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The formation and structures of the methyl-bridged complexes $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$ and $[Cp^*TiMe_2(\mu\text{-}Me)TiMe_2Cp^*][MeB(C_6F_5)_3]$

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Abstract

Reaction of the compound Cp^*TiMe_3 ($Cp^* = \eta^5$-pentamethylcyclopentadienyl) with the potent Lewis acid $B(C_6F_5)_3$ results in methyl carbanion abstraction from the titanium and formation of the corresponding complex $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$, in which a methyl group bridges the titanium and boron atoms. The isotopically labelled compounds $Cp^*Ti(CH_2D)_3$, $Cp^*Ti(CH_2D)_2(\mu\text{-}CH_2D)B(C_6F_5)_3$, $Cp^*Ti(^{13}CH_3)_3$, and $Cp^*Ti(^{13}CH_3)_2(\mu\text{-}^{13}CH_3)B(C_6F_5)_3$ have also been prepared to provide NMR probes of the possibility of α-agostic bonding in these compounds, and while the answer appears to be 'no', a caveat on the use of this type of experiment is proposed. The compounds Cp^*TiMe_3 and $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$ react further to form the novel but unstable methyl-bridged species $[Cp^*TiMe_2(\mu\text{-}Me)TiMe_2Cp^*][MeB(C_6F_5)_3]$, which has been characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy.

Keywords: Titanium; Olefin; Polymerization; Agostic

1. Introduction

There has in recent years been reported considerable research into the utilization of titanocene, zirconocene and hafnocene derivatives as homogeneous catalysts for the polymerization of olefins (see, for instance Ref. [1] and Ref. [2] for recent theoretical considerations at the density functional level), and it has been shown that the best catalysts incorporate as necessary structural features the presence of a coordinated alkyl or hydride ligand, a vacant site, and a positive charge. Indeed, 16-electron complexes of the type $[Cp'_2MR(L)]^+$ (M = Ti, Zr, Hf; Cp' = substituted η^5-cyclopentadienyl group; R = alkyl group; L = labile ligand) form probably the most extensively studied and best understood class of homogeneous catalysts for the coordination (Ziegler–Natta) polymerization of olefins. Interestingly, and perhaps as anticipated, electronically less saturated, sterically less hindered monocyclopentadienyl complexes of the general stoichiometries $[Cp'MRL_2]^{2+}$ or $[Cp'MR_2L]^+$ (Cp' = substituted cyclopentadienyl) also behave as very reactive Ziegler–Natta olefin polymerization catalysts for a number of monomers (see Refs. [3–10] (for recent examples) and Refs. [11–16]).

We have reported in a preliminary communication that treatment of the compounds Cp^*MMe_3 (M = Ti, Zr, Hf; $Cp^* = \eta^5$-pentamethylcyclopentadienyl) with the potent Lewis acid $B(C_6F_5)_3$ results in methyl carbanion abstraction and formation of the corresponding complexes $[Cp^*MMe_2][BMe(C_6F_5)_3]$ [11]. Rather similar results have been reported elsewhere for this and analogous systems [3,4,8–10]. The titanium compound, $[Cp^*TiMe_2][MeB(C_6F_5)_3]$, is of considerable interest as it behaves as a very good Ziegler–Natta catalyst or catalyst precursor for the polymerization of ethylene [4,10,12,14], 1,5-hexadiene [15] and norbornene [15], and of styrene to syndiotactic polystyrene [5,6,8,9,12,14]. Interestingly, this titanium system also behaves as an excellent carbocationic initiator for the polymerization of α-methylstyrene [14], vinyl ethers [16], *N*-vinylcarbazole [16] and isobutylene [13], and of styrene to atactic polystyrene [14]. However, because of

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thermal lability, $[Cp^*TiMe_2][BMe(C_6F_5)_3]$ has been little characterized.

We now extend our preliminary findings [11], which suggested that $[Cp^*TiMe_2][MeB(C_6F_5)_3]$ assumes the methyl-bridged structure $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$ in solution. The isotopically labelled compounds $Cp^*Ti(CH_2D)_3$, $Cp^*Ti(CH_2D)_2(\mu\text{-}CH_2D)B(C_6F_5)_3$, $Cp^*Ti(^{13}CH_3)_3$, and $Cp^*Ti(^{13}CH_3)_2(\mu\text{-}^{13}CH_3)B(C_6F_5)_3$ are prepared to assess the possibility of α-agostic methyl ligands in these compounds, and a caveat on the use of this type of experiment is discussed. We also describe the reaction of $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$ with Cp^*TiMe_3 to form the unusual methyl-bridged species $[Cp^*TiMe_2(\mu\text{-}Me)TiMe_2Cp^*][MeB(C_6F_5)_3]$. In a subsequent paper, we shall discuss reactions of $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$ and its zirconium and hafnium analogues with aromatic solvents to form complexes of the type $[Cp^*MMe_2(\eta^6\text{-arene})][MeB(C_6F_5)_3]$ (M = Ti, Zr, Hf).

