_2Ti$	$C_{32}H_{52}ClF_6OSi_2Ti$	$C_{59}H_{99}F_{12}MgSi_4Ti$	$C_{28}H_{43}F_6Si_2Ti$	$C_{34}H_{53}F_6Si_2Ti$
Molecular weight	669.61	634.15	1268.79	597.70	679.84
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	C2/c (No. 15)	C2/c (No. 15)	$P2_1/c$ (No. 14)
a, Å	13.1440(4)	8.8880(3)	28.880(1)	25.6470(6)	33.2710(3)
b, Å	12.9040(4)	16.2990(6)	14.7880(5)	9.1290(3)	12.5410(3)
c, Å	19.6960(7)	25.836(1)	16.6460(4)	15.3230(5)	17.5700(8)
β, °	108.134(2)	96.086(1)	101.217(2)	121.631(2)	91.283(1)
V, Å^3; Z	3174.7(2); 4	3721.7(2); 4	6973.3(4); 4	3054.63(16); 4	7329.3(4); 8
D_{calc}, g cm^{-3}	1.401	1.260	1.209	1.300	1.232
μ, mm^{-1}	0.566	0.419	0.372	0.411	0.351
Color and habit	red fragment	black block	blue prism	blue plate	black block
Crystal size, mm^3	0.25×0.25×0.23	0.50×0.50×0.23	0.4×0.25×0.2	0.25×0.25×0.10	0.50×0.38×0.35
T, K	150(2)	150(2)	150(2)	150(2)	293(2)
θ_{min}; θ_{max}, °	1.65; 27.89	1.48; 24.06	1.00; 25.00	3.12; 26.01	1.00; 27.48
No. diffrns collected	7533	5839	6143	2988	16 687
No. unique diffrns	4519	3951	4751	2444	11 343
No. of parameters	364	377	382	173	805
$R(F)$; $wR(F^2)$ all data	13.01; 13.57	11.54; 21.65	8.51; 20.65	8.10; 14.80	8.89; 12.06
GooF (F^2), all data	1.028	1.064	1.124	1.158	1.026
$R(F)$; $wR(F^2)$ [I > 2σ(I)]	5.80; 10.77	7.33; 19.03	6.37; 19.26	6.48; 14.14	4.99; 10.53
$\Delta\rho$, e Å^{-3}	0.515; −0.525	1.013; −0.525	0.865; −0.401	0.620; −0.438	0.532; −0.436

the positions of atoms of the complex were well resolved including the hydride bridges, which appeared on difference Fourier map as maxima of rather high electron density (≈ 1.6 e Å^{-3}). To describe this electron density, the scattering factor for neutral hydrogen was insufficient (the H1 and H2 had very low temperature factors during refinement while leaving high maxima on the difference Fourier map), and the use of the scattering factor for hydride (H$^-$) led to no improvement. The best agreement was obtained when the scattering factor for He was used in the final refinement. This gave reasonable displacement factors, low residual maxima, and a better R-factor (by 1%). This description, however, does not allow to draw conclusions on the distribution of electron density in the Ti–H–Mg bridge because of low precision of the structure analysis due to a poor scattering power of the crystal (diffraction intensities rapidly decreasing with decreasing θ). A similar effect was not observed in crystal structure determination of other complexes of this type[18,19,21]. Relevant crystallographic data for all the compounds are given in Table IV. CCDC 215220 (for **1**), CCDC 215218 (for **2**), CCDC 254672 (for **3**), CCDC 254671 (for **5**), and CCDC 253643 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

REFERENCES

1. a) Long N. J.: *Metallocenes*. Blackwell Science, Oxford 1998; b) Beckhaus R. in: *Metallocenes* (A. Togni and R. L. Halterman, Eds), Vol. 1, Chap. 4, p. 153. Wiley-VCH, Weinheim 1998; c) Rosenthal U., Burlakov V. V. in: *Titanium and Zirconium in Organic Synthesis* (I. Marek, Ed.), Chap. 10, p. 355. Wiley-VCH, Weinheim 2002.
2. De Wolf J. M., Blaauw R., Meetsma A., Teuben J. H., Gyepes R., Varga V., Mach K., Veldman N., Spek A. L.: *Organometallics* **1996**, *15*, 4977.
3. a) Bercaw J. E., Marvich R. H., Bell R. G., Brintzinger H. H.: *J. Am. Chem. Soc.* **1972**, *94*, 1219; b) Bercaw J. E.: *J. Am. Chem. Soc.* **1974**, *96*, 5087; c) Cohen S. A., Auburn P. R., Bercaw J. E.: *J. Am. Chem. Soc.* **1983**, *105*, 1136.
4. Hitchcock P. B., Kerton F. M., Lawless G. A.: *J. Am. Chem. Soc.* **1998**, *120*, 10264.
5. Horáček M., Kupfer V., Thewalt U., Štěpnička P., Polášek M., Mach K.: *Organometallics* **1999**, *18*, 3572.
6. Horáček M., Hiller J., Thewalt U., Polášek M., Mach K.: *Organometallics* **1997**, *16*, 4185.
7. Lukešová L., Horáček M., Štěpnička P., Fejfarová K., Gyepes R., Císařová I., Kubišta J., Mach K.: *J. Organomet. Chem.* **2002**, *663*, 134.
8. a) Pool J. A., Lobkovsky E., Chirik P. J.: *Nature* **2004**, *427*, 527; b) Hanna T. E., Keresztes I., Lobkovsky E., Bernskoetter W. H., Chirik P. J.: *Organometallics* **2004**, *23*, 3448; c) Hanna T. E., Lobkovsky E., Chirik P. J.: *J. Am. Chem. Soc.* **2004**, *126*, 14688.
9. Varga V., Mach K., Polášek M., Sedmera P., Hiller J., Thewalt U., Troyanov S. I.: *J. Organomet. Chem.* **1996**, *506*, 241.

