C−H Bond Activation Processes in Cationic and Neutral Titanium Benzyl Compounds with Cyclopentadienyl−Arene Ligands

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Received August 13, 2002

Titanium tribenzyl complexes with cyclopentadienyl−arene ligands, (η^5-$C_5H_4CMe_2Ar$)Ti(CH_2Ph)$_3$ (Ar = 3,5-$Me_2C_6H_3$ (**1**), Ph (**2**)), were synthesized. Reaction of **1** with either $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$ affords the cation [(η,$^5\eta$-$C_5H_4CMe_2$-3,5-$Me_2C_6H_3$)Ti(η-CH_2Ph)$_2$]$^+$ (**3**), in which the pendant arene group and the benzyl ligands show fluxional behavior. Reaction of **2** with $B(C_6F_5)_3$, leads to rapid ortho cyclometalation of the pendant arene to give the contact ion pair [(η^5:η^1-$C_5H_4CMe_2C_6H_4$)Ti(η^1-CH_2Ph)][η^6-$PhCH_2B(C_6F_5)_3$] (**4**) and toluene. Reaction of **2** with $[Ph_3C][B(C_6F_5)_4]$ also leads to ligand ortho metalation, giving [(η^5:η^1-$C_5H_4CMe_2C_6H_4$)-Ti(η^2-CH_2Ph)][$B(C_6F_5)_4$] (**5**) with a η^2-benzyl group. Thermolysis of compounds **1** and **2** (50 °C, 50 h) results in the ortho-cyclometalated dibenzyl species (η^5:η^1-$C_5H_4CMe_2Ar'$)Ti-(CH_2Ph)$_2$ (Ar′ = 3,5-$Me_2C_6H_2$ (**6**), C_6H_4 (**7**)) and toluene. The thermolysis of **1** follows first-order kinetics ($k \approx 10^{-5}$ s^{-1} at 333 K) with $\Delta H^{\ddagger} = 24 \pm 2$ kcal mol^{-1} and $\Delta S^{\ddagger} = -5 \pm 5$ cal mol^{-1} K^{-1}. For the thermolysis of the related titanium trialkyl (η^5-$C_5H_4CMe_2Ph$)Ti-(CH_2SiMe_3)$_3$ (**9**), activation parameters of $\Delta H^{\ddagger} = 21 \pm 2$ kcal mol^{-1} and $\Delta S^{\ddagger} = -18 \pm 4$ cal mol^{-1} K^{-1} were found. Deuterium labeling studies with (η^5-$C_5H_4CMe_2C_6D_5$)Ti(CH_2Ph)$_3$ (**2-*d*$_5$**) show that thermolysis of the neutral compound involves initial formation of an alkylidene intermediate, followed by *o*-CH addition to the Ti=C bond. In the corresponding cationic species, ortho cyclometalation proceeds via direct σ-bond metathesis.

Introduction

Monocyclopentadienyl (half-sandwich) titanium alkyl compounds, used in combination with methylalumoxane or other cocatalysts, are especially known for their ability to act as (pro)catalysts for the syndiotactic polymerization of styrene,[1] although they also show interesting behavior in the polymerization of other olefins.[2] For example, Cp*$TiMe_3$ is an effective procatalyst for the polymerization of propene to give high-molecular-weight atactic polypropene with a narrow polydispersity.[2b] Remarkably, it was also observed to produce butyl chain branched polyethene from ethene homopolymerization.[2c]

Recently we have been investigating monocyclopentadienyl titanium complexes with a pendant arene group attached to the cyclopentadienyl ligand. Not only can this pendant arene coordinate to the metal center in the cations [(η^5:η^6-$C_5H_4CMe_2Ar$)$TiMe_2$]$^+$ (Ar = Ph, 3,5-$Me_2C_6H_3$)[3] but it also turns these systems into highly active catalysts for the trimerization of ethene to 1-hexene.[4] In this paper we describe the synthesis and thermal decomposition of various (η^5-$C_5H_4CMe_2Ar$)-Ti(CH_2Ph)$_3$ complexes and their dialkyl cations. Decomposition of both the neutral and cationic complexes with Ar = Ph leads to ortho metalation of the pendant arene group, but the pathways to this metalation are different: for the cationic systems direct σ-bond metathesis occurs, whereas in the neutral trialkyls the reaction is initiated by rate-determining α-H abstraction followed by the subsequent addition of the arene *o*-CH bond to the alkylidene intermediate.

Results and Discussion

Synthesis and Characterization of (η^5-$C_5H_4CMe_2Ar$)Ti(CH_2Ph)$_3$. The cyclopentadienyl−arene titanium tribenzyl compounds (η^5-$C_5H_4CMe_2Ar$)Ti(CH_2-Ph)$_3$ (Ar = 3,5-$Me_2C_6H_3$ (**1**), Ph (**2**)) are readily accessible by the reaction of the appropriate titanium trichloride[3] with 3 equiv of benzylmagnesium bromide in diethyl ether. Crystallization from pentane afforded **1** and **2** as air- and moisture-sensitive red crystals in around 70% yield. They were fully characterized by 1D and 2D NMR techniques and elemental analysis. The methylene

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(1) (a) Ishihara, T.; Seimiga, T.; Kuramoto, M.; Uoi, M. *Macromolecules* **1986**, *19*, 2464. (b) Ishihara T.; Kuramoto, M.; Uoi, M. *Macromolecules* **1988**, *21*, 3256.

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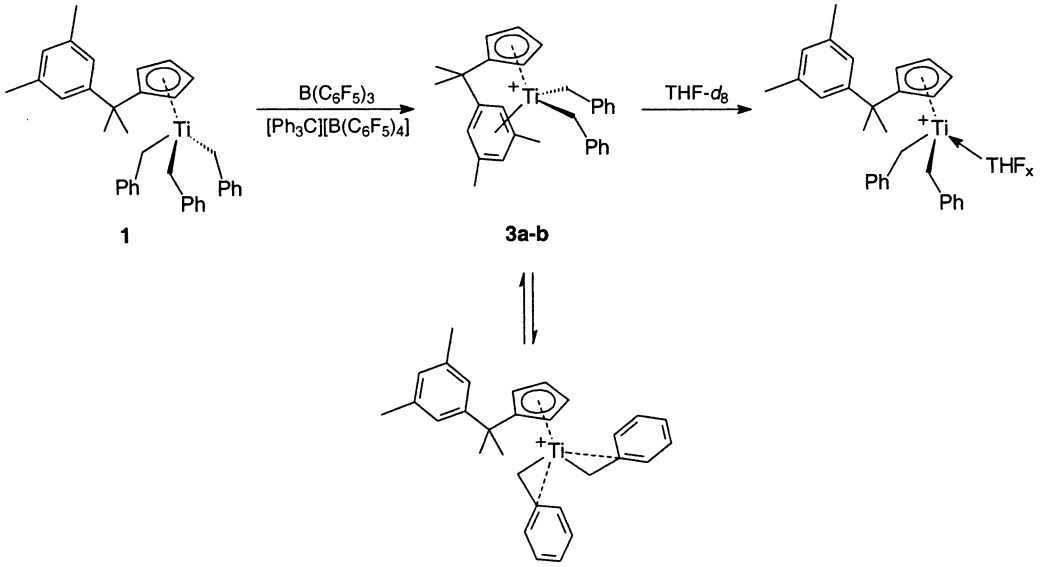
10.1021/om0206554 CCC: $22.00
Publication on Web 11/02/2002

Scheme 1



benzyl proton resonance appears as one singlet at δ 2.99 and 2.97 ppm for **1** and **2**, respectively. The corresponding methylene ^{13}C NMR resonances are found at δ 93.5 ppm for both compounds, with a $^1J_{CH}$ coupling constant of 123−124 Hz. These spectroscopic data are similar to those of other monocyclopentadienyl titanium tribenzyl complexes,[3b,5] in which the methylene $^1J_{CH}$ value of 122−126 Hz is indicative of η^1 coordination of the benzyl ligands.

Cationic Species from (η^5-$C_5H_4CMe_2$-3,5-$Me_2C_6H_3$)-$Ti(CH_2Ph)_3$ (1). The reaction of the tribenzyl compound **1** with the Lewis acid $B(C_6F_5)_3$ in bromobenzene-d_5 was studied by NMR spectroscopy. At −30 °C this results in the rapid formation of the ionic complex [(η^5:η-$C_5H_4CMe_2$-3,5-$Me_2C_6H_3$)Ti(η-$CH_2Ph)_2$]-[$PhCH_2B(C_6F_5)_3$] (**3a**; Scheme 1). ^{1}H and ^{19}F NMR data are consistent with the abstraction of one benzyl group to give the free $[PhCH_2B(C_6F_5)_3]^-$ anion.[6] Interaction of the pendant arene group on the cyclopentadienyl ligand with the metal center in the cation is indicated by the increase in the separation of the two CH ^{1}H NMR signals of the monosubstituted cyclopentadienyl ring ($\Delta\delta$ = 1.62 ppm in **3a**, $\Delta\delta$ = 0.29 ppm in **1**). This increase is related to the constrained geometry associated with the simultaneous bonding of both cyclopentadienyl and arene moieties to the metal. This effect was also observed for *ansa*-metallocenes of the type [$X(C_5H_4)_2$]-$TiCl_2$ (X = $(CH_2)_3$, $GeMe_2$, $SiMe_2$, CH_2), where the separation of the two sets of Cp protons increases with decreasing Cp(centroid)−Ti−Cp(centroid) angle.[7] In contrast with this observation, the benzyl CH_2 protons do not show the expected AB pattern but one broad singlet resonance, and the rather large $^1J_{CH}$ coupling constant of 148 Hz suggests some η^2 character of these groups.[8] For the zirconium species [(η^5:η^6-$C_5H_4CMe_2$-4-MeC_6H_4)$Zr(CH_2Ph)_2$][$B(C_6F_5)_4$],[9] the two resonances of the diastereotopic benzyl methylene protons are barely separated ($\Delta\delta$ = 0.01 ppm), but the observed $^1J_{CH}$ coupling constant of 127 Hz unequivocally indicates η^1 coordination.[10] The NMR spectroscopic data probably indicate highly fluxional character of the coordination mode of the aromatic moieties in **3a** (i.e. the hapticity of the two benzyl groups and the arene functionality; Scheme 1) on the NMR time scale, yielding an average NMR spectrum of an *ansa* complex with η^1-benzyl ligands and an isomer with η^2-benzyl groups in which the π-arene coordination is weakened or lost. Bochmann and co-workers recently demonstrated similar behavior for the closely related species [(η^5:η-$C_5H_4CHPh_2$)Ti(η-$CH_2Ph)_2$][$B(C_6F_5)_4$] in CD_2Cl_2, for which the two different structures could be observed separately by NMR spectroscopy at −90 °C.[3b]

Addition of a drop of THF-d_8 to a C_6D_5Br solution of **3a** shows a shift of the cyclopentadienyl proton resonances back to the chemical shifts normal for a η^5-Cp−arene ligand (δ 6.11 and 5.90 ppm), indicating release of the arene moiety in the presence of a hard Lewis base to give a [(η^5-$C_5H_4CMe_2$-3,5-$Me_2C_6H_3$)Ti(η^1-$CH_2Ph)_2$-(THF-$d_8)_x$][$PhCH_2B(C_6F_5)_3$] species (Scheme 1). The Ti−benzyl methylene proton resonances form an AB system (δ 3.19 and 2.18 ppm), with a $^2J_{HH}$ value of 9.2 Hz, and the corresponding methylene carbon resonance is a triplet at δ 107.0 ppm ($^1J_{CH}$ 129 Hz), indicative of η^1

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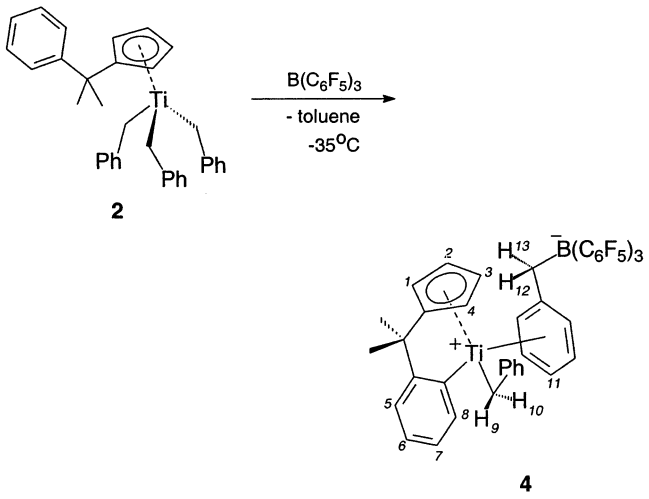
Scheme 2



coordination of the benzyl ligands in the presence of THF.[10]

Compound **3a** is reasonably stable at −30 °C in bromobenzene-d_5 but rapidly decomposes at ambient temperature ($t_{1/2} \approx 10$ min) to give paramagnetic species and liberation of toluene, as seen by NMR spectroscopy. After 20 h deep brown-green crystals had formed which, from a unit cell determination by X-ray diffraction, were identified as $\{[(\eta^5{:}\eta^6\text{-}C_5H_4CMe_2\text{-}3,5\text{-}Me_2C_6H_3]Ti(\mu\text{-}Br)]_2\}[B(C_6F_5)_4]$, the same product as formed in the decomposition of $[(\eta^5{:}\eta^6\text{-}C_5H_4CMe_2\text{-}3,5\text{-}Me_2C_6H_3)TiMe_2][MeB(C_6F_5)_3]$ in C_6D_5Br solution.[3a]

Reaction of $(\eta^5\text{-}C_5H_4CMe_2\text{-}3,5\text{-}Me_2C_6H_3)Ti(CH_2Ph)_3$ (**1**) with $[Ph_3C][B(C_6F_5)_4]$ in C_6D_5Br resulted in the release of 1 equiv of 1,1,1,2-tetraphenylethane and the formation of the ionic species $[(\eta^5{:}\eta\text{-}C_5H_4CMe_2\text{-}3,5\text{-}Me_2C_6H_3)Ti(\eta\text{-}CH_2Ph)_2][B(C_6F_5)_4]_2$ (**3b**). The NMR data for the cation are identical with those of **3a**. This suggests that the rapid equilibrium between the different coordination modes of the aromatic moieties in the cations is apparently not influenced by the counterion.

