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Note

The reaction of $Cp_2^*ZrMe_2$ with $[CPh_3][B(C_6F_5)_4]$: triphenylethane does *not* form η^n-arene complexes with $[Cp_2^*ZrMe]^+$

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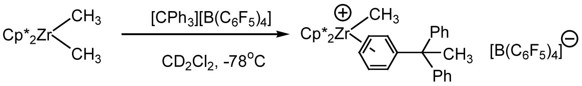
Abstract

In response to a recent paper concerning the formation of a putative arene complex, $[Cp_2^*Zr(CH_3)\eta\text{-}C_6H_5C(C_6H_5)_2CH_3][B(C_6F_5)_4]$ from the reaction of $Cp_2^*ZrMe_2$ with $[CPh_3][B(C_6F_5)_4]$ in CD_2Cl_2 at −78 °C, we present data showing that this reaction leads in fact to a mixture of $[(Cp_2^*ZrMe)_2(\mu\text{-}Me)][B(C_6F_5)_4]$ and $[Cp_2^*ZrMe\cdots B(C_6F_5)_4]$, while NMR signals attributed to η-arene coordination of triphenylethane are due to unreacted CPh_3^+ ($Cp^* = \eta\text{-}C_5Me_5$). © 2002 Published by Elsevier Science B.V.

Keywords: Zirconocene cations; Triphenylmethyl cation; Arene coordination

In a recent paper [1], Casey and Carpenetti presented low-temperature NMR spectroscopic data which were interpreted as evidence for the coordination of one of the phenyl rings of triphenylethane to $[Cp_2^*ZrCH_3]^+$ (Eq. (1)), as indicated by ^{1}H-NMR signals at δ 7.67 (*ortho*), 7.87 (*meta*) and 8.25 (*para*) (CD_2Cl_2, −78 °C). Surprisingly, there was no interchange between bound and free phenyl groups up to the decomposition temperature of ca. 0 °C, and there was no displacement of the coordinated arene by added toluene. On addition of THF, the low-field resonances disappeared.



(1)

The data were illustrated by a partial ^{1}H-NMR of the aromatic region (fig. 1 of ref. [1]). However, this spectrum had a rather familiar appearance since we had observed a similar pattern numerous times before, in cases where the reaction of a metallocene dialkyl with $[CPh_3][B(C_6F_5)_4]$ had not gone to completion. Indeed, the ^{1}H-NMR values quoted in [1] for the 'coordinated' phenyl ring are essentially identical to those reported [2] for pure $[CPh_3][B(C_6F_5)_4]$. Similarly, the ^{13}C-NMR signals of δ 130.5, 139.6, 142.9 and 143.5 quoted in [1] compare well with δ 129.8, 138.8, 142.4 and 142.7 for the *o*-, *i*-, *m*- and *p*-C resonances, respectively, of $[CPh_3][B(C_6F_5)_4]$ (CD_2Cl_2, −78 °C).

We decided therefore to reproduce the reaction between $Cp_2^*ZrMe_2$ (**1**) and $[CPh_3][B(C_6F_5)_4]$ (**2**). Following the reaction of an equimolar mixture of **1** and **2** in CD_2Cl_2 at −78 °C showed the formation of two zirconocene products (Fig. 1): the homobinuclear cation, $[(Cp_2^*ZrMe)_2(\mu\text{-}Me)]^+$ $[B(C_6F_5)_4]^-$ (**3**), as indicated by signals for the bridging (δ −2.31) and terminal (δ −0.17) methyl signals with relative intensities of 1:2, and the (possibly solvated) mononuclear product, $[Cp_2^*ZrMe^+\cdots B(C_6F_5)_4]$ (**4**), as evidenced by a peak at δ 0.37 [5,6] (Scheme 1). These signals are accompanied by those for free triphenylethane and unreacted trityl cation. If **1** and **2** are combined in a 2:1 molar ratio, only the spectrum of **3** is observed, with no indication of **4** and no signals in the 7.6–8.3 ppm region. Homobinuclear methyl-bridged titanocene and zirconocene cations are known for a variety of Cp ligands [2–4], and cation **3** has previously been reported by Marks et al. [5].