2. Experimental

All experiments were carried out under nitrogen using standard Schlenk line techniques, a Vacuum Atmospheres glove box and dried, thoroughly deoxygenated solvents. ^1H, ^{13}C and ^{19}F NMR spectra were run using a Bruker AM 400 spectrometer operating at 400.14 MHz, 100.6 MHz, and 376.5 MHz respectively; ^1H and $^{13}C\{^1H\}$ NMR spectra are referenced with respect to internal TMS using residual proton resonances or carbon resonances, respectively, of the solvents; ^{19}F spectra are referenced to external $CFCl_3$.

The compounds Cp^*TiMe_3 [17] and $B(C_6F_5)_3$ [18] were prepared as described previously; $LiCH_2D$ as described in Ref. [19] but using CH_2DI prepared from the reaction of CH_2I_2 with Bu_3SnD.

2.1. $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$

A solution of 0.511 g of $B(C_6F_5)_3$ (1.0 mmol) in 200 ml of hexanes, cooled to 195 K, was added dropwise over 45 min to a well stirred solution of 0.228 g Cp^*TiMe_3 (1.0 mmol) in 20 ml of hexanes, cooled to 195 K. The resulting yellow suspension was stirred for 30 min at 195 K, but an attempt to filter the product resulted in decomposition to a dark solid with gas evolution. All work with this compound was therefore carried out in situ on NMR-scale samples prepared in NMR tubes.

As a representative procedure, a solution of 23 mg of $B(C_6F_5)_3$ (0.045 mmol) in 0.3 ml of CD_2Cl_2 was added to a solution of 10 mg Cp^*TiMe_3 (0.044 mmol) in 0.3 ml of CD_2Cl_2 at 195 K in an NMR tube. The orange reaction mixture was maintained at 195 K for a few minutes, then placed in the probe of an AM-400 NMR spectrometer at 223 K where it was examined by ^1H, ^{13}C and ^{19}F NMR spectroscopy. ^1H NMR (CD_2Cl_2 at 223 K): δ 1.97 (s, 15H, Cp^*), 1.53 (s, 6H, TiMe), 1.19 (br s, 3H, μ-Me). $^{13}C\{^1H\}$ NMR (CD_2Cl_2 at 223 K): δ 147.3 (d, J_{CF} 240 Hz, *o*-CF), 136.2 (d, J_{CF} 259 Hz, *p*-CF), 135.6 (d, J_{CF} 257 Hz, *m*-CF), 131.0 (Cp^* ring C), 80.1 (Ti–Me), 12.6 (Cp^* Me). ^{19}F NMR (CD_2Cl_2 at 223 K): δ −125.7 (m, 2F, *o*-F), −130.8 (t, 1F, *p*-F), −156.2 (d, 2F, *m*-F).

When an approximately one molar equivalent of $B(C_6F_5)_3$ was added to a solution of $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$, separate ^{19}F resonances were observed for $B(C_6F_5)_3$ (δ −129.9 (m, 2F, *o*-F), −147.3 (t, 1F, *p*-F), −163.0 (d, 2F, *m*-F) at 223 K) and the $[\mu\text{-}MeB(C_6F_5)_3]$ group in the temperature range 193–273 K. While the resonances of $B(C_6F_5)_3$ remained well-resolved multiplets over this range of temperature, broadening only above ca. 270 K, those of the $[\mu\text{-}MeB(C_6F_5)_3]$ group broadened considerable above ca. 223 K but did not change their chemical shifts significantly.

2.2. $Cp^*Ti(CH_2D)_3$, $Cp^*Ti(CH_2D)_2(\mu\text{-}CH_2D)B(C_6F_5)_3$

$LiCH_2D$ was prepared by treating 5 g Li metal suspension with 10 g CH_2DI in 60 ml ethyl ether at −78 °C. The reaction mixture was stirred at 195 K for 2 h, then allowed to warm to room temperature and stirred overnight. The resulting solution of $LiCH_2D$ was then allowed to react with a suspension of Cp^*TiCl_3 in hexane at 0 °C to form $Cp^*Ti(CH_2D)_3$ which was purified as previously described for the d_0 isotopomer [17]. ^1H NMR: δ 1.94 (s, 15H, Cp^*), 0.69 (1:1:1 t, J_{HD} 1.45 Hz, 6H, Ti–Me). In an NMR experiment, carried out as above for the synthesis of $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$, 10 mg of $Cp^*Ti(CH_2D)_3$ in 0.5 ml of CD_2Cl_2 at 195 K was treated with an equimolar amount (23 mg) of $B(C_6F_5)_3$ to form $Cp^*Ti(CH_2D)_2(\mu\text{-}CH_2D)B(C_6F_5)_3$. ^1H NMR at 223 K: δ 1.98 (s, 15H, Cp^*), 1.50 (s, 4H, TiMe), 1.18 (br s, 2H, μ-Me).