Generation of cationic species from $(\eta^5\text{-}C_5H_4CMe_2Ph)Ti(CH_2Ph)_3$ (2). The reaction of the tribenzyl complex **2** with $B(C_6F_5)_3$ in bromobenzene-d_5 at −30 °C results in the release of 1 equiv of toluene and the formation of an ionic species that was characterized as the contact ion pair $[(\eta^5{:}\eta^1\text{-}C_5H_4CMe_2C_6H_4)Ti(\eta^1\text{-}CH_2Ph)][\eta^6\text{-}PhCH_2B(C_6F_5)_3]$ (**4**; Scheme 2), in which the pendant aromatic group has been ortho-cyclometalated. In contrast to the ionic dimethyl compounds $[(\eta^5{:}\eta^6\text{-}C_5H_4CMe_2Ar)TiMe_2][MeB(C_6F_5)_3]$[3] and **3a**,**b**, compound **4** is also soluble in benzene and toluene and was obtained analytically pure as a green microcrystalline solid from the reaction of **2** with $B(C_6F_5)_3$ in pentane.

The Ti−C ^{13}C NMR resonance of the cyclometalated pendant arene group is found at δ 199.7 ppm, which is comparable to the chemical shift found for the ipso carbon of the Ti−Ph group in the neutral metallocenes $[Me_2Si(\eta^5\text{-}C_5Me_4)_2]TiPh_2$ (δ 199.6 ppm, $CDCl_3$, 25 °C) and $(\eta^5\text{-}C_5H_4CMe_3)_2TiPh_2$ (δ 191.9 ppm, C_6D_6, 25 °C).[11] The complex **4** has an asymmetric structure in solution (toluene-d_8, −30 °C), due to the η^6 coordination of the $[PhCH_2B(C_6F_5)_3]^-$ anion to the metal center. This can be seen by ^{19}F NMR, where the $\Delta(\delta_{m-F}-\delta_{p-F})$ shift difference is 4.2 ppm, indicative of a contact-ion pair,[12] and by ^1H NMR, where separate resonances are seen for all aromatic and benzylic protons of the anion. The Ti−benzyl group is η^1 bound, as can be seen from the $^2J_{HH}$ coupling constant of 10 Hz and the $^1J_{CH}$ coupling constant of 126 Hz of the benzyl methylene group, both of which are characteristic of η^1-benzyl coordination.[10]

From its low-temperature (−30 °C) $^1H,^1H$ NOESY spectrum the structure of **4** in solution can be determined (see Scheme 2 for the numbering of the H atoms in **4**). The methylene protons of the benzyl of the $[PhCH_2B(C_6F_5)_3]^-$ anion (12 and 13) show a correlation with the two β-protons of the cyclopentadienyl ring (2 and 3). Methylene proton 13 (δ 3.39 ppm) interacts with both protons 2 and 3, while 12 (δ 2.8 ppm) only correlates with 3. The methylene proton of the titanium−benzyl ligand (9, δ 2.80 ppm) displays NOE interactions with the Ph *m-H* (8), adjacent to the Ph *o-C*$_{ipso}$. Additionally, the other methylene proton (10, δ 0.81 ppm) correlates with the *p-H* (11) of the benzyl ligand of the anion. From the NOE interactions it can be concluded that in solution at low temperature complex **4** adopts a structure in which the benzyl methylene group of the coordinated anion is directed toward the cyclopentadienyl ligand and the methylene protons of the metal-bound benzyl group are pointing away from the cyclopentadienyl moiety. At ambient temperature considerable line broadening is observed, suggesting fluxional behavior of the remaining benzyl ligand and the coordinated anion.

In the closely related cationic cyclopentadienyl−amido titanium benzyl complexes $\{[\eta^5{:}\eta^1\text{-}C_5H_4(CH_2)_2NR]Ti(CH_2Ph)\}[PhCH_2B(C_6F_5)_3]$ (R = Me, *i*-Pr, *t*-Bu) the anion is not coordinated to the titanium center.[13] In these cyclopentadienyl−amido systems the nitrogen lone pair can serve as an additional 2-electron π-donor, thus affording a 12-electron cationic species, as opposed to the formally 10-electron cation in **4**.[14] Possibly, the additional 2-electron π-donation is sufficient to favor the solvent-separated ion pair for the Cp−amido systems (even for small substituents on the amido nitrogen), whereas for the highly electron-deficient Cp-aryl system the η^6 coordination of the anion (to give a 16-electron species) is preferred.

Upon reaction of $[Ph_3C][B(C_6F_5)_4]$ with the tribenzyl complex **2** in bromobenzene-d_5 at −30 °C, 1 equiv of 1,1,1,2-tetraphenylethane and 1 equiv of toluene are

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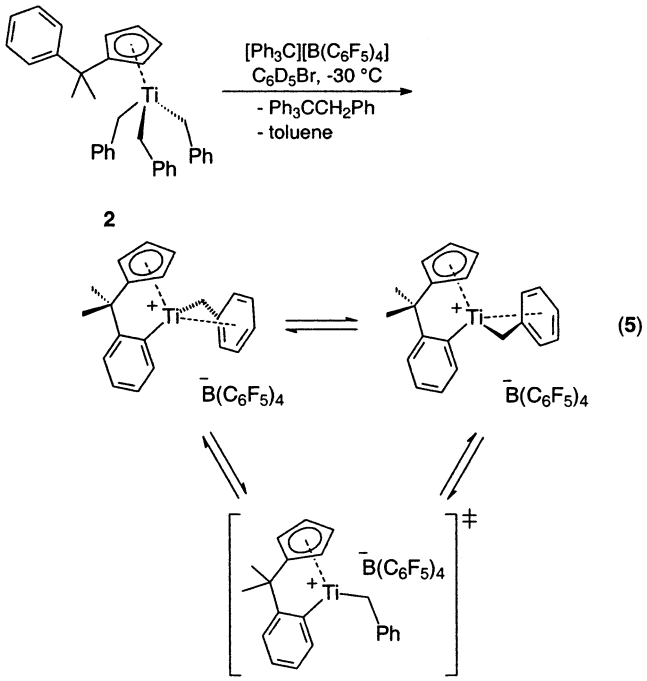
(13) For R = Me, an equilibrium between a coordinated and a noncoordinated state was observed. See: (a) Sinnema, P.-J.; Van der Veen, L.; Spek, A. L.; Veldman, N.; Teuben, J. H. *Organometallics* **1997**, *16*, 4245. (b) Sinnema, P.-J.; Hessen, B.; Teuben, J. H. *Macromol. Rapid Commun.* **2000**, *21*, 562. (c) Sinnema, P.-J.; Lielkelema, K.; Staal, O. K. B.; Hessen, B.; Teuben, J. H. *J. Mol. Catal.* **1998**, *128*, 143. (d) Sinnema, P.-J. Ph.D. Dissertation, University of Groningen, 1999.

(14) In metal−(σ-aryl) complexes, such as **4**, π-donation of the aryl π-system is of relatively little importance. See: (a) Morse, P. M.; Girolami, G. S. *J. Am. Chem. Soc.* **1989**, *111*, 4114. (b) Girolami, G. S.; Nelsen, M. J. *Abstracts of Papers*, 213th National Meeting of the American Chemical Society, San Francisco, April 1997; American Chemical Society: Washington, DC, 1997; INOR 710. (c) Bouwkamp, M.; Van Leusen, D.; Meetsma, A.; Hessen, B. *Organometallics* **1998**, *17*, 3645.

Scheme 3



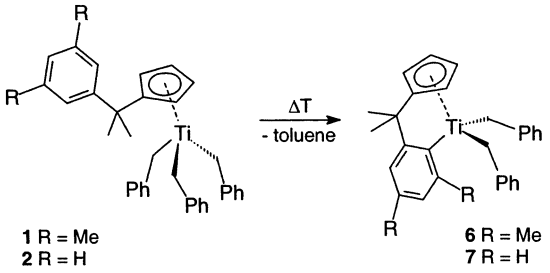
liberated, and an ionic species with an ortho-cyclometalated pendant arene group and a η^2-coordinated benzyl ligand, $[(\eta^5{:}\eta^1\text{-}C_5H_4CMe_2C_6H_4)Ti(\eta^2\text{-}CH_2Ph)][B(C_6F_5)_4]$ (**5**; Scheme 3), is formed.

The ^{13}C NMR resonance of the Ti-bound aryl carbon is observed at δ 215.8 ppm and the methylene resonance of the benzyl ligand at δ 88.1 ppm, the latter with a $^1J_{CH}$ coupling constant of 154 Hz, indicative of η^2-benzyl coordination.[8] At −30 °C the benzyl methylene proton resonances are observed as two broad signals ($W_{1/2}$ = 37 Hz), and four broadened resonances ($W_{1/2}$ = 33 Hz) are seen for the cyclopentadienyl protons. This implies that compound **5** has an asymmetric structure with the η^2-benzyl ligand bound in the cleft between the cyclopentadienyl and arene moieties (Scheme 3). At ambient temperature the Cp and methylene protons each coalesce into broad signals, indicating fluxionality of the benzyl ligand to give an average C_s symmetry.

Reactions of the analogous titanium trimethyl species $(\eta^5\text{-}C_5H_4CMe_2Ph)TiMe_3$ with $B(C_6F_5)_3$[15] or $[Ph_3C][B(C_6F_5)_4]$[3b] cleanly afford the cationic species $[(\eta^5{:}\eta^6\text{-}C_5H_4CMe_2Ph)TiMe_2]^+$. No indications for rapid ortho cyclometalation of the ancillary ligand have been observed for this compound. Apparently, the benzyl ligands in **4** help to induce metalation of the cyclopentadienyl−arene ligand. The benzyl ligands appear to weaken the coordination of the pendant arene group by binding in a multihapto fashion (as seen above in the behavior of **3**), and consequently facilitate the Cp−arene ligand ortho cyclometalation. This pathway is not available for the dimethyl analogues.

Thermolysis of the Neutral $(\eta^5\text{-}C_5H_4CMe_2Ar)Ti(CH_2Ph)_3$ Complexes. Warming benzene-d_6 solutions of the titanium tribenzyl complexes $(\eta^5\text{-}C_5H_4CMe_2Ar)Ti(CH_2Ph)_3$ (Ar = 3,5-$Me_2C_6H_3$ (**1**), Ph (**2**)) for 50 h at 50 °C and monitoring the reactions by NMR spectroscopy reveal gradual liberation of 1 equiv of toluene and

Scheme 4



the formation of titanium dibenzyl species with an ortho-cyclometalated pendant arene group, $(\eta^5{:}\eta^1\text{-}C_5H_4CMe_2\text{-}3,5\text{-}Me_2C_6H_2)Ti(CH_2Ph)_2$ (**6**) and $(\eta^5{:}\eta^1\text{-}C_5H_4CMe_2C_6H_4)Ti(CH_2Ph)_2$ (**7**; Scheme 4).[16]

The ^{13}C NMR spectra show the Ar *o*-C_{ipso} resonances of the cyclometalated arene group at δ 201.7 ppm for **6** and δ 200.6 ppm for **7**. The observed benzyl methylene $^2J_{HH}$ (9.5 Hz for **6** and 10 Hz for **7**), and $^1J_{CH}$ coupling constants (125 and 122 Hz, respectively) indicate η^1 coordination of the benzyl groups.[10]

Attempts to isolate **6** and **7** from preparative-scale thermolysis reactions (50 °C) in hexane or benzene reproducibly afforded viscous oils, which could not be crystallized. Isolation of the pure titanium dibenzyl species appears to be thwarted by the occurrence of further degradation via a secondary decomposition process, leading to product mixtures. Indeed, prolonged thermolysis of benzene-d_6 solutions of **1** or **2** (>12 h at 80 °C) leads to full decomposition of the initially formed cyclometalated dibenzyl species **6** and **7**. At the final stage of the decomposition (no changes of the ^1H NMR spectrum could be observed for 1 day), 1.3 (±0.1) equiv of toluene per titanium had been formed, as seen by comparison with an internal ferrocene standard. In addition, there is evidence for the formation of paramagnetic titanium species.[17] Oxidation of the product mixture with excess lead(II) chloride, a method used to cleanly oxidize Ti(III) to Ti(IV),[18] only revealed a complicated mixture of diamagnetic products that could not be characterized. This suggests that the secondary decomposition process leads to a mixture of paramagnetic species.

Reaction of **7** (prepared in situ in d_6-benzene) with 1 equiv of $B(C_6F_5)_3$ leads to benzyl abstraction, affording the ionic species **4**. Correspondingly, **7** reacts with $[Ph_3C][B(C_6F_5)_4]$ in d_5-bromobenzene to give compound **5**. Treatment of $(\eta^5{:}\eta^1\text{-}C_5H_4CMe_2\text{-}3,5\text{-}Me_2C_6H_2)Ti(CH_2Ph)_2$ (**6**) with $[Ph_3C][B(C_6F_5)_4]$ or $B(C_6F_5)_3$ in C_6D_5Br yields extremely thermally labile species that decompose within seconds, even at −30 °C, while in benzene-d_6, a brown oil separates from solution. Monitoring the

(15) Deckers, P. J. W. Ph.D. Dissertation, University of Groningen, 2002.