Under low-temperature conditions, the reaction of the binuclear cation **3** with **2** is slow, and a fraction of the initial amount of **2** remains unreacted. However, on warming to −40 °C compound **3** is fully converted to

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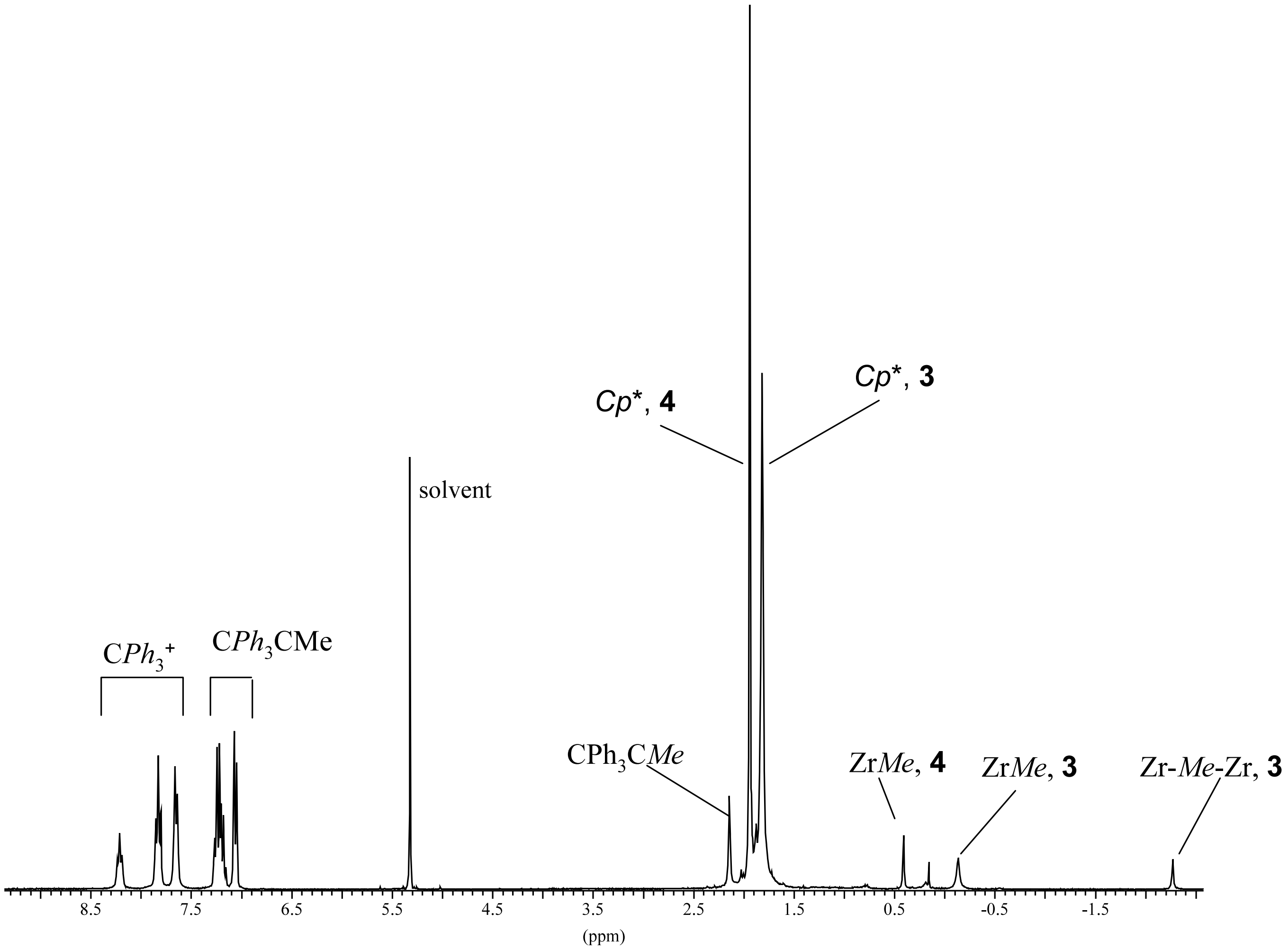
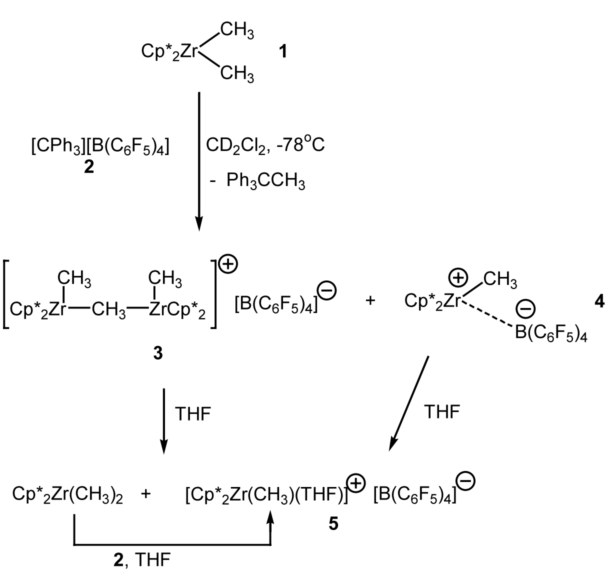