2.3. $Cp^*Ti(^{13}CH_3)_3$, $Cp^*Ti(^{13}CH_3)_2(\mu\text{-}^{13}CH_3)B(C_6F_5)_3$

$Li^{13}CH_3$ was prepared by reaction of 0.9 g Li metal with 1 g $^{13}CH_3I$ in 20 ml of 70 ml of ethyl ether at 195 K. The reaction mixture was stirred for 2 h at 195 K, allowed to reach room temperature over several hours, then filtered and allowed to react with 0.57 g Cp^*TiCl_3 as above to form $Cp^*Ti(^{13}CH_3)_3$. ^1H NMR: δ 1.94 (s, 15H, Cp^*), 0.71 (d, J_{HC} 119 Hz, 9H, Ti–Me). In an NMR experiment, carried out as above for the synthesis of $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$, 10 mg (0.042 mmol) of $Cp^*Ti(^{13}CH_3)_3$ and an equimolar amount of $B(C_6F_5)_3$ (23 mg) were combined in 0.5 ml of CD_2Cl_2 to form

$Cp^*Ti(^{13}CH_3)_2(\mu\text{-}^{13}CH_3)B(C_6F_5)_3$. ^1H NMR (CD_2Cl_2 at 223 K): δ 1.95 (s, 15H, Cp^*), 1.52 (d, J_{CH} 125 Hz, 6H, TiMe), 1.20 (br d, J_{CH} 114 Hz, 3H, μ-Me). $^{13}C\{^1H\}$ NMR (CD_2Cl_2 at 223 K): δ 131.0 (Cp^* ring C), 80.1 (vs, Ti–Me), 44.3 (br, μ-Me), 12.6 (Cp^* Me).

2.4. $[Cp^*TiMe_2(\mu\text{-}Me)TiMe_2Cp^*][MeB(C_6F_5)_3]$

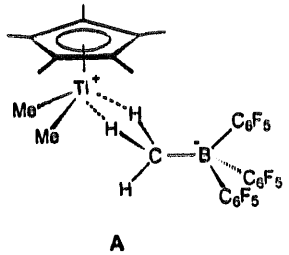
To a solution of $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$ (prepared as above from 10 mg of Cp^*TiMe_3 and 23 mg of $B(C_6F_5)_3$), in 0.4 ml CD_2Cl_2 in an NMR tube at 195 K, was added an equimolar amount of Cp^*TiMe_3 (10 mg) in 0.2 ml CD_2Cl_2). ^1H NMR (CD_2Cl_2 at 193 K): δ 2.00 (br s, 30H, Cp^*), 1.40 (br s, 12H, TiMe), 0.33 (br s, 3H, BMe), 0.08 (v br s, 3H, TiMeTi). On raising the temperature, coalescence between the resonances at δ 1.40 and 0.08 was observed at ca. 258 K; the averaged resonance began to narrow at 273 K, above which temperature decomposition became significant. $^{13}C\{^1H\}$ NMR (CD_2Cl_2 at 223 K): δ 129.1 (Cp^* ring C), 12.7 (Cp^* Me). ^{19}F NMR (CD_2Cl_2 at 223 K): δ −123.6 (m, 2F, *o*-F), −126.4 (t, 1F, *p*-F), −156.70 (d, 2F, *m*-F).

3. Results and discussion

3.1. Synthesis and structure of $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$

Treatment of Cp^*TiMe_3 with an equimolar amount of $B(C_6F_5)_3$ in CD_2Cl_2 at low temperature results in immediate abstraction of a methyl ligand (as the carbanion) from the titanium by the very electrophilic borane. On the basis of its chemistry and spectroscopic properties, the yellow product has the stoichiometry $[Cp^*TiMe_2][BMe(C_6F_5)_3]$; it has not been isolated in the solid state at room temperature, but can be studied by NMR spectroscopy in CD_2Cl_2 in the temperature range 193–273 K. While the new compound decomposes above ca. 273 K in this solvent, as indicated by the appearance of new Cp^* resonances in the ^1H NMR spectrum, it does survive, for minutes at least, at room temperature in chlorobenzene-d_5.

On the basis of its NMR spectra, the material exists at low temperature in CD_2Cl_2 as the zwitterionic species $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$ (A).