(16) For other examples of thermally induced ortho cyclometalation with comparable ligands, see: (a) Erker, G.; Mühlenbrend, T. *J. Organomet. Chem.* **1987**, *319*, 201. (b) Djakovitch, L.; Herrmann. W. A. *J. Organomet. Chem.* **1997**, *545/546*, 399. (c) Licht, E. H.; Alt, H. G.; Karim, M. M. *J. Organomet. Chem.* **2000**, *599*, 261. (d) Bulls, A. R.; Bercaw, J. E.; Manriquez, J. M.; Thompson, M. E. *Polyhedron* **1988**, *7*, 1409. (e) Licht, E. H.; Alt, H. G.; Milius, W.; Abu-Orabi, S. *J. Organomet. Chem.* **1998**, *560*, 69. (f) Djakovitch, L.; Herrmann, W. A. *J. Organomet. Chem.* **1998**, *562*, 71.

(17) The ^1H NMR spectrum obtained after complete thermolysis (24 h, 80 °C) only showed the toluene resonances. No precipitation was observed.

(18) (a) Luinstra, G. A.; Teuben, J. H. *J. Chem. Soc., Chem. Commun.* **1990**, 1470. (b) Van Leusen, D.; Beetstra, D. J.; Hessen, B.; Teuben, J. H. *Organometallics* **2000**, *19*, 4084.

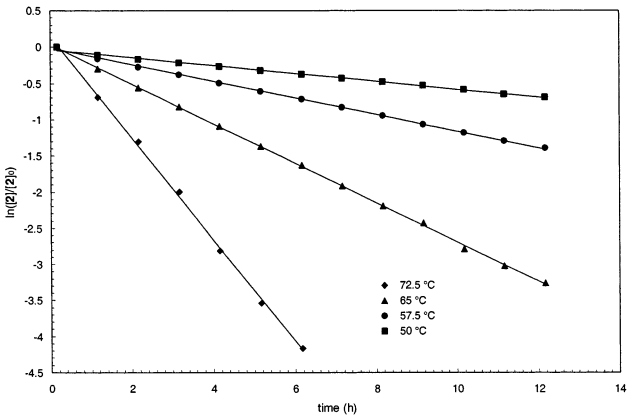


Figure 1. First-order kinetic plots of the thermolysis of **2** in C_6D_6 at different temperatures.

Table 1. Rate Constants of the Thermolysis of (η^5-$C_5H_4CMe_2Ph$)$Ti(CH_2Ph)_3$ (2)

T (°C)	solvent	[**2**] (10^{-2} M)	k_1 (10^{-5} s^{-1})	k_2 (10^{-6} s^{-1})
72.5	C_6D_6	2.6	19.5	14.8
65.0	C_6D_6	2.6	7.6	8.0
57.5	C_6D_6	2.6	3.2	2.6
50.0	C_6D_6	2.6	1.5	1.3
65.0	C_6D_6	1.3	7.5	–
65.0	C_6D_{12}	2.7	7.2	7.0
65.0	THF-d_8	2.5	5.6	16.7

reactions by ^{1}H NMR shows that additional toluene is liberated and that unidentified paramagnetic titanium species are formed. The decomposition pathway of **6** with $B(C_6F_5)_3$ appears to be different from that of [(η^5:η-$C_5H_4CMe_2$-3,5-$Me_2C_6H_3$)Ti(η-CH_2Ph)$_2$][$PhCH_2B(C_6F_5)_3$] (**3a**), since the ^{19}F NMR resonances of the $[B(C_6F_5)_4]^-$ anion, the formation of which accompanies the decomposition of the latter, are not observed here.

Kinetic Investigation of the Thermolysis of (η^5-$C_5H_4CMe_2Ph$)$Ti(CH_2Ph)_3$ (2). Despite the occurrence of secondary decomposition reactions, the kinetics of the initial thermolysis process could be investigated by monitoring the disappearance of the titanium tribenzyl complex (η^5-$C_5H_4CMe_2Ph$)$Ti(CH_2Ph)_3$ (**2**) in benzene-d_6 relative to an internal ferrocene standard. The reaction follows simple first-order kinetics for over 3 half-lives in the temperature range 50.0−72.5 °C (Figure 1), and the rate constants k_1 are independent of initial concentration (Table 1). The kinetic parameters were determined from an Eyring plot (of four k_1 determinations over the cited temperature range) as $\Delta H^{\ddagger} = 24 \pm 2$ kcal mol^{-1} and $\Delta S^{\ddagger} = -5 \pm 5$ cal mol^{-1} K^{-1} (Figure 2)[19]

The kinetics of the secondary degradation process were initally investigated in C_6D_6 at 72.5 °C for starting compound **2** by monitoring the disappearance of the initial thermolysis product (η^5:η^1-$C_5H_4CMe_2C_6H_4$)Ti-$(CH_2Ph)_2$ (**7**) relative to the internal ferrocene standard, after full conversion of **2**. The secondary process also follows simple first-order kinetics in **7** with a rate constant k_2 of 1.3×10^{-5} s^{-1}, an order of magnitude smaller than that found for the conversion of **2** to **7** at this temperature (Table 1). Assuming that the titanium tribenzyl species **2** is cleanly converted to the dibenzyl

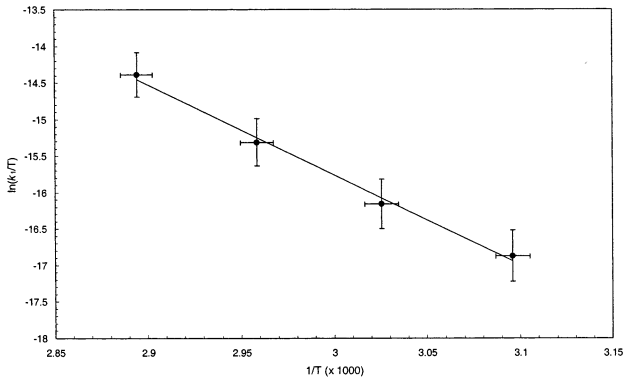


Figure 2. Eyring plot of the thermolysis of **2** in C_6D_6 (with error bars).

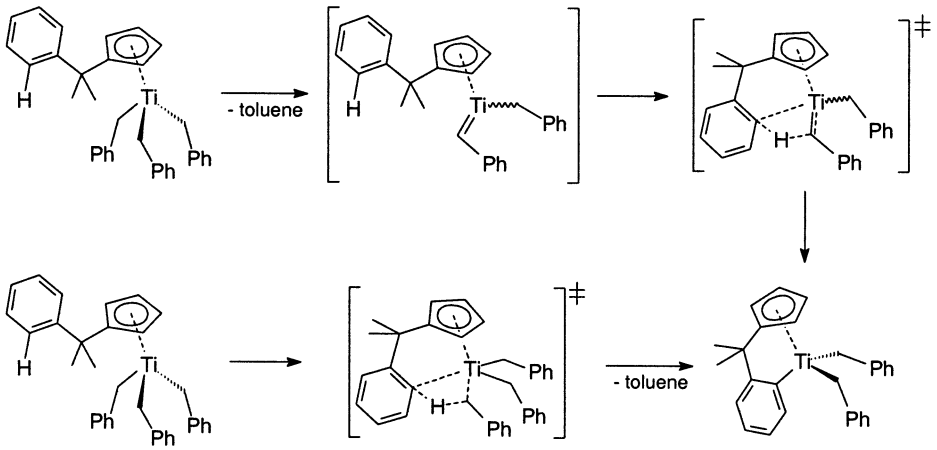
compound **7**, followed by a secondary decomposition of **7**, the overall disappearance of a diamagnetic signal relative to the internal standard can be used to determine the rate constant of the secondary degradation process, since all the organometallic species are completely soluble at the concentrations used and both decomposition processes are cleanly first-order and, thus, independent of concentration. Indeed, monitoring the disappearance of diamagnetic titanium species in C_6D_6 at 72.5 °C affords simple first-order kinetics with $k_2 = 1.5 \times 10^{-5}$ s^{-1}, equal (within experimental error) to the rate constant determined for the decomposition of **7**, thus indicating that there is no direct conversion of **2** to the secondary decomposition product. Similar analysis of the data from the experiments at other temperatures (Table 1) allowed the determination of the kinetic parameters for the secondary degradation process as $\Delta H^{\ddagger} = 24 \pm 2$ kcal mol^{-1} and $\Delta S^{\ddagger} = -11 \pm 5$ cal mol^{-1} K^{-1}.

Monitoring the thermolysis of **2** in cyclohexane-d_{12} and in THF-d_8 at 65.0 °C showed that the decomposition processes follow first-order kinetics in these solvents as well (Table 1). The rate constants in C_6D_{12} of $k_1 = 7.2 \times 10^{-5}$ s^{-1} and $k_2 = 7.0 \times 10^{-6}$ s^{-1} are close to those measured at 65 °C in benzene-d_6 ($k_1 = 7.6 \times 10^{-5}$ s^{-1}, $k_2 = 8.0 \times 10^{-6}$ s^{-1}). The disappearance of **2** in THF-d_8 proceeds at a slightly slower rate of $k_1 = 5.8 \times 10^{-5}$ s^{-1}. In contrast, the secondary degradation process takes place significantly more rapidly in THF ($k_2 = 1.7 \times 10^{-5}$ s^{-1}) than in benzene-d_6 and cyclohexane-d_{12}. These observations suggest either participation of THF solvent in the secondary decomposition process or significant differences in the polarity of the transition state for the two independent thermolysis processes, resulting in a lower rate constant in THF for the conversion of **2** to **7** but a higher rate constant for the degradation of **7**.

The first-order kinetics observed in the course of ortho cyclometalation of the ancillary ligand in the titanium tribenzyl species **2** to give **7** is consistent with an intramolecular pathway. The two most likely pathways for this transformation are (a) rate-determining formation of an electronically unsaturated benzylidene intermediate followed by rapid intramolecular addition of the aryl *o*-CH bond to the Ti=C bond (Scheme 5; top) and (b) direct σ-bond metathesis (Scheme 5, bottom). For the cyclometalation of the Cp−arene ligand in (η^5-$C_5H_4CMe_2Ph)_2Zr(C_6H_5)_2$, Erker and co-workers proposed initial formation of an η^2-benzyne intermediate followed by C−H bond addition.[16a] In contrast, cyclo-

(19) The errors in the kinetic parameters were calculated from the error propagation formulas derived from the Eyring equation. See: Morse, P. M.; Spencer, M. D.; Wilson, S. R.; Girolami, G. S. *Organometallics* **1994**, *13*, 1646.

Scheme 5



metalation in the half-sandwich niobium compound (η^5-$C_5H_4CMe_2Ph$)Nb{=N[2,6-(*i*-Pr)$_2C_6H_3$]}$(NMe_2)_2$ proceeds via direct σ-bond metathesis.[16b]

The kinetic parameters as determined for thermolysis of **2** of $\Delta H^{\ddagger} = 24 \pm 2$ kcal mol^{-1} and $\Delta S^{\ddagger} = -5 \pm 5$ cal mol^{-1} K^{-1} can be consistent with a pathway via a benzylidene intermediate. Bercaw and co-workers showed conclusively that the conversion of $Cp^*_2Hf(CH_2Ph)_2$ to $Cp^*_2Hf(CH_2$-*o*-$C_6H_4)$ proceeds through a benzylidene intermediate.[20] The entropy of activation of 1 ± 3 cal mol^{-1} K^{-1} for this reaction is similar to that observed for the disappearance of **2**. Other examples of processes involving alkylidene intermediates show similarly small entropy of activation values,[21] in contrast to most examples of direct σ-bond metathesis ($\Delta S^{\ddagger} = -10$ to -25 cal mol^{-1} K^{-1}).[22] However, the kinetic parameters are not conclusive proof as such for a reaction sequence involving an alkylidene intermediate. Reactions proceeding via an alkylidene can in some cases exhibit large negative entropies of activation,[23] and others, for which the involvement of an alkylidene species is highly unlikely, show very small $\Delta S^{\ddagger}$ values.[24] For example, Berg and co-workers recently found kinetic parameters similar to ours for the ortho cyclometalation of the pendant arene group in [(PhCHMe)N($CH_2CH_2CMe_2O$)$_2$]-$Zr(CH_2Ph)_2$. Although the entropy of activation suggests the possibility of a benzylidene intermediate, isotopic labeling experiments conclusively proved a direct σ-bond metathesis pathway.[25]

Deuterium Labeling Studies. To establish the mechanism of the ligand cyclometalation in the decomposition of **2**, isotopic labeling experiments were carried out. The partially labeled compound (η^5-$C_5H_4CMe_2C_6D_5$)Ti(CH_2Ph)$_3$ (**2-*d*$_5$**) was prepared via the same route as its nondeuterated analogue, but using C_6D_5Li instead of PhLi. The ^{1}H and ^{13}C NMR data of **2-*d*$_5$** are identical with those of **2** except for the signals of the perdeuteriophenyl group.

Thermolysis of **2-*d*$_5$** in benzene-d_6 (14 h, 65 °C) was monitored by ^{1}H and ^{13}C NMR spectroscopy. This revealed the gradual formation of 1 equiv of toluene, identified as being exclusively $C_6H_5CH_3$, and the formation of the titanium dibenzyl (η^5:η^1-$C_5H_4CMe_2C_6D_4$)Ti-(CH_2Ph)(CHDPh) (**7-*d*$_{4/1}$**). The methylene proton resonances of the Ti−CH_2Ph group in **7-*d*$_{4/1}$** are found at the same chemical shifts as those in **7**. The corresponding methylene ^{13}C NMR resonance consists of two singlets of equal intensity at δ 90.6 and 90.5 ppm (90.5 ppm for **7**), one for each of the two diastereomers (syn- and anticlinal; Scheme 6).[26] The methylene ^{1}H NMR resonances of the Ti−CHDPh group show a small upfield isotope shift ($\Delta\delta = -0.06$ ppm) and are observed as two singlets (the H−D coupling is not resolved) of equal intensity, indicating that the two diastereomers are formed in a 1:1 ratio (vide infra). The methylene carbon resonance is observed as a triplet at δ 89.6 ppm (isotope shifted by $\Delta\delta = -0.9$ ppm) with a $^1J_{CD}$ coupling constant of 19 Hz. Comparable isotope shifts and $^1J_{CD}$ coupling constants have been observed for the methylene group of the neopentyl ligand of (η^5-C_5H_5)$_2$Ti-($CHDCMe_3$)(C_6D_5).[23c]

The observations conclusively rule out a direct σ-bond metathesis pathway, which would have led to the formation of (η^5-$C_5H_4CMe_2C_6D_4$)Ti(CH_2Ph)$_2$ and α-*d*-toluene. The results confirm the involvement of a benzylidene intermediate (Scheme 5; top). Phosphines are known to be able to stabilize electronically unsaturated alkylidene species,[27] but attempts to trap the reactive benzylidene intermediate with PMe_3 in our systems failed, resulting only in the formation of ill-defined paramagnetic titanium species.

