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Communications

Effectiveness in Catalyzing Carboalumination Can Be Inferred from the Rate of Dissociation of M/Al Dimers

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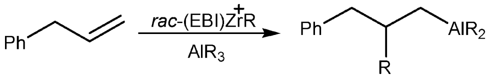
Summary: The rate constants for the dissociation of $AlMe_3$ *from* [**2**][$B(C_6F_5)_4$] *and related M/Al dimers have been determined by selective population inversion* (^1H *NMR). The results predict—correctly—that (EBI)ZrMe*$^+$ *will be a better carboalumination catalyst than (EBTHI)-ZrMe*$^+$.

Transfer of alkyl groups from Zr to Al must occur when Zr is used to catalyze chain growth in aluminum alkyls[1−3] and when Zr is used to catalyze carboalumination of olefins (eq 1).[4,5] Little is known about the mechanism of such transmetalation reactions, but they seem likely to involve intermediates with alkyl bridges between Zr and Al. Such μ-alkyl heterobimetallics are probably also formed when trialkylaluminum compounds are used as impurity scavengers with metallocene catalysts for olefin polymerization[6,7] and from the trialkylaluminum compounds often present[8] when commercially available aluminoxanes are used to activate such catalysts.



(1)

These Zr/Al heterobimetallics appear to be involved in chain transfer[9,10] and have been assumed to be “dormant” and incapable of inserting olefin themselves.[11−15] We have therefore examined the kinetics of exchange between trimethylaluminum and these adducts, first observed by Bochmann,[15] of the general formula $[Cp_2M(\mu\text{-}Me)_2AlMe_2]^+$ (**2**), where M = Ti, Zr, Hf.

The species that takes up olefin in both polymerization and carboalumination reactions is believed to be a

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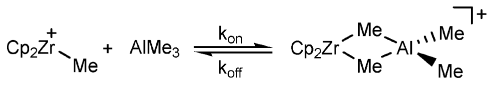
Table 1. Rate Constants for Dissociation of $AlMe_3$ from [2][$B(C_6F_5)_4$]

	[**2**] (mM)	[$AlMe_3$] (mM)	k_{off} (M^{-1} s^{-1})
[$Cp_2Ti(\mu\text{-}Me)_2AlMe_2$]$^+$ (**2a**)	1.1	1.7	2.9(6)
	0.5	1.7	3.3(1)
[$Cp_2Zr(\mu\text{-}Me)_2AlMe_2$]$^+$ (**2b**)	2.2	2.5	0.113(8)
	1.1	2.1	0.141(9)
	1.1	1.1	0.126(5)
	0.5	1.2	0.118(6)
[$Cp_2Hf(\mu\text{-}Me)_2AlMe_2$]$^+$ (**2c**)	1.1	1.0	0
[(EBTHI)$Zr(\mu\text{-}Me)_2AlMe_2$]$^+$ (**2d**)	1.1	0.8	0.018(9)
	1.1	0.8	0.010(9)
[(EBI)$Zr(\mu\text{-}Me)_2AlMe_2$]$^+$ (**2e**)	1.0	1.8	0.18(1)
	1.0	0.9	0.15(1)
	0.5	0.9	0.17(1)

coordinatively unsaturated cation (such as the zirconocene methyl cation **1b** in eq 2). Such cations can



(2)

1b **2b**

be trapped by aluminum alkyls (such as $AlMe_3$ in eq 2) to form adducts such as **2**, which must dissociate and reform the cation (e.g., **1b**) before olefin insertion can continue. The rate at which the adduct dissociates (rate constant k_{off} in eq 2) restricts the rate at which an alkyl ligand can be transferred from M to Al.

The equilibrium in eq 2 generally lies to the right. No free cation **1** is observed in the proton NMR spectrum for any of the systems **2** in Table 1 once 1 equiv of $AlMe_3$ has been added. We have therefore measured k_{off}, the rate constant for regeneration of the catalytically active cations **1**.