A

Thus the ^1H NMR spectrum (193 K) exhibits resonances at δ 1.97, (15H), 1.53 (6H) and ca. 1.1 (br, 3H), which are attributable to the Cp^*, Ti–Me and μ-Me resonances respectively, while its $^{13}C\{^1H\}$ NMR spectrum exhibits resonances at δ 130.6 (Cp^* ring C), 79.6 (Ti–Me), 12.4 (Cp^* Me), 147.3 (*o*-CF), 136.2 (*p*-CF), and 135.6 (*m*-CF). Although the μ-Me and *ipso*-C_6F_5 resonances could not be detected, the spectra are very different from those of the parent compound Cp^*TiMe_3 (^1H NMR in CD_2Cl_2 at 298 K: δ 1.95 (Cp^*), 0.73 (TiMe); $^{13}C\{^1H\}$ NMR in CD_2Cl_2 at 298 K: δ 124.2 (Cp^* ring C), 61.3 (Ti–Me), 12.1 (Cp^* Me)). The ^{19}F NMR spectrum (CD_2Cl_2 at 223 K: δ −125.7 (*o*-F), −130.8 (*p*-F), −156.2 (*m*-F)) is also very different from that of $B(C_6F_5)_3$ (CD_2Cl_2 at 223 K: δ −129.9 (*o*-F), −147.3 (*p*-F), −163.0 (*m*-F)), and the chemical shift of the μ-Me group differs from that of free borate, $[BMe(C_6F_5)_3]^-$ (δ 0.32). The μ-Me resonance is rather broad at room temperature, broadens further as the temperature is lowered below 298 K, but begins to narrow below ca. 260 K, all with essentially no change in chemical shift. The phenonemon is probably a result of quadrupolar relaxation by the $^{10,11}B$ nuclei [20]. Presumably because of the latter reason, the μ-Me ^{13}C resonance is too broad to be detected without isotopic enrichment (see below).

The two ^{13}C-enriched compounds $Cp^*Ti(^{13}CH_3)_3$ and $Cp^*Ti(^{13}CH_3)_2(\mu\text{-}^{13}CH_3)B(C_6F_5)_3$ have facilitated identification of the Ti–Me ^{13}C resonances, in particular the broad μ-Me of the latter at δ 44.3, and have permitted determination of $^1J_{CH}$ of the two types of TiMe group of A (see below). Isotopically enriched $Cp^*Ti(^{13}CH_3)_2(\mu\text{-}^{13}CH_3)B(C_6F_5)_3$ has previously been utilized in connection with our mechanistic research on olefin polymerization by A [14].

Spin saturation experiments were carried out on a solution of A in CD_2Cl_2 at 223 K; the Ti–Me and μ-Me resonances of A were irradiated, and difference spectra were inspected for transfer of saturation. Interestingly, while no transfer between these two resonances was observed, implying that the $B(C_6F_5)_3$ does not 'hop' from one methyl group to another, irradiation of the μ-Me resonance resulted in enhancement of a vanishingly weak resonance at ca. δ 0.38, the chemical shift of free borate anion (Fig. 1). It follows that the borate anion, $[BMe(C_6F_5)_3]^-$, of A does dissociate to some extent in solution, and that slow (on the NMR time scale) exchange between free and coordinated borate ensues. It is for this reason that the above-mentioned, temperature-dependent broadening of the μ-Me resonance is confidently attributed to quadrupolar effects [20] rather than to chemical exchange.

As further evidence that dissociation of $B(C_6F_5)_3$ from A does not occur, addition of one molar equivalent of $B(C_6F_5)_3$ to a solution of A has no effect on the ^1H NMR spectrum but does result in separate sets of ^{19}F

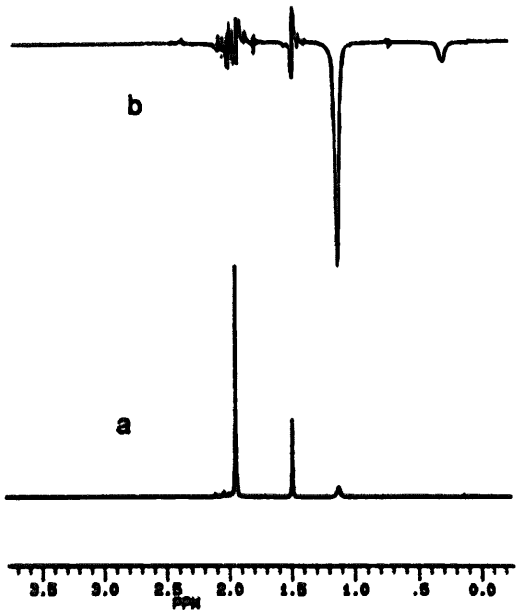


Fig. 1. (a) ^{1}H NMR spectra of A at 223 K. (b) Difference spectrum of A at 223 K with irradiation of the μ-Ti–Me resonance at δ 1.12.