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(22) (a) Buchwald, S. L.; Nielsen, R. B. *J. Am. Chem. Soc.* **1988**, *110*, 3171. (b) Bruno, J. W.; Smith, G. M.; Marks, T. J.; Fair, C. K.; Schultz, A. J.; Williams, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 40. (c) Smith, G. M.; Carpenter, J. D.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 6805. (d) Bruno, J. W.; Marks, T. J.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 7357. (e) Hayes, P. G.; Piers, W. E.; Lee, L. W. M.; Knight, L. K.; Parvez, M.; Elsegood, M. J. R.; Clegg, W. *Organometallics* **2001**, *20*, 2533.

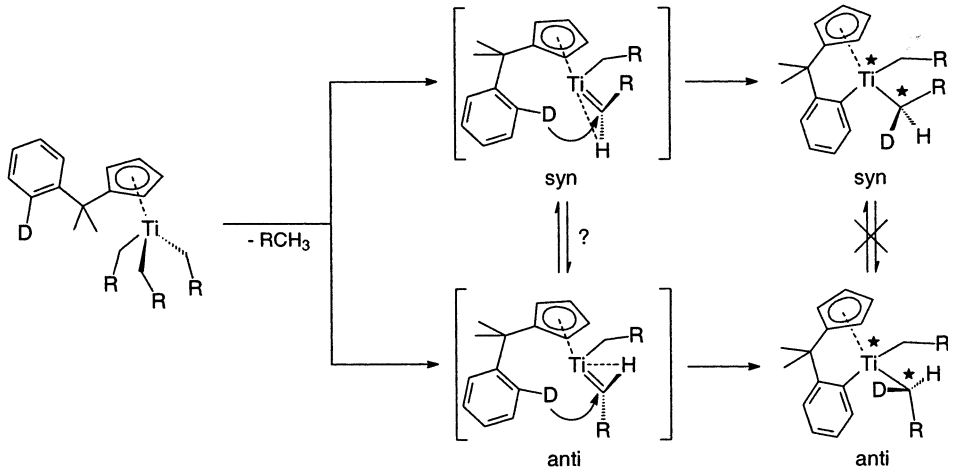
(23) (a) Amor Nait Ajjou, J.; Rice, G. L.; Scott, S. L. *J. Am. Chem. Soc.* **1998**, *120*, 13436. (b) Cheon, J.; Rogers, D. M.; Girolami, G. S. *J. Am. Chem. Soc.* **1997**, *119*, 6804. (c) Van der Heijden, H.; Hessen, B. *J. Chem. Soc., Chem. Commun.* **1995**, 145. (d) Legzdins, P.; Veltheer, J. E.; Young, M. A.; Batchelor, R. J.; Einstein, F. W. B. *Organometallics* **1995**, *14*, 407. (e) Schock, L. E.; Brock, C. P.; Marks, T. J. *Organometallics* **1987**, *6*, 232.

(24) (a) Fryzuk, M. D.; Haddad, T. S.; Rettig, S. J. *Organometallics* **1991**, *10*, 2027. (b) Cummins, C. C.; Baxter, S. M.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 8731.

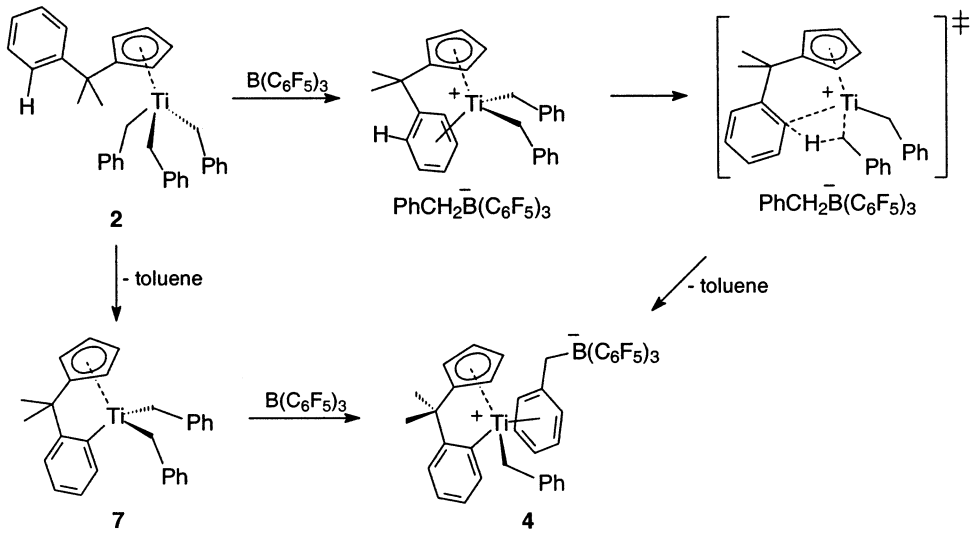
(25) Shao, P.; Gendron, R. A. L.; Berg, D. J.; Bushnell, G. W. *Organometallics* **2000**, *19*, 509.

(26) The synclinal and anticlinal diastereomers of the cyclometalated species are defined with respect to the orientation of the alkylidene substituents in the two possible alkylidene rotamers they are formed from (synclinal, alkylidene substituent pointing towards the Cp ligand; anticlinal, pointing away).

Scheme 6



Scheme 7



Only a very small deuterium isotope effect (k_H/k_D = 1.23 ± 0.05 at 65.0 °C) is observed for the thermolysis of **2-*d*$_5$**, indicating that the aryl ortho C−H/D bond is not broken in the transition state of the rate-determining step. For direct σ-bond metathesis, kinetic isotope effects of 5.2−6.6 have been reported.[22a,b] The small kinetic isotope effect gives additional evidence for the proposed benzylidene pathway.

In contrast to the observations made above for the ortho cyclometalation in the neutral complexes, the reaction of **2-*d*$_5$** with $B(C_6F_5)_3$ in C_6D_6 results in the selective formation of α-*d*-toluene and the contact ion pair $[(\eta^5{:}\eta^1\text{-}C_5H_4CMe_2C_6D_4)Ti(\eta^1\text{-}CH_2Ph)][\eta^6\text{-}PhCH_2B(C_6F_5)_3]$ (**4-*d*$_4$**). The ^{1}H NMR resonance of the CH_2D group in α-*d*-toluene is observed as a triplet at δ 2.08 ppm with a $^2J_{HD}$ coupling constant of 2.2 Hz, and the corresponding methyl ^{13}C NMR resonance is a triplet at δ 21.2 ppm with a $^1J_{CD}$ coupling constant of 19 Hz. Compound **4-*d*$_4$** has the same NMR characteristics as its nondeuterated analogue, except for the resonances of the perdeuteriophenyl ring.

The formation of α-*d*-toluene indicates that the ortho cyclometalation of the pendant arene group in the cationic species proceeds via σ-bond metathesis, in contrast to the benzylidene pathway identified for the ligand cyclometalation in the thermolysis of the neutral compound $(\eta^5\text{-}C_5H_4CMe_2Ph)Ti(CH_2Ph)_3$ (**2**) to **7**. Thus $B(C_6F_5)_3$ initially abstracts a benzyl group from the titanium tribenzyl species to form the *ansa*-cyclopentadienyl−phenyl titanium dibenzyl cation, which subsequently gives ortho C−H/D bond activation to afford the cyclometalated cationic species $\{[\eta^5{:}\eta^1\text{-}C_5H_4CMe_2C_6(H/D)_4]Ti(CH_2Ph)\}^+$ (Scheme 7) (the same product is obtained via benzyl abstraction with $B(C_6F_5)_3$ from the cyclometalated neutral species **7**; vide supra). The reaction is accompanied by a distinctive color change from brown to green. Although the reaction is too fast to determine the rate constants for the process, this color change allows a qualitative assessment of the isotope effect at ambient temperature. Solutions of **2** turn green within 10 s of the addition of $B(C_6F_5)_3$, whereas solutions of **2-*d*$_5$**/$B(C_6F_5)_3$ take about 3 min after mixing for a full color change. These observations suggest ortho C−H/D bond activation in the rate-determining step, confirming the proposed σ-bond metathesis pathway.

(27) (a) Cámpora, J.; Buchwald, S. L. *Organometallics* **1993**, *12*, 4182. (b) Bennett, M. A.; Schwemlein, H. P. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1296. (c) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047. (d) Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 7411.

Thermolysis of Other (η^5-$C_5H_4CMe_2Ph$)Ti(CH_2R)$_3$ Complexes (R = CMe_3, $SiMe_3$). For comparison with the (η^5-$C_5H_4CMe_2Ph$)Ti(CH_2Ph)$_3$ (**2**) system, the thermolysis behavior of two other trialkyl complexes (η^5-$C_5H_4CMe_2Ph$)Ti(CH_2R)$_3$ (R = CMe_3, $SiMe_3$) was studied. These alkyl groups are known to readily undergo α-H abstraction processes.[21c,28] A reaction of (η^5-$C_5H_4CMe_2Ph$)$TiCl_3$ with 3 equiv of $LiCH_2CMe_3$ in C_6D_6, performed in an NMR tube at ambient temperature, shows rapid release of 1 equiv of neopentane and formation of the ortho-cyclometalated titanium dialkyl species (η^5:η^1-$C_5H_4CMe_2C_6H_4$)Ti(CH_2CMe_3)$_2$ (**8**). Diagnostic for the formation of the ortho-cyclometalated pendant arene group is the ^{13}C NMR resonance for Ti−C_{ipso} observed at δ 195.5 ppm. The resonances for the diastereotopic methylene protons of the neopentyl ligands form an AB system at δ 2.72 and 2.26 ppm ($^2J_{HH}$ = 10.5 Hz). Repeated attempts to isolate **8** from reactions on a preparative scale afforded viscous oils that could not be crystallized, probably due to secondary degradation processes similar to those observed for the benzyl species.[29] In contrast with the tribenzyl complex **2**, the corresponding trineopentyl compound, (η^5-$C_5H_4CMe_2Ph$)Ti(CH_2CMe_3)$_3$, could not be isolated, even at −78 °C.

Treatment of (η^5-$C_5H_4CMe_2Ph$)$TiCl_3$ with 3 equiv of $LiCH_2SiMe_3$ in C_6D_6 at ambient temperature affords the titanium trialkyl species (η^5-$C_5H_4CMe_2Ph$)Ti(CH_2SiMe_3)$_3$ (**9**). The coordination chemical shifts of the ancillary ligand are comparable to those of **2**, and the ^1H NMR resonance of the methylene protons of the neosilyl ligands is found as a singlet at δ 1.73 ppm. Compound **9** can be obtained on a preparative scale in good yield from (η^5-$C_5H_4CMe_2Ph$)$TiCl_3$ and 3 equiv of $ClMgCH_2SiMe_3$ in diethyl ether as a brown oil of >95% purity (NMR), which could not be crystallized.

Warming benzene-d_6 solutions of **9** at 50 °C for 70 h leads to liberation of 1 equiv of tetramethylsilane and the formation of the titanium dineosilyl species with an ortho-cyclometalated arene group, (η^5:η^1-$C_5H_4CMe_2C_6H_4$)Ti(CH_2SiMe_3)$_2$ (**10**). The Ti−C_{ipso} ^{13}C NMR resonance is observed at δ 198.6 ppm, and the methylene proton resonances of the neosilyl ligands appear as two doublets at δ 2.27 and 2.05 ppm ($^2J_{HH}$ = 10.8 Hz).

The mechanistic aspects of the formation of the neopentyl and neosilyl ortho-cyclometalated dialkyl titanium complexes **8** and **10** are similar to those previously outlined for the dibenzyl species **7**. Reaction of (η^5-$C_5H_4CMe_2C_6D_5$)$TiCl_3$ with 3 equiv of $LiCH_2CMe_3$ on an NMR-tube scale gives release of 1 equiv of neopentane-d_0 and the formation of the titanium dialkyl species (η^5:η^1-$C_5H_4CMe_2C_6D_4$)Ti(CH_2CMe_3)($CHDCMe_3$) (**8-*d*$_{4/1}$**), similar to the conversion of the deuterated tribenzyl compound **2-*d*$_5$** to **7-*d*$_{4/1}$**, indicating the presence of a neopentylidene intermediate. In contrast to the dibenzyl species **7-*d*$_{4/1}$**, the two diastereomers of **8-*d*$_{4/1}$** are not formed in a 1:1 ratio. The methylene proton resonance of the Ti−$CHDCMe_3$ group appears as two singlets at δ 2.65 and 2.18 ppm in the ratio 15:85.