Fig. 1. ^{1}H-NMR spectrum of a mixture of **1** and **2** (molar ratio 1:1) (300.13 MHz, CD_2Cl_2, −60 °C). Under these conditions, products **4** and **3** are formed in a relative ratio of 1.28:1.



Scheme 1.

mononuclear **4**. There is also some evidence for the onset of decomposition in the chlorinated solvent at that temperature. The assumption of the presence of excess **2** in the spectra given in [1] would account for a number of observations, such as the reported failure to observe an exchange between 'free' and 'coordinated' phenyl groups of Ph_3CMe or with toluene, and the inability to freeze out a lower-symmetry coordination mode on cooling **1**–**2** mixtures to −135 °C.

The addition of THF to the mixtures of **3** and **4** generated in the above experiment leads to the formation of $[\mathrm{Cp}^*_2\mathrm{ZrMe(THF)}]^+$ (**5**) [7]. In the case of **3**, this reaction proceeds with the liberation of **1** which readily reacts with any remaining **2** to give more **5**. This reaction sequence explains Casey's observation that the low field signals disappear on THF addition, and only resonances for free triphenylethane are seen.

Arene π-coordination would, of course, be difficult in a sterically highly hindered metallocene such as $[\mathrm{Cp}^*_2\mathrm{ZrMe}]^+$. There are, however, a few authenticated cases in more open environments. In 1990, we reported the first arene complex of a zirconium(IV) alkyl, $Zr(CH_2Ph)_3(\eta\text{-}C_6H_5BPh_3)$, where a much wider chemical shift range was observed, δ 6.22 (*para*), 6.59 (*meta*) and 8.25 (*ortho*) (400 MHz, CD_2Cl_2, −40 °C) [8]. Horton described BPh_4^- anion coordination for a number of complexes $L_2ZrMe(\eta\text{-}C_6H_5BPh_3)$, where a similarly wide range of chemical shifts is observed, and suspected η^2- or η^3-bonding for steric reasons [9]. Cationic half-sandwich complexes of zirconium and hafnium form rather stable 16-electron η^6-complexes with toluene [10–12].