resonances for borane and borate in the temperature range 193–273 K. All six resonances are well-resolved multiplets exhibiting F–F coupling below 230 K, but those of A begin to broaden above 230 K, those of $B(C_6F_5)_3$ above ca. 273 K. Since the resonances of free $B(C_6F_5)_3$ broaden in any case above ca. 273 K, our observations on the mixture do not imply chemical exchange of any kind. Instead, the observed broadening of both sets of resonances probably arises from the effects of $^{10,11}B$–^{19}F spin–spin coupling, with an intermediate rate of quadrupolar induced relaxation [20]. Intramolecular exchange between non-equivalent pairs of *o*- and *m*-fluorine atoms, which might arise from freezing out of propeller-like conformations of the borane [21], cannot be a factor since only one resonance is observed at low temperature for each *o*- and *m*-fluorine site.

Since the early work of Marks and coworkers [22], the highly electrophilic borane $B(C_6F_5)_3$ has been extensively used to abstract methyl groups from neutral dimethyl metallocene compounds in order to form cationic complexes which might serve as olefin polymerization initiators (Eq. (1)).

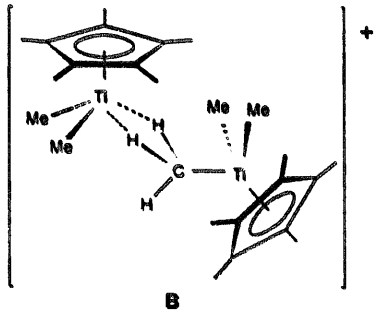
$$Cp'_2ZrMe_2 + B(C_6F_5)_3 \rightarrow [Cp'_2ZrMe][BMe(C_6F_5)_3] \quad (1)$$

where $Cp' = C_5H_5$, substituted cyclopentadienyl.

Recent crystal structures [22–24] of compounds of stoichiometry $[Cp'_2ZrMe][BMe(C_6F_5)_3]$ show that the compounds contain μ-BMe groups in which two of the BMe hydrogen atoms bond to the transition metal cation in an agostic fashion [19,25], as shown for A. Although distinct resonances for the bridging and terminal methyl hydrogen atoms cannot be distinguished in the ^{1}H NMR spectra of any such species, in all cases the μ-BMe resonance is broader than the terminal metal–methyl resonance and is usually found to higher field as well. Since A appears to be very similar chemically [1–10] and structurally to the crystallographically characterized metallocene analogues [22–24], the structure suggested seems quite reasonable. Interestingly, the room temperature ^{1}H NMR spectrum of the compound $(\eta^5\text{-}1,2\text{-}C_5Me_2H_3)_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3$ exhibits separate sets of resonances for the ring 3,5-hydrogen atoms and ring methyl groups, indicating that the $\{(\eta^5\text{-}1,2\text{-}C_5Me_2H_3)_2ZrMe\}$ moiety retains a pyramidal structure on the NMR time scale and thus that the borate anion is firmly coordinated. Exchange broadening of the ring methyl, terminal ZrMe and μ-Me resonances is observed at higher temperatures, but the degree of broadening varies. These observations have been interpreted in terms of two exchange processes, one involving ion-pair dissociation/reorganization, the other ZrMe/BMe methyl exchange [24]. In comparison, our NMR investigations of A suggest that TiMe/BMe methyl exchange does not occur, but that ion-pair dissociation/recombination does. The latter conclusion is consistent with observations that the borate ligand of A is coordinated sufficiently weakly that it is readily displaced by a number of Lewis bases [14], olefins [12–16] and arenes [11].

3.2. Synthesis and structure of $[Cp^*TiMe_2(\mu\text{-}Me)TiMe_2Cp^*][MeB(C_6F_5)_3]$

Treatment of A with an equimolar amount of Cp^*TiMe_3 in CD_2Cl_2 at 195 K results in displacement of the borate from the titanium cation and formation of what appears to be a methyl-bridged species, $[Cp^*TiMe_2(\mu\text{-}Me)TiMe_2Cp^*][MeB(C_6F_5)_3]$, in which the cation assumes structure B.



B

Thus the ^{1}H NMR spectrum (193 K) exhibits resonances at δ 2.00, (30H), 1.40 (12H), 0.33 (~ 3H) and ca. 0.08 (br, ~ 3H), which are attributable to the Cp^*, Ti–Me,

free borate and μ-Me protons respectively, while the $^{13}C\{^1H\}$ NMR spectrum (193 K) exhibits resonances at δ 128.7 (Cp^* ring), 78.9 (Ti–Me) and 12.5 (Cp^* Me). The ^{19}F NMR spectrum (193 K) exhibits only the resonances of the free borate at δ −124.0 (br s, 2F, *o*-F), −126.8 (t, 1F, *p*-F), −156.59 (br s, 2F, *m*-F).