Addition of the ortho C−D bond to the Ti=C bond is expected to proceed selectively in a cis fashion[30] to generate the cyclometalated species **7-*d*$_{4/1}$** and **8-*d*$_{4/1}$** with two stereogenic centers, giving rise to diastereomers (Scheme 6). Apparently, the two possible isomers of the neopentylidene intermediate (syn and anti)[26] are not formed in equal quantities. On the basis of arguments formulated by Gibson for tetrahedral alkylidene complexes with one dominant π-donor ligand that possesses two orbitals of π-symmetry, such as Cp, the substituent on the alkylidene ligand in the electronically most favorable isomer is expected to point in the direction of that π-donor (synclinal rotamer).[31] For the monocyclopentadienyl group 4 alkylidene species [η^5:η^1-$C_5H_4CH_2CH_2N(t\text{-}Bu)$]Ti(=CHR)($PMe_3$)[13a] and {$\eta^5$-$C_5H_3$-1,3-[$SiMe_2CH_2P(i\text{-}Pr)_2$]$_2$}Zr(=CHR)Cl[32] (and its Hf analog),[33] NOESY NMR spectroscopy and X-ray analysis, respectively, indeed indicate the formation of the synclinal rotamer. The orientation is supplemented by agostic interaction of the α-H with the metal center[34] and is generally retained in the solution structure. On the other hand, ready syn/anti isomerization has been reported for Mo(CHR)(NAr)(OR′)$_2$ species ($\Delta G^{\ddagger}$ = 16−18 kcal mol^{-1}),[35] even at temperatures as low as −70 °C,[36] and Re(CR)(CHR′)(OR″)$_2$ species ($\Delta G^{\ddagger}$ = 25−30 kcal mol^{-1}),[37] and the molybdenum complexes were found to display a marked difference in reactivity between the anti and the syn isomer, e.g. in olefin metathesis.[38]

On the basis of the data available we cannot establish whether, in the transformation of (η^5-$C_5H_4CMe_2C_6D_5$)Ti(CH_2Ph)$_3$ (**2-*d*$_5$**) to **7-*d*$_{4/1}$**, the benzylidene intermediate is immediately formed as a 1:1 syn/anti mixture or if rapid rotation around the Ti=C bond,[39] combined with a difference in reactivity between the syn and anti rotamers, leads effectively to the observed 1:1 diastereomer mixture. This lower distereoselectivity may also be associated with the higher reaction temperatures required for the decomposition of **2** compared to that of **8**.

The instantaneous ortho cyclometalation of the transient trineopentyl complex (η^5-$C_5H_4CMe_2Ph$)Ti(CH_2CMe_3)$_3$ precludes a kinetic study of this system. An analysis of the reaction kinetics for the thermolysis of the neosilyl complex **9** was conducted by ^1H NMR, for reactions at 50.0, 57.5, 65.0, and 72.5 °C, relative to an internal ferrocene standard. In all instances, the primary thermolysis of **9** follows first-order kinetics (Table 2) and an overall disappearance of the diamagnetic

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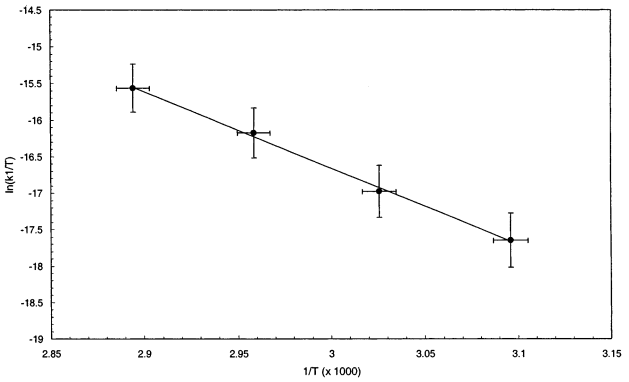

Figure 3. Eyring plot of the thermolysis of **9** in C_6D_6 (with error bars).

Table 2. Rate Constants of the Thermolysis of (η^5-$C_5H_4CMe_2Ph$)$Ti(CH_2SiMe_3)_3$ (9) in C_6D_6

T (°C)	[**9**] (10^{-2} M)	k_1 (10^{-5} s^{-1})
72.5	2.6	6.0
65.0	2.7	3.2
57.5	2.5	1.4
50.0	2.6	0.7

signal by a secondary process can be observed, similar to the decomposition pattern observed for the benzyl derivative **2**. The corresponding Eyring plot is shown in Figure 3, from which the activation parameters $\Delta H^{\ddagger} = 21 \pm 2$ kcal mol^{-1} and $\Delta S^{\ddagger} = -18 \pm 4$ cal mol^{-1} K^{-1} are obtained for the primary process.

The general trend reported in the literature for the relative rates of alkylidene formation from metal dialkyl complexes follows the order neopentyl > neosilyl > benzyl, which reflects faster rate-determining α-H abstraction for complexes with alkyl ligands that provide greater steric congestion at the metal center. For example, for the first-order decomposition of $Ta(CH_2R)_5$ (R = Ph, $SiMe_3$, CMe_3), the rate constants follow the order Ph ($k = 4.3 \times 10^{-5}$ s^{-1}, at 313 K)[40] < $SiMe_3$ ($k = 3.5 \times 10^{-4}$ s^{-1}, 311 K)[21c] < CMe_3 (too fast to monitor).[21c] Our results indicate a deviation from this trend for the complexes studied here. Whereas the neopentyl species eliminates neopentane very rapidly, even at low temperatures, comparison of the first-order rate constants in Tables 1 and 2 for the other trialkyl species reveals a slower rate of α-H abstraction (expressed in the rate constant k_1) of neosilyl **9** versus benzyl **2** over the temperature range studied. Similar behavior has been observed by Fryzuk and co-workers for the {η^5-C_5H_3-1,3-[$SiMe_2CH_2P(i\text{-}Pr)_2$]$_2$}$Zr(CH_2R)_2Cl$ (R = Ph, $SiMe_3$, CMe_3) system, in which a reversal of the trend in rates is observed (Ph > $SiMe_3$ > CMe_3).[32b] In these compounds coordination of the two sterically demanding phosphine groups, attached to sidearms on the Cp ligand, is required in the transition state for alkylidene formation. This becomes less favorable with increasing bulk of the alkyl ligands and helps to explain the otherwise anomalous observation that the more sterically demanding alkyl ligands are thermally less reactive.

While the enthalpies of activation, associated with the rate-determining α-H abstraction step, are similar for the benzyl and neosilyl complexes (24 kcal mol^{-1} for **2** and 21 kcal mol^{-1} for **9**), a large difference in the entropy of activation is observed. As mentioned above, the $\Delta S^{\ddagger}$ value of −5 cal mol^{-1} K^{-1} for the initial decomposition of the tribenzyl complex **2** is in accord with the small negative values of −1 to −10 cal mol^{-1} K^{-1} typically observed for the majority of C−H bond abstraction processes studied.[21] The result for the trineosilyl compound **9** ($\Delta S^{\ddagger} = -18$ cal mol^{-1} K^{-1}) shows considerable departure from these values but compares well with the activation parameters found for the thermolysis of {η^5-C_5H_3-1,3-[$SiMe_2CH_2P(i\text{-}Pr)_2$]$_2$}$Zr(CH_2Ph)_2Cl$ ($\Delta H^{\ddagger} = 19$ kcal mol^{-1}, $\Delta S^{\ddagger} = -22$ cal mol^{-1} K^{-1}).[32b] The more negative entropy of activation for **9** suggests a more ordered transition state for alkylidene formation with respect to that of **2**. Applying Fryzuk's arguments (vide supra) for our systems, the pendant arene group may perform a similar function as the pendant phosphine arms in those systems in the alkylidene formation. Interaction of the arene moiety with the metal center could facilitate α-H elimination and give a more negative entropy of activation due to the more ordered transition state. It may be noted that in $Cp(O-PR_2)Ti(CH_2CMe_3)_2$ systems (O−PR_2 = phosphino-alkoxide ligand), the pendant phosphine is not coordinated to the titanium center in the dineopentyl compound but does coordinate in the neopentylidene complex $Cp(O-PR_2)Ti(=CHCMe_3)$.[41] Similarly, it may be possible that multihapto (probably η^2) coordination of the benzyl ligands in the tribenzyl species **2** can help to induce α-H elimination. The availability of three benzyl groups in **2** that can potentially facilitate alkylidene formation (in addition to the pendant arene on the Cp ligand) could then lead to a less strongly negative entropy of activation compared to that for the trialkyl **9**. Another system in which benzyl-assisted α-H elimination may occur is in the transformation of $Cp^*W(NO)(CH_2CMe_3)(CH_2R)$ (R = CMe_3, Ph) in benzene-d_6 to give neopentane and $Cp^*W(NO)(CHDR)(C_6D_5)$ via rate-limiting alkylidene formation and subsequent C−D addition of benzene-d_6. The first-order rate constant is higher for the mixed benzyl/neopentyl species than for the sterically more demanding dineopentyl species.[39]

Conclusions

The cationic dibenzyl species [(η^5:η^6-$C_5H_4CMe_2Ph$)$Ti(CH_2Ph)_2$]$^+$ decomposes rapidly at ambient temperature by metalation of the pendant arene group on the cyclopentadienyl ligand, via a σ-bond metathesis pathway. The observation that the cationic dimethyl species [(η^5:η^6-$C_5H_4CMe_2Ph$)$TiMe_2$]$^+$ is more stable toward cyclometalation than the dibenzyl analogue suggests that initial displacement of the coordinated arene is required for cyclometalation. In the [(η^5:η^6-$C_5H_4CMe_2Ph$)$Ti(CH_2Ph)_2$]$^+$ cation this is likely to be compensated for or assisted by η^2 bonding of the benzyl group(s), something which is not possible for the analogous dimethyl cationic species.

The neutral (η^5-$C_5H_4CMe_2Ph$)$Ti(CH_2R)_3$ (R = Ph, CMe_3, $SiMe_3$) complexes decompose via rate-determining α-H elimination to give alkylidene intermediates, followed by rapid intramolecular addition of the *o*-CH bond of the pendant arene group to the Ti=C bond of the intermediate. The unusual order of reactivity (R =

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CMe_3 > Ph > $SiMe_3$), combined with the significantly negative entropy of activation for the R = $SiMe_3$ system, suggest that here interaction of the aromatic moieties (either the pendant arene group or the metal-bound benzyl groups in the case of R = Ph) with the metal center can assist the α-H elimination process, possibly through alleviating the electron deficiency of the incipient 12-electron CpTi−alkyl−alkylidene species.

Experimental Section

General Comments. All experiments were carried out under a purified nitrogen atmosphere using standard Schlenk and glovebox techniques. Deuterated solvents (Aldrich, Acros) were either degassed and dried over 4 Å molecular sieves (C_6D_5Br) or dried over Na/K alloy and vacuum-transferred before use (C_6D_6, toluene-d_8, THF-d_8). Diethyl ether and pentane (Aldrich) were distilled from Na/K alloy prior to use. Methylene chloride (Aldrich) was dried on 4 Å molecular sieves before use.

The starting materials (η^5-$C_5H_4CMe_2Ar$)$TiCl_3$,[3] $B(C_6F_5)_3$,[42] $[Ph_3C][B(C_6F_5)_4]$,[43] $LiCH_2CMe_3$,[44] and $LiCH_2SiMe_3$[45] were prepared according to published procedures. $C_5H_4(SiMe_3)CMe_2C_6D_5$ was prepared analogously to $C_5H_4(SiMe_3)CMe_2Ph$,[3b] and $PhCH_2$-MgBr was prepared from Mg and $PhCH_2Br$ (Aldrich, used as received) in diethyl ether.

NMR spectra were recorded on Varian Gemini 200/300 and Unity 500 spectrometers in NMR tubes equipped with a Teflon (Young) valve. The ^1H NMR spectra were referenced to resonances of residual protons in the deuterated solvents (δ 7.15 ppm for C_6D_6, δ 2.15 ppm for methyl resonance of toluene-d_8, δ 7.28 ppm for downfield signal of C_6D_5Br, δ 7.24 ppm for $CDCl_3$). The ^{13}C NMR spectra were referenced to the carbon resonances of the deuterated solvent (δ 128 ppm for C_6D_6, δ 137.5 ppm for C_{ipso} for toluene-d_8, δ 122.4 ppm for C_{ipso} for C_6D_5Br). Chemical shifts (δ) are given relative to tetramethylsilane (downfield shifts are positive); J values are given in hertz. Elemental analyses were performed at the Microanalytical Department of the University of Groningen. Given values are the average of at least two independent determinations. For the compounds **1, 2**, and **2-*d*$_5$** the found carbon content is consistently and reproducibly too low, whereas the values for Ti and H are in reasonable agreement. We have observed this phenomenon previously for Ti compounds with all-carbon ligation. It is likely to be associated with the formation of inert Ti carbides upon combustion.

Preparation of (η^5-$C_5H_4CMe_2$-3,5-$Me_2C_6H_3$)$Ti(CH_2Ph)_3$ (1). To a stirred solution of 0.48 g (1.31 mmol) of the corresponding titanium trichloride in diethyl ether (−40 °C) was added 3.94 mmol of $PhCH_2MgBr$ dropwise as a solution in diethyl ether (1.26 M). The reaction mixture was warmed to room temperature and was subsequently stirred for 3 h. The volatiles were removed in vacuo, and the residue was stirred with 10 mL of pentane, which was subsequently pumped off. The red solid was extracted with pentane, and concentration and cooling to −40 °C gave dark red crystals of **1** in 70% yield (0.49 g, 0.92 mmol). ^1H NMR (500 MHz, C_6D_6): δ 7.15 (t, $^3J_{HH}$ = 7.5, 6H, Bz *m-H*), 6.95 (s, 2H, Ar *o-H*), 6.90 (t, $^3J_{HH}$ = 7.5, 3H, Bz *p-H*), 6.82 (d, $^3J_{HH}$ = 7.5, 6H, Bz *o-H*), 6.70 (s, 1H, Ar *p-H*), 5.80 (ps t, $^3J_{HH}$ = 2.8, 2H, Cp *H*), 5.51 (ps t, $^3J_{HH}$ = 2.8, 2H, Cp *H*), 2.99 (s, 6H, Ti−CH_2), 2.16 (s, 6H, ArCH_3), 1.45 (s, 6H, C(CH_3)$_2$). ^{13}C NMR (125.7 MHz, C_6D_6): δ 149.4 (s, Ar C_{ipso}), 149.2 (s, Bz C_{ipso}), 147.3 (s, Cp C_{ipso}), 137.7 (s, Ar *m*-C_{ipso}), 128.8 (dm, $^1J_{CH}$ = 156, Bz *m-C*H, overlap with solvent), 128.3 (dm, $^1J_{CH}$ = 131, Ar *p-C*H, overlap with solvent), 127.0 (dm, $^1J_{CH}$ = 153, Bz *o-C*H), 124.5 (d, $^1J_{CH}$ = 155, Ar *o-C*H), 123.0 (d, $^1J_{CH}$ = 160, Bz *p-C*H), 118.4 (dm, $^1J_{CH}$ = 171, Cp *C*H), 113.5 (dm, $^1J_{CH}$ = 172, Cp *C*H), 93.5 (t, $^1J_{CH}$ = 124, Ti-*C*H_2), 40.4 (s, *C*(CH$_3$)$_2$), 30.3 (q, $^1J_{CH}$ = 122, C(*C*H$_3$)$_2$), 21.6 (q, $^1J_{CH}$ = 126, Ar*C*H$_3$). Anal. Calcd for $C_{37}H_{40}Ti$: C, 83.44; H, 7.57; Ti, 8.99. Found: C, 82.54; H, 7.62; Ti, 8.76.