10. Horáček M., Štěpnička P., Gyepes R., Císařová I., Tišlerová I., Zemánek J., Kubišta J., Mach K.: *Chem. Eur. J.* **2000**, *6*, 2397.
11. Horáček M., Císařová I., Čejka J., Karban J., Petrusová L., Mach K.: *J. Organomet. Chem.* **1999**, *577*, 103.
12. Lukešová L., Horáček M., Štěpnička P., Gyepes R., Císařová I., Kubišta J., Mach K.: *J. Organomet. Chem.* **2004**, *689*, 1919.
13. Kupfer V., Thewalt U., Horáček M., Petrusová L., Mach K.: *Inorg. Chem. Commun.* **1999**, *2*, 540.
14. Horáček M., Gyepes R., Císařová I., Polášek M., Varga V., Mach K.: *Collect. Czech. Chem. Commun.* **1996**, *61*, 1307.
15. Luinstra G. A., Teuben J. H.: *Chem. Commun.* **1990**, 1470.
16. Mach K., Raynor J. B.: *J. Chem. Soc., Dalton Trans.* **1992**, 683.
17. Lukens W. W., Smith III R. M., Andersen R. A.: *J. Am. Chem. Soc.* **1996**, *118*, 1719.
18. Mach K., Gyepes R., Horáček M., Petrusová L., Kubišta J.: *Collect. Czech. Chem. Commun.* **2003**, *68*, 1877.
19. a) Troyanov S. I., Varga V., Mach K.: *J. Chem. Soc., Chem. Commun.* **1993**, 1174; b) Gyepes R., Mach K., Císařová I., Loub J., Hiller J., Šindelář P.: *J. Organomet. Chem.* **1995**, *497*, 33.
20. a) Samuel E., Harrod J. F., Gourier D., Dromzee Y., Robert F., Jeannin Y.: *Inorg. Chem.* **1992**, *31*, 3252; b) Mach K., Varga V., Schmid G., Hiller J., Thewalt U.: *Collect. Czech. Chem. Commun.* **1996**, *61*, 1285.
21. Gyepes R., Hiller J., Thewalt U., Polášek M., Šindelář P.: *J. Organomet. Chem.* **1996**, *516*, 177.
22. Brintzinger H. H.: *J. Am. Chem. Soc.* **1967**, *89*, 6871.
23. Kenworthy J. G., Myatt J., Symons M. C. R.: *J. Chem. Soc. A* **1971**, 1020.
24. Troyanov S. I., Varga V., Mach K.: *J. Organomet. Chem.* **1993**, *461*, 85.
25. Kupfer V., Thewalt U., Tišlerová I., Štěpnička P., Gyepes R., Kubišta J., Horáček M., Mach K.: *J. Organomet. Chem.* **2001**, *620*, 39.
26. a) Fischer J. M., Piers W. E., Young V. G.: *Organometallics* **1996**, *15*, 2410; b) Bercaw J. E., Brintzinger H. H.: *J. Am. Chem. Soc.* **1971**, *93*, 2046; c) Vondrák T., Mach K., Varga V., Terpstra A.: *J. Organomet. Chem.* **1992**, *425*, 27.
27. Horáček M., Štěpnička P., Kubišta J., Fejfarová K., Gyepes R., Mach K.: *Organometallics* **2003**, *22*, 861.
28. Horáček M., Gyepes R., Kubišta J., Mach K.: *Inorg. Chem. Commun.* **2004**, *7*, 155.
29. Horáček M., Císařová I., Lukešová L., Kubišta J., Mach K.: *Inorg. Chem. Commun.* **2004**, *7*, 713.
30. Kirchbauer F. G., Pellny P.-M., Sun H., Burlakov V. V., Arndt P., Baumann W., Spannenberg A., Rosenthal U.: *Organometallics* **2001**, *20*, 5289.
31. Langmaier J., Samec Z., Varga V., Horáček M., Mach K.: *J. Organomet. Chem.* **1999**, *579*, 348.
32. Lukešová L., Štěpnička P., Fejfarová K., Gyepes R., Císařová I., Horáček M., Kubišta J., Mach K.: *Organometallics* **2002**, *21*, 2639.
33. Antropiusová H., Dosedlová A., Hanuš V., Mach K.: *Transition Met. Chem. (London)* **1981**, *6*, 90.
34. Otwinowski Z., Minor W.: *HKL Denzo and Scalepack Program Package*. Nonius BV, Delft 1997. For a reference, see: Otwinowski Z., Minor W.: *Methods Enzymol.* **1997**, *276*, 307.
35. Altomare A., Burla M. C., Camalli M., Cascarano G., Giacovazzo C., Guagliardi A., Polidori G.: *J. Appl. Crystallogr.* **1994**, *27*, 435.
36. Sheldrick G. M.: *SHELXL97*, Program for Crystal Structure Refinement from Diffraction Data. University of Göttingen, Göttingen 1997.