Compound **B** thus appears to resemble the dinuclear compounds $[\{Cp'_2ZrMe\}(\mu\text{-Me})\{ZrMeCp'_2\}][B(C_6F_5)_4]$, formed by abstracting a single methyl group from the corresponding neutral dimethyl compounds with trityl tetrakis(pentafluorophenyl)borate [26], and the mixed metal compound $(^iPr_2CH_2CH^i_2Pr_2)Pt(\mu\text{-Me})_2YbCp^*_2$, prepared by reacting Cp^*_2Yb with $PtMe_2(^iPr_2CH_2CH^i_2Pr_2)$ [27]. A crystal structure of the latter compound unambiguously demonstrates the presence of agostic-type bonding as in **B**, thus establishing a precedent for the putative structure.

The formation of **B** is reversible, as addition of one molar equivalent of $B(C_6F_5)_3$ converts **B** quantitatively to **A** (^1H NMR). This result suggests the following series of equilibria:

$$Cp^*TiMe_3 + B(C_6F_5)_3 \rightleftarrows Cp^*TiMe_2(\mu\text{-Me})B(C_6F_5)_3\,(\mathbf{A}) \quad (2)$$

$$Cp^*TiMe_2(\mu\text{-Me})B(C_6F_5)_3 + Cp^*TiMe_3 \rightleftarrows [Cp^*TiMe_2(\mu\text{-Me})TiMe_2Cp^*]^+\,(\boldsymbol{B}) + [MeB(C_6F_5)_3]^- \quad (3)$$

Consistent with this conclusion, although ^1H NMR spectra of mixtures of **A** and **B** (formed by adding less than one molar equivalent of Cp^*TiMe_3 to a solution of **A** at 193 K) exhibit separate sets of resonances for the

