



Exchange of alkyl and *tris*(2-mercapto-1-*t*-butylimidazolyl)hydroborato ligands between zinc, cadmium and mercury



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Dedicated with respect to Mike Mingos on the occasion of his 70th birthday. Happy birthday, Mike!

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ABSTRACT

The *tris*(2-mercaptoimidazolyl)hydroborato ligand, [Tm^{Bu^t}], has been used to investigate the exchange of alkyl and sulfur donor ligands between the Group 12 metals, Zn, Cd and Hg. For example, [Tm^{Bu^t}]₂Zn reacts with Me₂Zn to yield [Tm^{Bu^t}]ZnMe, while [Tm^{Bu^t}]CdMe is obtained readily upon reaction of [Tm^{Bu^t}]₂Cd with Me₂Cd. Ligand exchange is also observed between different metal centers. For example, [Tm^{Bu^t}]CdMe reacts with Me₂Zn to afford [Tm^{Bu^t}]ZnMe and Me₂Cd. Likewise, [Tm^{Bu^t}]HgMe reacts with Me₂Zn to afford [Tm^{Bu^t}]ZnMe and Me₂Hg. However, whereas the [Tm^{Bu^t}] ligand transfers from mercury to zinc in the methyl system, [Tm^{Bu^t}]HgMe/Me₂Zn, transfer of the [Tm^{Bu^t}] ligand from zinc to mercury is observed upon treatment of [Tm^{Bu^t}]₂Zn with HgI₂ to afford [Tm^{Bu^t}]HgI and [Tm^{Bu^t}]ZnI. These observations demonstrate that the phenomenological preference for the [Tm^{Bu^t}] ligand to bind one metal rather than another is strongly influenced by the nature of the co-ligands.

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Introduction

The exchange of alkyl, aryl and cyclopentadienyl groups between metal centers is an important method for synthesizing a variety of organometallic compounds [1]. For example, transition metal alkyl compounds are often synthesized *via* metathesis of a transition metal halide compound with main group metal alkyls such as RLi, RMgX, and R₂Zn. In addition to their use in the synthesis of organometallic compounds of transition metals, main group metal alkyl compounds have found other applications. For example, Et₂Zn [2] is an important chain transfer agent in olefin polymerization for the control of molecular weight distributions [3]; furthermore, it has also been used as an effective means to shuttle growing polymer chains between different catalyst centers, thereby affording a novel method for forming block copolymers [4]. Here we describe a series of reactions that involve exchange of alkyl and other ligands between Group 12 metals.

Results and discussion

While zinc [3–6] and, to a lesser extent, cadmium [5,7] dialkyls have important applications, the mercury counterparts find little utility due to their extreme toxicity [8]. One of the factors responsible for the toxicity of organomercury compounds is the high affinity of mercury for sulfur [8–10] such that it binds effectively to the cysteine residues in proteins and enzymes [11], and also displaces zinc from cysteine rich structural and catalytic sites [9,12,13]. Therefore, in addition to examining alkyl group exchange, it is also pertinent to examine exchange reactions involving sulfur ligands.

Previous studies have demonstrated that *tris*(2-mercaptoimidazolyl)hydroborato ligands, [Tm^R] [14–18], are a useful class of L₂X [19] [S₃] donors that provide a sulfur-rich coordination environment for a variety of metals (Fig. 1). For example, the *t*-butyl derivative, [Tm^{Bu^t}], has been used to synthesize a variety of zinc [20–22], cadmium [21,23] and mercury [21,24] complexes, which provides a basis for us to investigate alkyl exchange reactions of these metals [25].

Whereas the aforementioned synthetic use of main group alkyls involves the exchange of alkyl groups between different metals, alkyl transfer between centers involving the same metal is also

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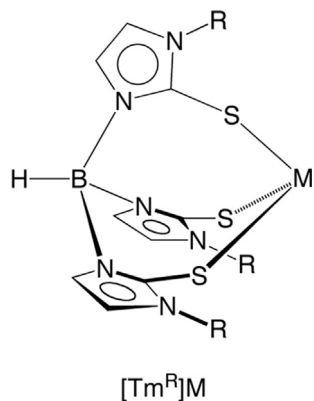
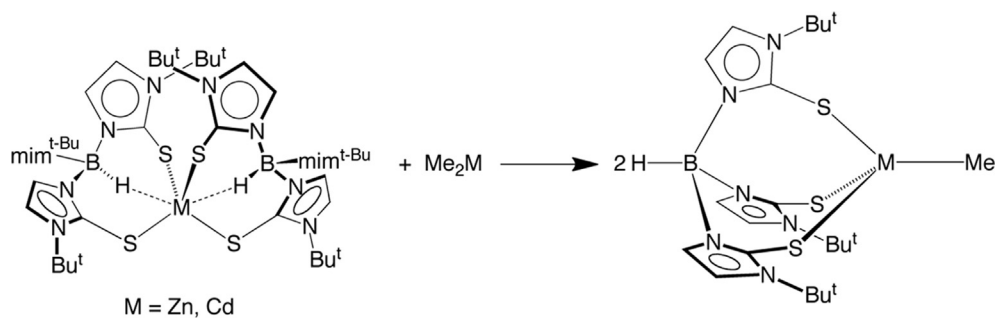


Fig. 1. $[\text{Tm}^{\text{R}}]$ ligands in their κ^3 -coordination mode.