Preparation of (η^5-$C_5H_4CMe_2Ph$)$Ti(CH_2Ph)_3$ (2). To a stirred solution of 0.52 g of (η^5-$C_5H_4CMe_2Ph$)$TiCl_3$ (1.54 mmol) in 30 mL of diethyl ether, cooled to −40 °C, was added a solution of benzylmagnesium bromide (4.62 mmol) in diethyl ether (1.26 M) dropwise. The mixture was warmed to room temperature and was stirred for 3 h. The solvent was removed in vacuo, after which the red solid was extracted with pentane. Cooling to −40 °C yielded red crystals of **2** (0.56 g, 1.11 mmol, 72%). ^1H NMR (500 MHz, C_6D_6): δ 7.17−7.11 (m, 10H, Ph *m-* and *o-H* and Bz *m-H*), 7.02 (m, 1H, Ph *p-H*), 6.90 (t, $^3J_{HH}$ = 7.5, 3H, Bz *p-H*), 6.81 (d, $^3J_{HH}$ = 7.5, 6H, Bz *o-H*), 5.74 (ps t, $^3J_{HH}$ = 2.8, 2H, Cp *H*), 5.50 (ps t, $^3J_{HH}$ = 2.8, 2H, Cp *H*), 2.97 (s, 6H, Ti−CH_2), 1.38 (s, 6H, C(CH_3)$_2$). ^{13}C NMR (125.7 MHz, C_6D_6): δ 149.6 (s, Ph C_{ipso}), 149.1 (s, Bz C_{ipso}), 146.7 (s, Cp C_{ipso}), 128.8 (dm, $^1J_{CH}$ = 158, Bz *m-C*H, overlap with solvent), 128.5 (d, $^1J_{CH}$ = 151, Ph *m-C*H, overlap with solvent), 127.0 (dm, $^1J_{CH}$ = 161, Bz *o-C*H), 126.5 (dm, $^1J_{CH}$ = 156, Ph *o-C*H), 126.4 (dm, $^1J_{CH}$ = 156, Ph *p-C*H), 123.0 (dm, $^1J_{CH}$ = 160, Bz *p-C*H), 118.4 (dm, $^1J_{CH}$ = 168, Cp *C*H), 113.5 (dm, $^1J_{CH}$ = 172, Cp *C*H), 93.5 (t, $^1J_{CH}$ = 123, Ti-*C*H_2), 40.5 (s, *C*(CH$_3$)$_2$), 30.2 (q, $^1J_{CH}$ = 122, C(*C*H$_3$)$_2$). Anal. Calcd for $C_{35}H_{36}Ti$: C, 83.32; H, 7.19; Ti, 9.49. Found: C, 82.63; H, 7.32; Ti, 9.35.

Generation of [(η^5:η-$C_5H_4CMe_2$-3,5-$Me_2C_6H_3$)$Ti(\eta$-$CH_2Ph)_2$][$PhCH_2B(C_6F_5)_3$] (3a). A solution of 37 mg (69 μmol) of (η^5-$C_5H_4CMe_2$-3,5-$Me_2C_6H_3$)$Ti(CH_2Ph)_3$ (**1**) in 0.25 mL of C_6D_5Br (−30 °C) was added to a solution of 36 mg (70 μmol) of $B(C_6F_5)_3$ in 0.25 mL of C_6D_5Br (−30 °C) to obtain a deep red solution of the cationic complex **3a**. ^1H NMR (500 MHz, C_6D_5Br, −30 °C): δ 7.18 (br, 2H, B−Bz *m-H*), 7.04 (br, 2H, B−Bz *o-H*, partial overlap with solvent), 6.99 (s, 6H, Ti−Bz *m-* and *p-H*), 6.62 (s, 1H, Ar *p-H*), 6.58 (s, 2H, Ar *o-H*), 6.46 (s, 2H, Cp *H*), 6.14 (s, 4H, Ti−Bz *o-H*), 4.84 (s, 2H, Cp *H*), 3.36 (br, 2H, B−CH_2), 2.88 (s, 4H, Ti−CH_2), 2.21 (s, 6H, ArCH_3), 1.03 (s, 6H, C(CH_3)$_2$). ^{13}C NMR (125.7 MHz, C_6D_5Br, −30 °C): δ 148.8 (d, $^1J_{CF}$ = 240, *o-C*F), 146.0 (s, Ar C_{ipso}), 144.8 (s, Cp C_{ipso}), 142.0 (s, Ar *m*-C_{ipso} or Ti−Bz C_{ipso}), 140.2 (s, Ar *m*-C_{ipso} or Ti−Bz C_{ipso}), 138.0 (d, $^1J_{CF}$ = 240, *p-C*F and s, B−Bz C_{ipso}), 137.0 (d, $^1J_{CF}$ = 240, *m-C*F), 136.8 (d, $^1J_{CH}$ = 164, Ti−Bz *m-C*H), 129.6−128.8 (Ti−Bz *p-C*H, Ar *p-C*H, B−Bz *o-C*H, B−Bz *p-C*H, B−Bz *m-C*H, overlap with solvent), 127.0 (d, $^1J_{CH}$ = 161, Ti−Bz *o-C*H), 123.1 (d, $^1J_{CH}$ = 180, Cp *C*H), 123.0 (d, $^1J_{CH}$ = 154, Ar *o-C*H), 119.7 (d, $^1J_{CH}$ = 174, Cp *C*H), 101.5 (t, $^1J_{CH}$ = 148, Ti−*C*H_2), 40.3 (s, *C*(CH$_3$)$_2$), 32.4 (br, B−*C*H_2), 28.7 (q, $^1J_{CH}$ = 127, C(*C*H$_3$)$_2$), 22.1 (q, $^1J_{CH}$ = 128, Ar*C*H$_3$). ^{19}F NMR (188.2 MHz, C_6D_5Br, −30 °C): δ −128.4 (*o-F*), −160.5 (*p-F*), −163.5 (*m-F*).

Reaction of 3a with THF-*d*$_8$. To a deep brown solution of **3a** in C_6D_5Br, prepared as described above, was added a drop of THF-d_8, resulting in a red solution of [(η^5-$C_5H_4CMe_2$-3,5-$Me_2C_6H_3$)$Ti(CH_2Ph)_2$(THF-d_8)$_x$][$PhCH_2B(C_6F_5)_3$]. ^1H NMR (500 MHz, C_6D_5Br/THF-d_8, −30 °C): δ 7.25−6.5 (18H, aromatic protons), 6.11 (s, 2H, Cp *H*), 5.90 (s, 2H, Cp *H*), 3.28 (br, 2H, B−CH_2), 3.19 (d, $^2J_{HH}$ = 9.2, 2H, Ti−CH_2), 2.19 (s, 6H, ArCH_3), 2.18 (2H, Ti−CH_2, overlapped by ArCH_3), 1.32 (s, 6H, C(CH_3)$_2$). ^{13}C NMR (125.7 MHz, C_6D_5Br/THF-d_8, −30 °C): δ 151.1, 148.7, 146.1, 142.1, 138.3 (s, Ar, Cp, Ti−Bz, and B−Bz C_{ipso}), 148.6 (d, $^1J_{CF}$ = 237, *o-C*F), 137.8 (d, $^1J_{CF}$ = 246, *p-C*F), 136.8 (d, $^1J_{CF}$ = 249, *m-C*F), 132−122 (aromatic *C*H, overlapped by solvent), 121.2 (d, $^1J_{CH}$ = 174, Cp *C*H), 117.4 (d, $^1J_{CH}$ = 169, Cp *C*H), 107.0 (t, $^1J_{CH}$ = 129, Ti−*C*H_2), 40.4 (s, *C*(CH$_3$)$_2$), 32.5 (br, B−*C*H_2), 30.2 (q, $^1J_{CH}$ = 126, C(*C*H$_3$)$_2$), 22.7 (q, $^1J_{CH}$ = 127, Ar*C*H$_3$).

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Generation of [(η^5:η-$C_5H_4CMe_2$-3,5-$Me_2C_6H_3$)Ti(η-CH_2Ph)$_2$][$B(C_6F_5)_4$] (3b). A solution of 25 mg (47 μmol) of **1** in 0.25 mL of C_6D_5Br (−30 °C) was added to a solution of 43 mg (48 μmol) of $B(C_6F_5)_3$ in 0.25 mL of C_6D_5Br (−30 °C) to obtain a deep brown solution containing the cationic complex **3b** and Ph_3CCH_2Ph. ^{1}H NMR (500 MHz, C_6D_5Br, −30 °C): δ 7.2−6.1 (33H, aromatic protons, ill-resolved), 6.33 (s, 2H, Cp *H*), 4.85 (s, 2H, Cp *H*), 3.78 (s, 2H, Ph_3CCH_2Ph), 2.90 (s, 4H, Ti−CH_2), 2.21 (s, 6H, ArCH_3), 1.04 (s, 6H, $C(CH_3)_2$). ^{13}C NMR (125.7 MHz, C_6D_5Br, −30 °C): δ 148.6 (d, $^1J_{CF}$ = 240, *o*-*C*F), 146.7, 146.0, 144.5, 144.0, 143.0, 141.7, 139.9, 138.4, 136.5 (s, Ar, Cp, Ti−Bz, B−Bz, and Ph_3CCH_2Ph C_{ipso}), 138.5 (d, $^1J_{CF}$ = 235, *p*-*C*F), 136.6 (d, $^1J_{CF}$ = 241, *m*-*C*F), 132−122 (aromatic *C*H and Cp *C*H, overlapped by solvent), 119.4 (d, $^1J_{CH}$ = 169, Cp *C*H), 101.2 (t, $^1J_{CH}$ = 147, Ti−CH_2), 58.6 (s, Ph_3CCH_2Ph), 45.9 (t, $^1J_{CH}$ = 128, Ph_3CCH_2Ph), 40.1 (s, $C(CH_3)_2$), 28.4 (q, $^1J_{CH}$ = 126, $C(CH_3)_2$), 21.8 (q, $^1J_{CH}$ = 128, ArCH_3).

Preparation of [(η^5:η^1-$C_5H_4CMe_2C_6H_4$)Ti(CH_2Ph)][η^6-$PhCH_2B(C_6F_5)_3$] (4). At −40 °C, a solution of (η^5-$C_5H_4CMe_2$-Ph)Ti(CH_2Ph)$_3$ (**2**; 430 mg, 0.85 mmol) in 20 mL of pentane was added to a solution of 440 mg (0.86 mmol) of $B(C_6F_5)_3$ in 20 mL of pentane. A green precipitate was instantaneously formed. The supernatant was decanted. The green residue was brought on a glass frit and was thoroughly rinsed with pentane to yield 520 mg (0.56 mmol, 66%) of analytically pure **4** (for labels, see Scheme 2). ^{1}H NMR (500 MHz, toluene-d_8, −30 °C): δ 6.88 (t, $^3J_{HH}$ = 7.7, 2H, Ti−Bz *m*-*H*), 6.73 (m, 3H, Ti−Bz *p*-*H* and H6,8), 6.65 (t, $^3J_{HH}$ = 7.5, 1H, H7), 6.46 (d, $^3J_{HH}$ = 8.1, 1H, H5), 6.44 (d, $^3J_{HH}$ = 8.1, 1H, B−Bz *o*-*H*), 6.28 (d, $^3J_{HH}$ = 7.7, 1H, B−Bz *o*-*H*′), 6.20 (t, $^3J_{HH}$ = 7.3, 1H, B−Bz *m*-*H*), 5.91 (d, $^3J_{HH}$ = 7.3, 2H, Ti−Bz *o*-*H*), 5.88 (s, 1H, *1*), 5.86 (t, 1H, H11, partial overlap), 5.84 (s, 1H, H4), 5.62 (t, $^3J_{HH}$ = 7, B−Bz *m*-*H*′), 5.11 (s, 1H, H3), 4.82 (s, 1H, H2), 3.39 (br, 1H, H13), 2.80 (d, $^2J_{HH}$ = 10, 1H, H9), 2.8 (br, 1H, H12, overlap with H9), 1.15 (s, 3H, $C(CH_3)_2$), 0.81 (d, $^2J_{HH}$ = 10, 1H, H10), 0.73 (s, 3H, $C(CH_3)_2$). ^{13}C NMR (125.7 MHz, toluene-d_8, −30 °C): δ 199.7 (Ph *o*-C_{ipso}), 170.9 (Cp C_{ipso}), 160.5, 157.3, 150.4 (Ph, Ti−Bz, B−Bz C_{ipso}), 148.5 (d, $^1J_{CF}$ = 238, *o*-*C*F), 139.0 (d, $^1J_{CF}$ = 238, *p*-*C*F), 137.4 (d, $^1J_{CF}$ = 238, *m*-*C*F), 134.7 (B−Bz *m*-*C*H), 132.0 (C6 or C8), 131.2 (B−Bz *o*-*C*H), 130.9 (B−Bz *m*-*C*H′), 128.5 (Ti−Bz *p*-*C*H, overlap with solvent), 127.7 (Ti−Bz *m*-*C*H, overlap with solvent), 126.5 (Ti−Bz *o*-*C*H), 125.5−124.5 (B−Bz *o*-*C*H′, C1, C5, C11, overlap with solvent), 124.0 (C6 or C8), 123.9 (C4), 122.6 (C7), 116.1 (C3), 111.2 (C2), 93.3 (Ti−CH_2, $^1J_{CH}$ = 126), 43.6 ($C(CH_3)_2$), 35.3 (br, B−CH_2), 29.7, 28.9 ($C(CH_3)_2$). ^{19}F NMR (188.2 MHz, C_6D_6): δ −132.8 (d, $^3J_{FF}$ = 22.8, 2F, *o*-*F*), −162.3 (t, $^3J_{FF}$ = 21.6, 1F, *p*-*F*), −166.5 (m, 2F, *m*-*F*). Anal. Calcd for $C_{46}H_{28}TiBF_{15}$: C, 59.77; H, 3.05; Ti, 5.18. Found: C, 59.61; H, 3.11; Ti, 5.08.