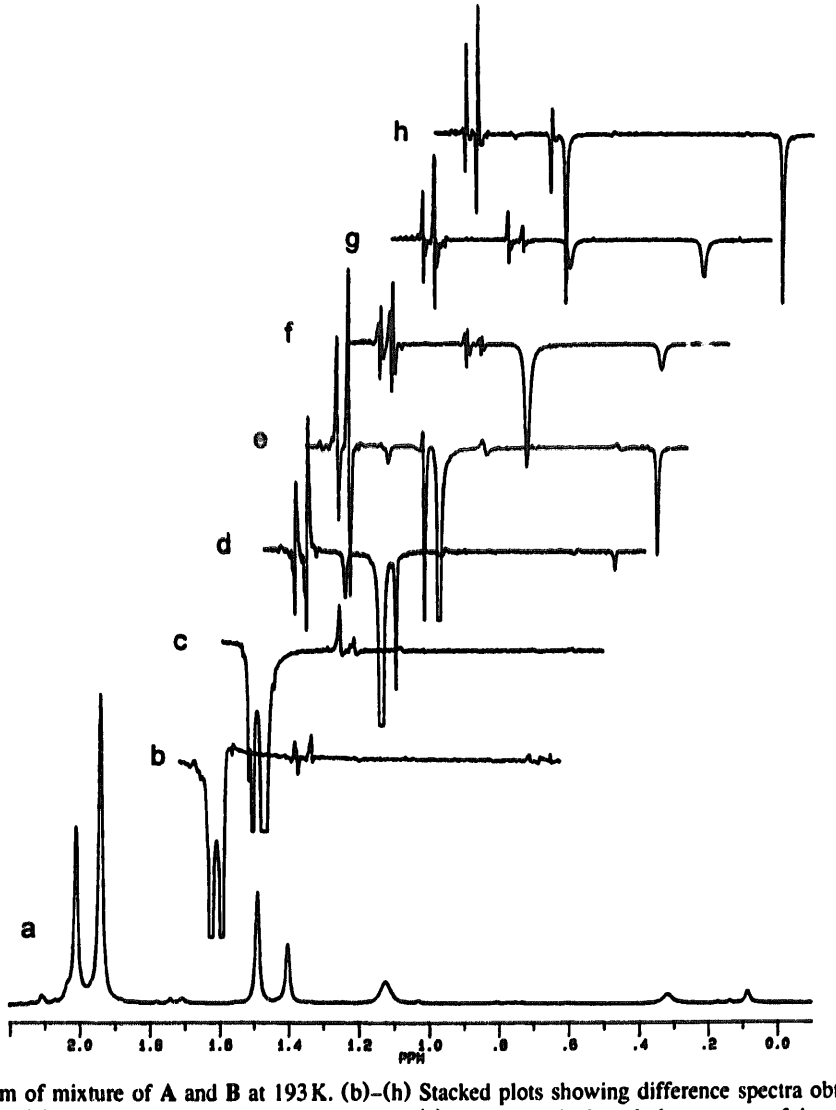


Fig. 2. (a) ^1H NMR spectrum of mixture of **A** and **B** at 193 K. (b)–(h) Stacked plots showing difference spectra obtained on irradiation of the Cp^* resonance of **B** at δ 2.01 (b), of the Cp^* resonance of **A** at δ 1.94 (c), of the terminal methyl resonance of **A** at δ 1.49 (d), of the terminal methyl resonance of **B** at δ 1.40 (e), of the bridging methyl resonance of **A** at δ 1.12 (f), of the free borate anion at δ 0.32 (g), and of the bridging methyl resonance of **B** at δ 0.08 (h). Note that (a) is an expanded scale relative to the scale of (b)–(h).

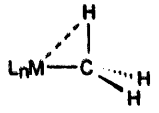
two species at 193 K (Fig. 2(a)), coalescence of the pairs of Cp*, terminal Ti–Me and μ-Me resonances occurs on raising the temperature to 273 K. Unfortunately, the appearance of new resonances on heating indicates the onset of significant thermal decomposition, and thus detailed interpretations of the NMR data are impossible. Broadening and partial coalescence of the ^{19}F resonances of the two compounds was also observed, although the greater chemical shift differences between the ^{19}F resonances of free and coordinated borate render the effects less dramatic and hence less compelling. [1]

A series of spin saturation experiments were carried out on a mixture of **A** and **B** at 193 K, and the resulting difference spectra are shown in Fig. 2. As can be seen, irradiation of the Cp* resonances of **A** and **B** demonstrates exchange between the Cp* groups (Fig. 2(b,c)), while similar irradiation of the terminal Ti–Me resonances of **A** and **B** demonstrates exchange between these groups as well (Fig. 2(d,e)). Interestingly, the experiments of Fig. 2(d,e) demonstrate significant exchange of the bridging methyl of **B** with the terminal methyl of **B**, but not to the same extent with the terminal methyl of **A**, conclusions confirmed by the experiment of Fig. 2(h). The experiments of Fig. 2(f,g) complement that of Fig. 1 in demonstrating mutual exchange of the bridging methyl group of **A** with the methyl group of the free borate anion but not with any other site. Thus there is extensive exchange between two species **A** and **B** even at 193 K, at which temperature all resonances in the ^1H NMR spectra are well resolved. The process involves exchange of anionic $[MeB(C_6F_5)_3]^-$ and neutral Cp^*TiMe_3 between $[Cp^*TiMe_2]^+$ cations, although observation of enhancement of an otherwise unobserved resonance at ca. δ 1.7 on irradiation of the terminal methyl resonances of **A** and **B** (experiments in Fig. 2(d,e)) suggests that the system is more complicated than it appears. The compound giving rise to the resonance at ca. δ 1.7 has not been identified.

Addition of two molar equivalents of Cp^*TiMe_3 to a solution of **B** at 193 K results in broadened resonances in the regions ca. δ 1.95 (v br), 1.45 (v br) and 0.34 (br), attributable to averaged Cp*, terminal TiMe and μ-Me groups respectively. However, there are also very broad resonances at ca. δ 0.6 and 0.15, of variable intensities from one experiment to another, and the nature of any new species in the solution remains speculative.

3.3. α-Agostic interactions in the compounds Cp^*TiMe_3 and $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$

As has been shown [19,25], α-CH bonds of alkyl ligands in electron deficient transition metal complexes often interact with vacant d orbitals to form two-electron, three-centered bonds, as in **C**.



C

As a result of such interactions, the metal center becomes electronically more saturated and hence less electrophilic, and the alkyl ligand distorts from the ideal in order to optimize overlap. To the extent that a structure such as **C** places the agostic hydrogen atom in close proximity to the metal atom, and may indeed constitute an intermediate en route to an α-elimination process to give a hydrido carbene complex, the agostic hydrogen atom undoubtedly assumes some hydride character (see below).