Other exchange processes can complicate the preparation of **2**. When the methyl cation **1b** was generated from Cp_2ZrMe_2 and $B(C_6F_5)_3$, the addition of $AlMe_3$ gave rapid redistribution to BMe_3,[16] $Cp_2Zr(CH_3)C_6F_5$, and an unidentified Al species (perhaps $Al(C_6F_5)_3$).[17−21] (The reported synthesis of $Al(C_6F_5)_3$ involves the reaction of $B(C_6F_5)_3$ and $AlMe_3$.[22]) Use of [Ph_3C][$B(C_6F_5)_4$][23−25] with Cp_2ZrMe_2 gave **1b** and then with $AlMe_3$ gave **2b** cleanly; therefore, [Ph_3C][$B(C_6F_5)_4$] was used to prepare **1** and **2** in all other cases.

We began by looking for exchange between free $AlMe_3$ and the "coordinated" $AlMe_3$ in **2**. We observed separate ^1H NMR resonance signals for each of the methyl groups of **2** and for free $AlMe_3$ (see Figure 1), implying that exchange was slow on the time scale of a conventional NMR experiment. However, a 2-D EXSY experiment confirmed exchange between the methyl groups of **2** and free $AlMe_3$.[26] We quantified the exchange (difficult for a three-site problem) with selective population inversion experiments, which can theoretically be used to find rate constants in systems involving any number of exchanging sites.[27] We observed no direct exchange between the terminal and bridging groups of **2** (with or without excess $AlMe_3$).

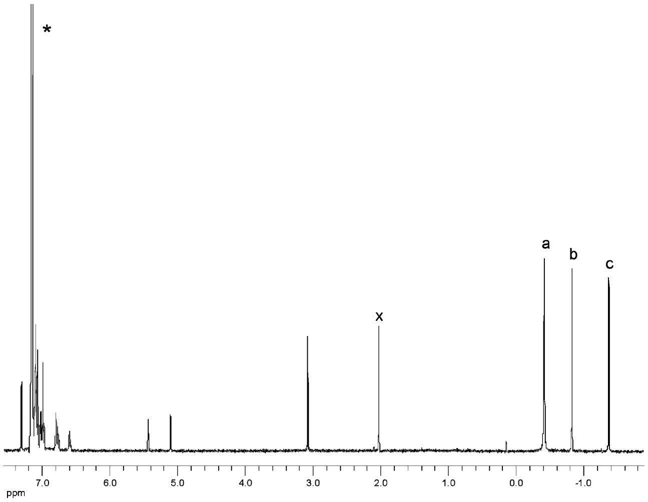
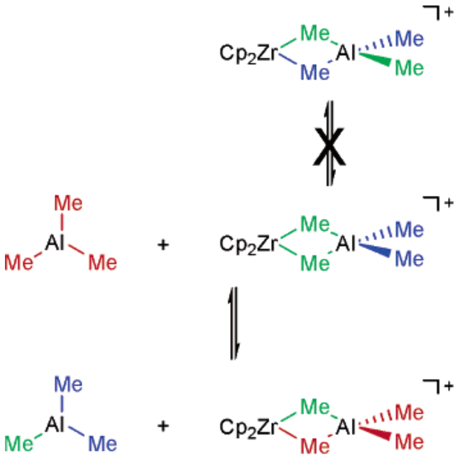


Figure 1. ^1H NMR spectrum of [**2e**][$B(C_6F_5)_4$] + $(AlMe_3)_2$ in C_6D_6 at room temperature. The peak marked with the letter a corresponds to $(Al\mathit{Me}_3)_2$, that with the letter b to [(EBI)$Zr(\mu\text{-}\mathit{Me})_2Al(Me)_2$][$B(C_6F_5)_4$], and that with the letter c to [(EBI)$Zr(\mu\text{-}Me)_2Al(\mathit{Me})_2$][$B(C_6F_5)_4$]. The asterisk denotes $C_6D_5\mathit{H}$, and the letter x denotes $\mathit{Me}CPh_3$. The remaining peaks are those of the EBI ligand.

Scheme 1. Observed Exchange of Free and Coordinated $AlMe_3$



The mechanism in Scheme 1 requires the coordination of another molecule of $AlMe_3$ after the dissociation of **2**. If the dissociation of **2** is indeed first order, the transfer of magnetization from the methyl groups of **2** to those of free $AlMe_3$ should be independent of [$AlMe_3$] and should occur (depending on which signal is inverted) with a rate constant equal to or twice the rate constant

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[16] BMe_3 appears to be the unidentified species that Shaughnessy and Waymouth[31] generated from the reaction of $Cp^*{}_2ZrMe_2$ or $(NMInd)_2ZrMe_2$ with $B(C_6F_5)_3$ and then $AlMe_3$. Al/B Me/C_6F_5 exchange is facile after methyl abstraction by $B(C_6F_5)_3$.