In summary, we have shown that the reaction of $Cp^*_2ZrMe_2$ and $[CPh_3][B(C_6F_5)_4]$ in CD_2Cl_2 at low temperatures leads to the formation of a mixture of the homobinuclear complex, $[(Cp^*_2ZrMe)_2(\mu\text{-}Me)][B(C_6F_5)_4]$ and a mononuclear compound, $[Cp^*_2ZrMe^+\cdots B(C_6F_5)_4]$. If the reagents are employed in a 1:1 ratio, excess $[CPh_3][B(C_6F_5)_4]$ is present in the mixture. *There is no evidence for the claimed coordination of triphenylethane* [13].

1. Experimental

All manipulations were performed under nitrogen using standard Schlenk techniques. Deuterated CH_2Cl_2 was stored over 4 Å molecular sieves and degassed by several freeze–thaw cycles. The compounds $Cp^*_2ZrMe_2$ [14] and $[CPh_3][B(C_6F_5)_4]$ [2] were prepared according to published procedures; the latter was recrystallised from CH_2Cl_2 and used as the solvate, **1**·CH_2Cl_2. NMR spectra were recorded on a Bruker Avance DPX300 spectrometer. ^1H- and ^{13}C-NMR spectra are referenced to residual solvent resonances.

1.1. $Cp^*_2ZrMe_2/[CPh_3][B(C_6F_5)_4]$ in a 1:1 ratio

Samples of 43 mg (0.11 mmol) crystalline **1**·CH_2Cl_2 and 111 mg (0.11 mmol) **2** were each dissolved in 0.3 ml CD_2Cl_2 and cooled to −78 °C. The two solutions were injected into a pre-cooled NMR tube. The NMR tube was shaken and inserted into the pre-cooled probe (−78 °C) of the NMR spectrometer.

3: ^1H-NMR (300.13 MHz, CD_2Cl_2, −78 °C): δ 1.79 (s, 60H, C_5Me_5), −0.17 (s, 6H, $ZrCH_3$), −2.31 (s, 3H, $\mu\text{-}CH_3$). ^{13}C- (74.47 MHz, CD_2Cl_2, −78 °C): δ 120.92 (C_5Me_5), 45.95 ($ZrCH_3$), 26.65 ($\mu\text{-}CH_3$), 11.33 (C_5Me_5). Ph_3CMe: ^1H-NMR (300.13 MHz, CD_2Cl_2, −78 °C): δ 7.23–7.21 (m, 9H, *m*, *p*-C_6H_5), 7.05 (m, 6H, *o*-C_6H_5), 2.14 (s, 3H, $(C_6H_5)_3CCH_3$). ^{13}C- (74.47 MHz, CD_2Cl_2, −78 °C): δ 148.29 (*i*-Ph), 128.02 (*o*-Ph), 127.41 (*m*-Ph), 125.54 (*p*-Ph), 51.51 (Ph_3CMe), 29.39 ($(C_6H_5)_3CMe$).

4: ^1H-NMR (300.13 MHz, CD_2Cl_2, −78 °C): δ 1.89 (s, 30H, C_5Me_5), 0.36 (s, 3H, ZrMe). ^{13}C- (74.47 MHz, CD_2Cl_2, −78 °C): δ 124.81 (C_5Me_5), 54.52 ($Zr\text{-}CH_3$), 11.08 (C_5Me_5).

1.2. $Cp^*_2ZrMe_2/[CPh_3][B(C_6F_5)_4]$ in a 3:1 ratio

Following a similar procedure to that described for the 1:1 ratio above, using 74 mg (0.19 mmol) **1**·CH_2Cl_2 and 70 mg (0.07 mmol) **2**. The ^1H-NMR spectrum shows the formation of **3**, together with unreacted **1**. The NMR data are identical to those given above.

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[13] Note added at the request of Casey et al.: "Casey and Carpenetti agree that their assignment of $[Cp^*_2Zr(CH_3)\eta\text{-}C_6H_5C(C_6H_5)_2CH_3][B(C_6F_5)_4]$ is incorrect. They believe that their claim of the corresponding hydride $[Cp^*_2Zr(H)\eta\text{-}C_6H_5C(C_6H_5)_2CH_3][B(C_6F_5)_4]$ is likely to be incorrect also".

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