α-Agostic interactions of type **C** are of interest here because their importance in many olefin polymerization processes [28] suggests their possible relevance in the ground state structure of **A**, which is one of the most versatile olefin polymerization initiators known [11–16]. Agostic interactions of type **C** may, in principle, be detected using NMR spectroscopy, since typical alkyl ligand distortions result in non-equivalence of hydrogen nuclei and/or in changes of the CH hybridization; thus, new resonances should appear and $^1J_{CH}$ and $^2J_{HH}$ should change significantly. Unfortunately, α-agostic interactions are usually sufficiently weak that exchange between α-hydrogen atoms occurs readily and, with methyl ligands, for instance, only uninformative, averaged ^1H NMR singlets are generally observed. To avoid the resulting ambiguities, Calvert and Shapley showed that partially deuterated, α-agostic methyl ligands exhibit temperature-dependencies in their chemical shifts which are much greater than those of non-agostic species [29]. As differences in zero-point energies between CH and CD bonds are greater for a terminal than for a weaker agostic bond, there is a thermodynamic preference in an α-agostic, partially deuterated methyl ligand for a deuterium to occupy a terminal position. This changes the average environment of the ^1H nuclei being

[1] The two sets of resonances were noted previously in the ^{19}F NMR spectrum of a solution believed to contain pure **A**, and were misinterpreted in terms of restricted rotation about the Ti–B axis [11]. It is now clear that, because of errors involved in weighing very small amounts of materials for NMR purposes, the solution contained a small excess of Cp^*TiMe_3, giving rise to the two sets of ^{19}F resonances.

observed, and hence their averaged chemical shifts and C–H coupling constants; these effects will be temperature-dependent, since the equilibrium population of α-agostic ^{1}H nuclei will increase as the temperaure is lowered. Since the agostic hydrogen atom of C assumes some hydride character, and since the chemical shifts of transition metal hydrides are normally at high field relative to methyl hydrogens, the effect of lowering the temperature is generally to move the observed ^{1}H resonance to higher field.

Calvert and Shapley initially utilized this technique of isotope perturbation of resonance (IPR) to demonstrate the presence of an α-agostic methyl ligand in the cluster compound $HOs_3(Me)(CO)_{10}$ [29], and the technique has since been applied to many other organometallic compounds [19,25]. For α-agostic CH_2D ligands, differences in ^{1}H chemical shifts between the CH_2D and the corresponding CH_3 groups are typically much greater than 0.1 ppm and decrease quite significantly as the temperature is raised from 200 to 300 K, effects which cannot be accounted for on the basis of secondary isotope effects.

Of relevance here, Green and coworkers found no NMR evidence for α-agostic interactions in the compounds $Ti(CH_2D)Cl_3(Me_2PCH_2CH_2PMe_2)$ [19,30], $(\eta^5\text{-}C_5Me_4Et)Ti(CH_2D)_3$ [19] and η^5-$CpTi(CH_2D)_3$ [19], although X-ray and neutron diffraction data [30] suggest that the first of these is at least weakly α-agostic. Since, however, successful application of the IPR method requires an agostic CH bond to be longer than a terminal CH bond while all three Ti–CH bond lengths in $Ti(CH_3)Cl_3(Me_2PCH_2CH_2PMe_2)$ are identical [30], failure of the method could be rationalized [19,30].

Consistent with these findings with $(\eta^5\text{-}C_5Me_4Et)Ti(CH_2D)_3$ and η^5-$CpTi(CH_2D)_3$, we find no evidence for α-agostic interactions in the compound $Cp^*Ti(CH_2D)_3$. The ^{1}H resonance of the CH_2D groups exhibits a normal chemical shift (ca. 0.04 ppm upfield from the CH_3 analogue) and normal CH (119 Hz) and HD (1.45 Hz) coupling constants, and the same temperature dependence of the CH_2D ^{1}H chemical shift as the Cp^* methyl resonance. Much more surprising, we also find no evidence for α-agostic interactions in $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$ (A), although the borate is bound very weakly and the $[Cp^*TiMe_2]^+$ species should be very electrophilic. However, the ^{1}H resonance of the terminal CH_2D groups of A exhibits a normal chemical shift (ca. 0.05 ppm upfield from the CH_3 analogue) and a normal CH coupling constant (125 Hz) although the CH_2D ^{1}H resonance is too broad at low temperatures for the HD coupling constant to be resolved. The CH_2D ^{1}H resonance exhibits the same temperature dependence of the ^{1}H chemical shift as the Cp^* methyl resonance.

As has been pointed out previously [19,30], absence of IPR evidence does not rule out the presence of an α-agostic hydrogen if the agostic and terminal hydrogens have near-identical CH bond lengths. In addition, significant variation of the averaged CH_2D ^{1}H chemical shift with changing temperature also requires that the agostic hydrogen atom assumes considerable hydridic character, with a chemical shift significantly different from that of the terminal methyl group. This requirement reasonably applies in classes of transition metal compounds for which terminal hydrides resonate at high field, but may not be reasonable for d^0 compounds. The hydride chemical shifts of the compounds $Cp_2^*MH_2$ (M = Ti, Zr, Hf) are δ 0.28 [31], 7.47 [32] and 15.57 [33] respectively, and thus the IPR method may not pertain to compounds of the Group 4 elements, such as the types under consideration here.

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