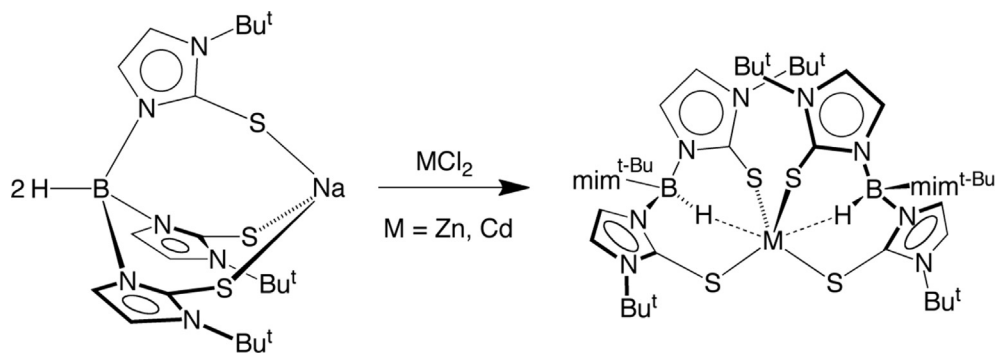
possible. For example, the Schlenk equilibrium involving the interconversion of Grignard reagents and the corresponding dialkyl magnesium compounds provides an excellent illustration of this type of transformation [26].

We have now demonstrated that a similar type of transformation exists between $[\text{Tm}^{\text{Bu}^t}]\text{MMe}$ and $[\text{Tm}^{\text{Bu}^t}]_2\text{M}/\text{Me}_2\text{M}$, and that the reaction lies heavily in favor of the heteroleptic derivative, $[\text{Tm}^{\text{Bu}^t}]\text{MMe}$. Thus, treatment of $[\text{Tm}^{\text{Bu}^t}]_2\text{Zn}$ [22] with Me_2Zn results in the facile formation of $[\text{Tm}^{\text{Bu}^t}]\text{ZnMe}$ [20a], as illustrated in Scheme 1. Likewise, $[\text{Tm}^{\text{Bu}^t}]\text{CdMe}$ [23] is rapidly obtained upon reaction of $[\text{Tm}^{\text{Bu}^t}]_2\text{Cd}$ [23] with Me_2Cd .

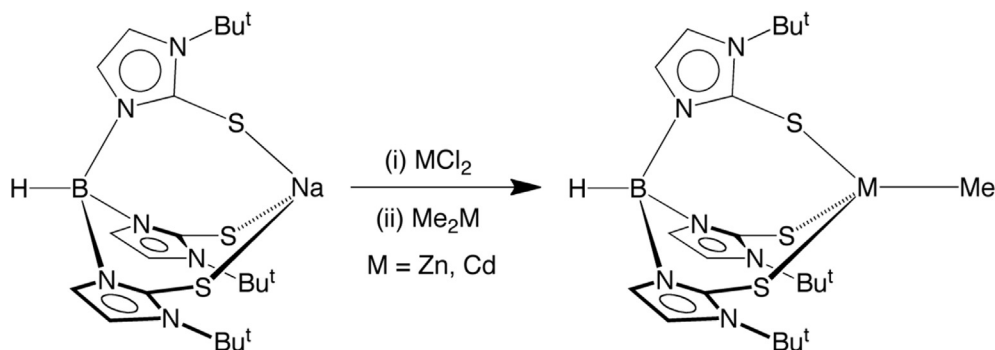
The formation of $[\text{Tm}^{\text{Bu}^t}]\text{ZnMe}$ and $[\text{Tm}^{\text{Bu}^t}]\text{CdMe}$ by these reactions provides a useful method of synthesis from the sodium complex because $[\text{Tm}^{\text{Bu}^t}]_2\text{M}$ may be generated via the reactions of $[\text{Tm}^{\text{Bu}^t}]\text{Na}$ [17,27] with MCl_2 ($\text{M} = \text{Zn}, \text{Cd}$), as illustrated in Scheme 2. Specifically, $[\text{Tm}^{\text{Bu}^t}]\text{MMe}$ can be obtained from $[\text{Tm}^{\text{Bu}^t}]\text{Na}$ in a single reaction flask via a two-step sequence that involves (i) treatment of 2 equivalents of $[\text{Tm}^{\text{Bu}^t}]\text{Na}$ with MCl_2 to generate $[\text{Tm}^{\text{Bu}^t}]_2\text{M}$, followed by (ii) treatment with Me_2M to afford $[\text{Tm}^{\text{Bu}^t}]\text{MMe}$ (Scheme 3). An important advantage of this method is that it does not require the use of the thallium reagent $[\text{Tm}^{\text{Bu}^t}]\text{Tl}$ [27]. Thus, although $[\text{Tm}^{\text{Bu}^t}]\text{MMe}$ may be synthesized directly via the reactions of Me_2M with $[\text{Tm}^{\text{Bu}^t}]\text{Tl}$, the latter compound is also synthesized from $[\text{Tm}^{\text{Bu}^t}]\text{Na}$ by treatment with $\text{Tl}(\text{OAc})$ [27]. As such, it is evident that the method of synthesis of $[\text{Tm}^{\text{Bu}^t}]\text{MMe}$ from $[\text{Tm}^{\text{Bu}^t}]\text{Na}$



Scheme 1. Formation of $[\text{Tm}^{\text{Bu}^t}]\text{MMe}$ by treatment of $[\text{Tm}^{\text{Bu}^t}]_2\text{M}$ with Me_2M ($\text{M} = \text{Zn}, \text{Cd}$).



Scheme 2. Formation of $[\text{Tm}^{\text{Bu}^t}]_2\text{M}$ from MCl_2 ($\text{M} = \text{Zn}, \text{Cd}$) and $[\text{Tm}^{\text{Bu}^t}]\text{Na}$.



Scheme 3. Synthesis of $[\text{Tm}^{\text{Bu}^t}]\text{MMe}$ from $[\text{Tm}^{\text{Bu}^t}]\text{Na}$ by sequential reaction with MCl_2 and Me_2M ($\text{M} = \text{Zn}, \text{Cd}$).

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