Generation of [(η^5:η^1-$C_5H_4CMe_2C_6H_4$)Ti(η^2-CH_2Ph)]-[$B(C_6F_5)_4$] (5). A solution of 10.2 mg (20 μmol) of **5** in 0.6 mL of bromobenzene-d_5 was added to 18.5 mg (20 μmol) of [Ph_3C]-[$B(C_6F_5)_4$] in an NMR tube equipped with a Teflon (Young) valve. This resulted in a brown solution containing Ph_3CCH_2Ph, toluene, and the thermally labile species **5**. ^{1}H NMR (500 MHz, C_6D_5Br, −30 °C): δ 7.8−6.6 (34H, aromatic protons, ill-resolved), 5.91 (br, $W_{1/2}$ = 33, 1H, Cp *H*), 5.52 (br, $W_{1/2}$ = 33, 1H, Cp *H*), 5.38 (br, $W_{1/2}$ = 33, 1H, Cp *H*), 4.79 (br, $W_{1/2}$ = 33, 1H, Cp *H*), 3.88 (br, $W_{1/2}$ = 37, 1H, Ti−CH_2), 3.77 (s, 2H, Ph_3CCH_2Ph), 2.16 (s, 4H, $C_6H_5CH_3$ and Ti−CH_2), 1.24 (br, 3H, $C(CH_3)_2$), 1.07 (br, 3H, $C(CH_3)_2$). ^{13}C NMR (125.7 MHz, C_6D_5Br, −30 °C): δ 215.8 (s, Ph *o*-C_{ipso}), 169.9, 158.2, 146.7, 142.2, 138.4 (s, Cp and aromatic C_{ipso}), 148.6 (d, $^1J_{CF}$ = 239, *o*-*C*F), 138.6 (d, $^1J_{CF}$ = 232, *p*-*C*F), 136.7 (d, $^1J_{CF}$ = 248, *m*-*C*F), 133.5−120.5 (aromatic *C*H, overlapped by solvent), 119.9, 118.6, 117.1, 115.5 (br, Cp *C*H), 88.0 (t, $^1J_{CH}$ = 154, Ti−CH_2), 58.6 (s, Ph_3CCH_2Ph), 45.9 (t, $^1J_{CH}$ = 128, Ph_3CCH_2Ph), 44.7 (s, $C(CH_3)_2$), 28.2, 27.9 (br, $C(CH_3)_2$). ^{1}H NMR (500 MHz, C_6D_5Br, 25 °C): δ 7.8−6.6 (36H, aromatic protons and Cp *H*, ill-resolved), 5.43 (br, $W_{1/2}$ = 56, 2H, Cp *H*), 3.82 (s, 2H, Ph_3CCH_2-Ph), 3.76 (br, $W_{1/2}$ = 160, 2H, Ti−CH_2), 2.16 (s, 3H, $C_6H_5CH_3$), 1.18 (s, 6H, $C(CH_3)_2$). ^{19}F NMR (188.2 MHz, C_6D_5Br, 25 °C): δ −132.8 (s, 2F, *o*-*F*), −162.9 (t, $^3J_{FF}$ = 21, 1F, *p*-*F*), −168.7 (s, 2F, *m*-*F*).

In Situ Preparation of (η^5:η^1-$C_5H_4CMe_2$-3,5-$Me_2C_6H_2$)-Ti(CH_2Ph)$_2$ (6). A solution of **1** in C_6D_6 (4.5×10^{-2} M) was kept at 50 °C for 50 h. Upon thermolysis the color of the solution changed from red to dark red. NMR spectroscopy indicates the formation of toluene and compound **6**. ^{1}H NMR (500 MHz, C_6D_6): δ 7.12 (t, $^3J_{HH}$ = 7.5, 4H, Bz *m*-*H*), 6.83 (t, $^3J_{HH}$ = 7.5, 2H, Bz *p*-*H*), 6.69 (s, 1H, Ar *p*-*H*), 6.65 (d, $^3J_{HH}$ = 7.5, 4H, Bz *o*-*H*), 6.58 (s, 1H, Ar *o*-*H*), 5.84 (ps t, $^3J_{HH}$ = 2.5, 2H, Cp *H*), 5.71 (ps t, $^3J_{HH}$ = 2.5, 2H, Cp *H*), 3.27 (s, 3H, ArCH_3, adjacent to Ti−C_{ipso}), 3.14 (d, $^2J_{HH}$ = 9.5, 2H, Ti−CH_2), 3.03 (d, $^2J_{HH}$ = 9.5, 2H, Ti−CH_2), 2.10 (s, 3H, ArCH_3, overlap with toluene), 1.37 (s, 6H, $C(CH_3)_2$). ^{13}C NMR (125.7 MHz, C_6D_6): δ 201.7 (Ar *o*-C_{ipso}), 171.8 (Cp C_{ipso}), 148.4 (Bz C_{ipso}), 148.0 (Ar C_{ipso}), 139.4 (Ar *m*-C_{ipso}, adjacent to Ti−C_{ipso}), 137.3 (Ar *m*-C_{ipso}), 128.6 (Bz *m*-*C*H), 127.6 (Ar *p*-*C*H), 125.3 (Bz *o*-*C*H), 122.5 (Bz *p*-*C*H), 121.7 (Ar *o*-*C*H), 119.5 (Cp *C*H), 116.7 (Cp *C*H), 94.1 ($^1J_{CH}$ = 122, Ti−CH_2), 43.3 ($C(CH_3)_2$), 29.8 ($C(CH_3)_2$), 26.1 (ArCH_3), 21.8 (ArCH_3, adjacent to Ti−C_{ipso}).

In Situ Preparation of (η^5:η^1-$C_5H_4CMe_2C_6H_4$)Ti(CH_2Ph)$_2$ (7). A solution of **2** in C_6D_6 (5×10^{-2} M) was kept at 50 °C for 50 h. Upon thermolysis the color of the solution changed from red to dark red. NMR spectroscopy indicates the formation of toluene and compound **7**. ^{1}H NMR (500 MHz, C_6D_6): δ 8.00 (d, $^3J_{HH}$ = 7.5, 1H, Ph *m*-*H*, adjacent to Ti−C_{ipso}), 7.12 (t, $^3J_{HH}$ = 7.5, 4H, Bz *m*-*H*), 7.02 (m, Ph *m*-*H*, overlap with toluene), 6.94 (t, $^3J_{HH}$ = 6.8, 1H, Ph *p*-*H*), 6.86 (t, $^3J_{HH}$ = 7.5, 2H, Bz *p*-*H*), 6.77 (d, $^3J_{HH}$ = 7.5, 1H, Ph *o*-*H*), 6.71 (d, $^3J_{HH}$ = 7.5, 4H, Bz *o*-*H*), 5.84 (ps t, $^3J_{HH}$ = 2.8, 2H, Cp *H*), 5.74 (ps t, $^3J_{HH}$ = 2.8, 2H, Cp *H*), 3.11 (d, $^2J_{HH}$ = 10, 2H, Ti−CH_2), 2.77 (d, $^2J_{HH}$ = 10, 2H, Ti−CH_2), 1.32 (s, 6H, $C(CH_3)_2$). ^{13}C NMR (125.7 MHz, C_6D_6): δ 200.6 (Ph *o*-C_{ipso}), 170.3 (Cp C_{ipso}), 148.8 (Ph C_{ipso}), 146.6 (Bz C_{ipso}), 129.7 (Ph *m*-*C*H′, adjacent to Ti−C_{ipso}), 129.7 (Ph *m*-*C*H), 128.8 (Bz *m*-*C*H), 127.2 (Bz *o*-*C*H), 123.8 (Ph *p*-*C*H), 123.7 (Ph *o*-*C*H), 122.9 (Bz *p*-*C*H), 119.3 (Cp *C*H), 114.5 (Cp *C*H), 90.5 ($^1J_{CH}$ = 125, Ti-CH_2), 43.9 ($C(CH_3)_2$), 29.3 ($C(CH_3)_2$).

Preparation of $C_5H_4(SiMe_3)CMe_2C_6D_5$. To a solution of 3.20 g (19.8 mmol) of bromobenzene-d_5 in 50 mL of diethyl ether was added 7.8 mL of a 2.5 M solution (19.7 mmol) of *n*-BuLi in hexanes. The mixture was stirred for 3 h. The mixture was cooled to −30 °C, and 2.4 mL (2.1 g, 19.8 mmol) of 6,6-dimethylfulvene was added. The yellowish suspension was warmed to room temperature and was stirred for an additional 3 h. The reaction mixture was cooled with an ice bath, and 1.2 equiv of trimethylsilyl chloride was added. The ice bath was removed, and the yellow-white suspension was stirred overnight. The reaction mixture was poured into 100 mL of ice−water. The organic and water layers were separated, and the water layer was extracted twice with 50 mL of light petroleum. The combined organic layers were dried over magnesium sulfate, and the low-boiling volatiles were removed using a rotary evaporator. The residue was distilled using a Kugelrohr apparatus. The product distilled at 130 °C at 0.4 Torr. Yield: 3.30 g (12.5 mmol, 64%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.35, 6.28, 6.13 (br, 1H, Cp *H*), 3.22 (s, 1H, Cp *H*), 1.53 (s, 6H, $C(CH_3)_2$), −0.06 (s, 9H, $Si(CH_3)_3$).

Preparation of (η^5-$C_5H_4CMe_2C_6D_5$)$TiCl_3$. The same procedure was followed as described for the preparation of the non-isotope-labeled analogue,[3b] using $C_5H_4(SiMe_3)CMe_2C_6D_5$ (3.20 g, 12.1 mmol) and $TiCl_4$ (1.3 mL, 2.3 g, 12 mmol). Yield: 2.67 g (7.8 mmol, 65%). ^{1}H NMR (300 MHz, C_6D_6): δ 6.27 (ps t, $^3J_{HH}$ = 2.8, 2H, Cp *H*), 5.99 (ps t, $^3J_{HH}$ = 2.8, 2H, Cp *H*), 1.53 ($C(CH_3)_2$). ^{13}C NMR (75.4 MHz, C_6D_6): δ 154.2 (Cp C_{ipso}), 123.3, 121.7 (Cp *C*H), 40.8 ($C(CH_3)_2$), 28.7 ($C(CH_3)_2$). Anal. Calcd for $C_{14}H_{10}D_5Cl_3Ti$: C, 49.09; H + D, 5.88; Ti, 13.98. Found: C, 49.13; H + D, 5.91; Ti, 13.87.[46]

Preparation of (η^5-$C_5H_4CMe_2C_6D_5$)Ti(CH_2Ph)$_3$ (2-*d*$_5$). The same procedure was followed as described for the preparation of **2**, using (η^5-$C_5H_4CMe_2C_6D_5$)$TiCl_3$ (1.11 g, 3.2 mmol) to afford the title compound in 75% yield (1.23 g, 2.4 mmol). ^{1}H NMR (300 MHz, C_6D_6): δ 7.15 (t, $^3J_{HH}$ = 7.7, 6H, Bz *m-H*), 6.91 (t, $^3J_{HH}$ = 7.3, 3H, Bz *p-H*), 6.82 (d, $^3J_{HH}$ = 7.3, 6H, Bz *o-H*), 5.75 (ps t, $^3J_{HH}$ = 2.7, 2H, Cp *H*), 5.50 (ps t, $^3J_{HH}$ = 2.7, 2H, Cp *H*), 2.97 (s, 6H, Ti−CH_2), 1.38 (s, 6H, C(CH_3)$_2$). ^{13}C NMR (75.4 MHz, C_6D_6): δ 149.1 (Bz C_{ipso}), 146.7 (Cp C_{ipso}), 128.8, 127.0, 123.0 (Bz *C*H), 118.4, 113.4 (Cp *C*H), 93.5 (Ti-*C*H$_2$), 40.4 (*C*(CH$_3$)$_2$), 30.1 (C(*C*H$_3$)$_2$). Anal. Calcd for $C_{35}H_{31}D_5Ti$: C, 82.49; H + D, 8.11. Found: C, 82.00; H + D, 8.12.[46]

In Situ Preparation of [η^5,η^1-$C_5H_4CMe_2C_6D_4$]Ti(CH_2Ph)(CHDPh) (7-*d*$_{4/1}$). A solution of 26.5 mg (52 μmol) of **2-*d*$_5$** in 0.6 mL of benzene in an NMR tube with a Teflon valve was warmed to 50 °C for 50 h. The color of the solution changed from red to dark red. ^{1}H NMR (300 MHz, C_6D_6): δ 7.12 (t, $^3J_{HH}$ = 7.7, 4H, Bz *m-H*), 6.86 (t, $^3J_{HH}$ = 7.3, 2H, Bz *p-H*), 6.71 (d, $^3J_{HH}$ = 7.3, 4H, Bz *o-H*), 5.85 (ps t, $^3J_{HH}$ = 2.6, 2H, Cp *H*), 5.74 (ps t, $^3J_{HH}$ = 2.6, 2H, Cp *H*), 3.11 (d, $^2J_{HH}$ = 9.9, 1H, Ti−CH_2), 3.05 (s, 0.5H, Ti−CDH_{anti}), 2.75 (d, $^2J_{HH}$ = 9.9, 1H, Ti−CH_2), 2.71 (s, 0.5H, Ti−CDH_{syn}), 1.32 (s, 6H, C(CH_3)$_2$). ^{13}C NMR (75.4 MHz, C_6D_6): δ 200.6 (Ph *o*-C_{ipso}), 170.2, 148.9 (Cp and Ph C_{ipso}), 146.6, 146.5 (Bz C_{ipso}), 128.8 (Bz *m*-*C*H), 127.2 (Bz *o*-*C*H), 122.9 (Bz *p*-*C*H), 119.3, 114.5 (Cp *C*H), 90.6, 90.5 (Ti-*C*H$_2$), 89.6 (t, $^1J_{CD}$ = 19, Ti-*C*DH), 43.9 (*C*(CH$_3$)$_2$), 29.3 (C(*C*H$_3$)$_2$).