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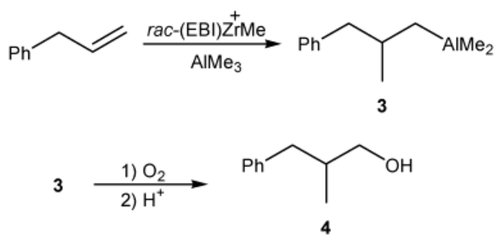
Scheme 2. Carboalumination of Allylbenzene

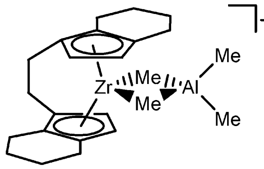


for dissociation of **2**. Selective inversion of the terminal methyl peak of **2**, and appropriate analysis of the return of magnetization to equilibrium,[28] gave the rate constants in Table 1; the measured **2**→$AlMe_3$ rate constants, which are independent of [$AlMe_3$] as predicted, must be k_{off}. (The $AlMe_3$ monomer/dimer equilibrium is rapidly maintained on the time scale of methyl exchange between Zr and Al.) Because **1** cannot be directly observed, and [**1**] cannot therefore be determined, it is impossible to determine k_{on}.

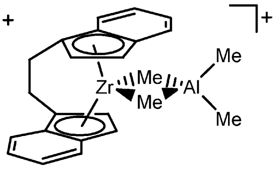
The decrease of the dissociation rate constants k_{off} in the order Ti > Zr > Hf is reasonable if we think of the dissociation of **2** as breaking a metal−ligand bond. It is more surprising that the k_{off} values decrease in the order ethylenebis(indenyl) (EBI) (**2e**) > Cp (**2b**) > ethylenebis(tetrahydroindenyl) (EBTHI) (**2d**). A variety of spectroscopic and thermodynamic data imply that bridged indenyl ligands are less effective donors than cyclopentadienyl ones,[29] and the reduction potentials of the dichlorides decrease in the order $(EBI)ZrCl_2 > Cp_2ZrCl_2 > (EBTHI)ZrCl_2$;[30] therefore, the electrophilicities of the alkylmetallocene cations **1** *decrease* in the order EBI > Cp > EBTHI.

The fact that the k_{off} value for the EBTHI cation **2d** is negligible is consistent with the fact that **2d** is a poor carboalumination catalyst. Shaughnessy and Waymouth[31] have reported "poor selectivity for carbometallated products" from 1,5-hexadiene, 1-hexene, 4-methyl-1-pentene, and diallylsilane with *rac*-(EBTHI)$ZrMe_2/B(C_6F_5)_3/AlMe_3$ in dichloroethane. While they did report a 78% yield of **4** from allylbenzene with the same catalyst and solvent (Scheme 2), we see no carboalumination activity (<5% reaction to form **3**) from allylbenzene with **1d** (9×10^{-4} M) and $AlMe_3$ (9×10^{-3} M) in C_6D_6.

The relatively large k_{off} value for **2e** suggests that the EBI cation **1e** will be a *much better* carboalumination catalyst. Indeed, we observe a k_{obs} value of 3.4×10^{-4} s^{-1} for the disappearance of allylbenzene, with [Zr] = 7×10^{-4} M and [Al] = 4×10^{-3} M in C_6D_6 at 300 K. This result and the rigidity of the **1e**/**2e** system make optically active **1e**/**2e** attractive as a catalyst for asymmetric carboalumination.



2d



2e

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Note Added in Proof. In a paper that has just appeared (Britovsek, G. J. P.; Cohen, S. A.; Gibson, V. C.; van Meurs, M. *J. Am. Chem. Soc.* **2004**, *126*, 10701−10712) a "dissociative or dissociative−interchange mechanism" has been called "most likely" for the substitution reactions of heterobimetallics like **2** with ethylene or a different AlR_3.

Supporting Information Available: Text and figures giving general experimental procedures and details of selective population inversion experiments, including data analysis using CIFIT. This material is available free of charge via the Internet at http://pubs.acs.org.

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