Generation of [(η^5,η^1-$C_5H_4CMe_2C_6D_4$)Ti(CH_2Ph)][η^6-$PhCH_2B(C_6F_5)_3$] (4-*d*$_4$). A solution of 16.5 (32 μmol) of **2-*d*$_5$** in 0.6 mL of benzene-d_6 was added to 16.7 mg (33 μmol) of $B(C_6F_5)_3$. The solution was transferred to an NMR tube equipped with a Teflon (Young) valve and investigated by NMR spectroscopy at 6 °C. ^{1}H NMR (500 MHz, C_6D_6, 6 °C): δ 6.90 (t, $^3J_{HH}$ = 7.7, 2H, Ti−Bz *m-H*), 6.73 (t, $^3J_{HH}$ = 7.3, 1H, Ti−Bz *p-H*), 6.51 (d, $^3J_{HH}$ = 7.7, 1H, B−Bz *o-H*), 6.33 (d, $^3J_{HH}$ = 7.7, 1H, B−Bz *o-H*′), 6.23 (t, $^3J_{HH}$ = 7.3, 1H, B−Bz *m-H*), 6.06 (t, $^3J_{HH}$ = 7.1, 1H, B−Bz *m-H*′), 5.95 (d, $^3J_{HH}$ = 7.3, 2H, Ti−Bz *o-H*), 5.89 (br, 1H, Cp *H*), 5.86 (br, 2H, B−Bz *p-H* and Cp *H*), 5.13 (d, $^3J_{HH}$ = 2.2, 1H, Cp *H*), 4.83 (m, 1H, Cp *H*), 3.28 (br, 1H, B−CH_2), 2.93 (br, 1H, B−CH_2), 2.83 (d, $^2J_{HH}$ = 9.9, 1H, Ti−CH_2), 2.08 (t, $^2J_{HD}$ = 2.2, 2H, $C_6H_5CH_2D$), 1.15 (s, 3H, C(CH_3)$_2$), 0.93 (d, $^2J_{HH}$ = 9.9, 1H, Ti−CH_2), 0.76 (s, 3H, C(CH_3)$_2$). ^{13}C NMR (125.7 MHz, C_6D_6, 6 °C): δ 200.0 (Ph *o*-C_{ipso}), 171.0, 160.6, 157.8, 150.4 (Cp, Ph, Ti−Bz, and B−Bz C_{ipso}), 148.5 (d, $^1J_{CF}$ = 235, *o*-*C*F), 138.9 (d, $^1J_{CF}$ = 250, *p*-*C*F), 137.4 (d, $^1J_{CF}$ = 239, *m*-*C*F), 133.9 (B−Bz *m*-*C*H), 131.2 (B−Bz *o*-*C*H), 130.8 (B−Bz *m*-*C*H′), 128.3 (Ti−Bz *m*-*C*H), 127.9 (Ti−Bz *p*-*C*H, overlap with solvent), 126.5 (Ti−Bz *o*-*C*H), 124.7, 124.1 (B−Bz *o*-*C*H′, B−Bz *p*-*C*H), 124.5, 124.1, 115.9, 111.4 (Cp *C*H), 94.2 (Ti−*C*H$_2$), 43.6 (*C*(CH$_3$)$_2$), 35.6 (br, B−*C*H$_2$), 29.6, 28.9 (C(*C*H$_3$)$_2$), 21.2 (t, $^1J_{CD}$ = 19, $C_6H_5CH_2D$).

In Situ Preparation of (η^5-$C_5H_4CMe_2C_6H_4$)Ti(CH_2CMe_3)$_2$ (8). A solution of 20.7 mg (61.3 μmol) of (η^5-$C_5H_4CMe_2Ph$)$TiCl_3$ in 0.5 mL of benzene-d_6 was added to 14.4 mg (184 μmol) of neopentyllithium to form the title compound, 1 equiv of neopentane, and 3 equiv of lithium chloride. To remove the LiCl, the benzene solution was filtered over a small piece of paper (predried at 75 °C) wedged in a Pasteur pipet. ^{1}H NMR (300 MHz, C_6D_6): δ 8.38 (d, $^3J_{HH}$ = 7.1, 1H, Ph *m-H*, adjacent to Ti−C_{ipso}), 7.01−6.82 (m, 3H, Ph *o*-, *m*-, *p-H*), 6.56 (ps t, $^3J_{HH}$ = 2.6, 2H, Cp *H*), 6.22 (ps t, $^3J_{HH}$ = 2.6, 2H, Cp *H*), 2.72 (d, $^2J_{HH}$ = 10.6, 2H, Ti−CH_2), 2.26 (d, $^2J_{HH}$ = 10.3, 2H, Ti−CH_2), 1.50 (s, 6H, C(CH_3)$_2$), 0.94 (s, 18H, C(CH_3)$_3$), 0.90 (s, 12H, C(CH_3)$_4$). ^{13}C NMR (75.4 MHz, C_6D_6): δ 195.5 (Ph *o*-C_{ipso}), 170.5, 145.7 (Ph and Cp C_{ipso}), 132.4, 128.8, 124.1, 123.5 (Ph *C*H), 117.0, 109.0 (Cp *C*H), 112.8 (Ti−*C*H$_2$), 38.6 (*C*(CH$_3$)$_2$), 34.1 (*C*(CH$_3$)$_3$), 33.9 (C(*C*H$_3$)$_3$), 31.6 (C(*C*H$_3$)$_2$), 29.8 (C(*C*H$_3$)$_4$), 29.5 (*C*(CH$_3$)$_4$).

Preparation of (η^5-$C_5H_4CMe_2Ph$)Ti(CH_2SiMe_3)$_3$ (9). To a solution of 1.03 g (3.05 mmol) of (η^5-$C_5H_4CMe_2Ph$)$TiCl_3$ in 70 mL of diethyl ether cooled to −70 °C was added 9.2 mmol of $ClMgCH_2SiMe_3$ dropwise as a 1.62 M solution in diethyl ether. The reaction mixture was warmed to room temperature and was stirred for 3 h. The volatiles were removed in vacuo, and the residue was extracted with pentane. The pentane was pumped off to afford 0.93 g (1.88 mmol, 62%) of the title compound as a brown oil. The purity of **9** is >95%, as seen by ^{1}H NMR. ^{1}H NMR (300 MHz, C_6D_6): δ 7.2−6.9 (m, 5H, Ph *H*), 6.05 (m, 2H, Cp *H*), 6.01 (m, 2H, Cp *H*), 1.73 (s, 6H, Ti−CH_2), 1.46 (s, 6H, C(CH_3)$_2$), 0.14 (s, 27H, Si(CH_3)$_3$). ^{13}C NMR (75.4 MHz, C_6D_6): δ 149.8, 144.4 (Ph and Cp C_{ipso}), 128.4, 126.5, 126.3 (Ph *C*H), 111.9, 109.87 (Cp *C*H), 85.8 (Ti−*C*H$_2$), 40.1 (*C*(CH$_3$)$_2$), 30.2 (C(*C*H$_3$)$_2$), 2.3 (Si(*C*H$_3$)$_3$).

In Situ Preparation of (η^5:η^1-$C_5H_4CMe_2C_6H_4$)Ti(CH_2SiMe_3)$_2$ (10). An NMR tube with a solution of **9** in C_6D_6 (6×10^{-2} M) was heated to 50 °C for 70 h. NMR spectroscopy reveals the formation of tetramethylsilane and **10**. ^{1}H NMR (300 MHz, C_6D_6): δ 8.26 (d, $^3J_{HH}$ = 7.0, 1H, Ph *m-H*, adjacent to Ti−C_{ipso}), 7.05−6.9 (m, 2H, Ph *m-H* and *p-H*), 6.81 (d, $^3J_{HH}$ = 7.7, 1H, Ph *o-H*), 6.43 (m, 2H, Cp *H*), 6.18 (m, 2H, Cp *H*), 2.27 (d, $^2J_{HH}$ = 11.0, 2H, Ti−CH_2), 2.05 (d, $^2J_{HH}$ = 10.6, 2H, Ti−CH_2), 1.47 (s, 6H, C(CH_3)$_2$), 0.01 (s, 18H, Si(CH_3)$_3$), −0.01 (s, 12H, Si(CH_3)$_4$). ^{13}C NMR (75.4 MHz, C_6D_6): δ 198.6 (Ph *o*-C_{ipso}), 170.5, 147.1 (Ph and Cp C_{ipso}), 131.4, 129.2, 124.0, 123.7 (Ph *C*H), 117.1, 109.9 (Cp *C*H), 88.0 (Ti−*C*H$_2$), 43.6 (*C*(CH$_3$)$_2$), 29.6 (C(*C*H$_3$)$_2$), 2.5 (Si(*C*H$_3$)$_3$), 0.0 (Si(*C*H$_3$)$_4$).

In Situ Preparation of (η^5:η^1-$C_5H_4CMe_2C_6D_4$)Ti(CH_2CMe_3)(CHDCMe$_3$) (8-*d*$_{4/1}$). A solution of 15.5 mg (46 μmol) of (η^5-$C_5H_4CMe_2C_6D_5$)$TiCl_3$ in 0.5 mL of benzene-d_6 was added to 10.8 mg (138 μmol) of neopentyllithium to form the title compound, 1 equiv of neopentane, and 3 equiv of lithium chloride. To remove the LiCl, the benzene solution was filtered over a small piece of paper (predried at 75 °C) wedged in a Pasteur pipet. ^{1}H NMR (500 MHz, C_6D_6): δ 6.56 (s, 2H, Cp *H*), 6.22 (s, 2H, Cp *H*), 2.73 (d, $^2J_{HH}$ = 10.3, 1H, Ti−CH_2), 2.65 (s, 0.15H, Ti−CDH_{anti}), 2.26 (d, $^2J_{HH}$ = 10.3, 1H, Ti−CH_2), 2.18 (s, 0.85H, Ti−CDH_{syn}), 1.50 (s, 6H, C(CH_3)$_2$), 0.94 (s, 18H, C(CH_3)$_3$), 0.90 (s, 12H, C(CH_3)$_4$). ^{13}C NMR (125.7 MHz, C_6D_6): δ 195.4 (Ph *o*-C_{ipso}), 170.4, 145.7 (Ph and Cp C_{ipso}), 117.0, 109.0 (Cp *C*H), 113.2, 113.0, 112.8 (Ti-*C*H$_2$), 111.8 (t, $^1J_{CD}$ = 17, Ti−*C*DH), 111.6 (t, $^1J_{CD}$ = 17, Ti−*C*DH), 38.6 (*C*(CH$_3$)$_2$), 34.1 (*C*(CH$_3$)$_3$), 33.9 (C(*C*H$_3$)$_3$), 31.6 (C(*C*H$_3$)$_2$), 29.8 (C(*C*H$_3$)$_4$), 29.5 (*C*(CH$_3$)$_4$).

Kinetic Experiments. In a typical experiment, the compound of interest (0.0188 mmol) was dissolved in 0.7 mL of benzene-d_6 (2.6×10^{-2} M) at ambient temperature, together with ferrocene (1.0 mg) used as internal standard. The solution was transferred to an NMR tube with a Teflon valve, which was then directly inserted into the (preheated) probe of the NMR spectrometer. The sample was given 20 min to equilibrate to the specified temperature. ^{1}H NMR spectra were recorded at regular intervals (1 h). The progress of thermolysis was monitored by integration of the Cp resonances in the ^{1}H NMR spectrum relative to the internal ferrocene standard. The rate constants were calculated via nonlinear-least-squares analysis of the plot of ln([*A*]/[*A*$_0$]) versus time using Microcal Origin 5.0 software (version 5.0; Microcal Software, Inc., 1991−1997). The maximum relative error found (2.1%) was used as the standard error for all determined k_1 rate constants. The temperature of the NMR probe was measured using a methanol temperature standard. At an NMR probe setting of 65 °C (for different experiments), the temperature was found to fluctuate between 65 ± 1 °C. The established error in the temperature of 1 K at this temperature was used for the whole temperature range.

OM0206554

(46) Since the detection method used in the elemental analysis cannot distinguish between D_2O and H_2O, the sample H + D content was calculated by multiplying the experimentally found H + D content with $(2n + m)/(n + m)$ for a sample containing *n* D and *m* H atoms.