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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 Me_2Zn to yield $[Tm^{Bu^t}]ZnMe$, while $[Tm^{Bu^t}]CdMe$ is obtained readily upon reaction of $[Tm^{Bu^t}]_2Cd$ with Me_2Cd. Ligand exchange is also observed between different metal centers. For example, $[Tm^{Bu^t}]CdMe$ reacts with Me_2Zn to afford $[Tm^{Bu^t}]ZnMe$ and Me_2Cd. Likewise, $[Tm^{Bu^t}]HgMe$ reacts with Me_2Zn to afford $[Tm^{Bu^t}]ZnMe$ and Me_2Hg. However, whereas the $[Tm^{Bu^t}]$ ligand transfers from mercury to zinc in the methyl system, $[Tm^{Bu^t}]HgMe/Me_2Zn$, transfer of the $[Tm^{Bu^t}]$ ligand from zinc to mercury is observed upon treatment of $[Tm^{Bu^t}]_2Zn$ with HgI_2 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.

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 R_2Zn. 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, Et_2Zn [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 L_2X [19] $[S_3]$ 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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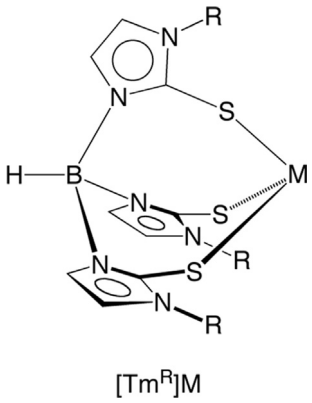
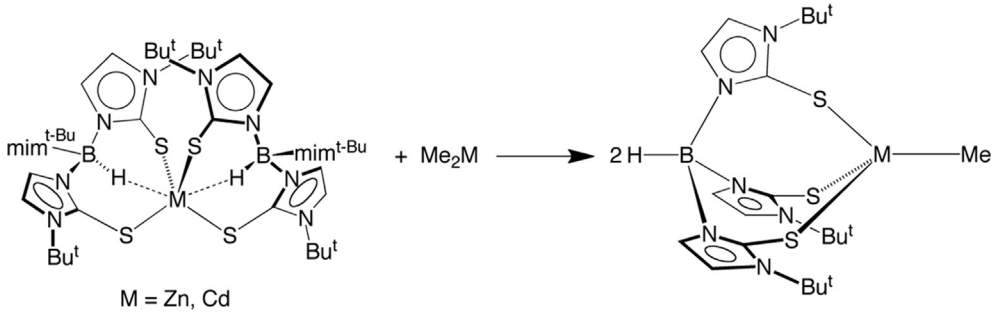


Fig. 1. [TmR] ligands in their κ^3-coordination mode.

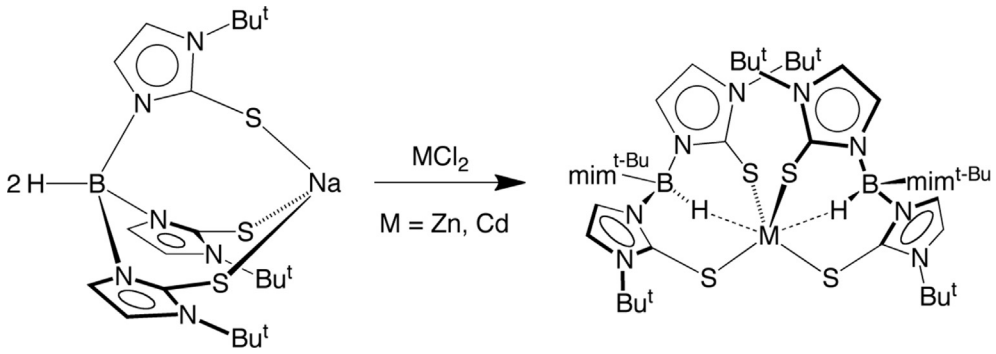
possible. For example, the Schlenk equilibrium involving the interconversion of Grignard reagents and the corresponding dialkyl magnesium compounds provides an excellent illustration of this type of transformation [26].

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

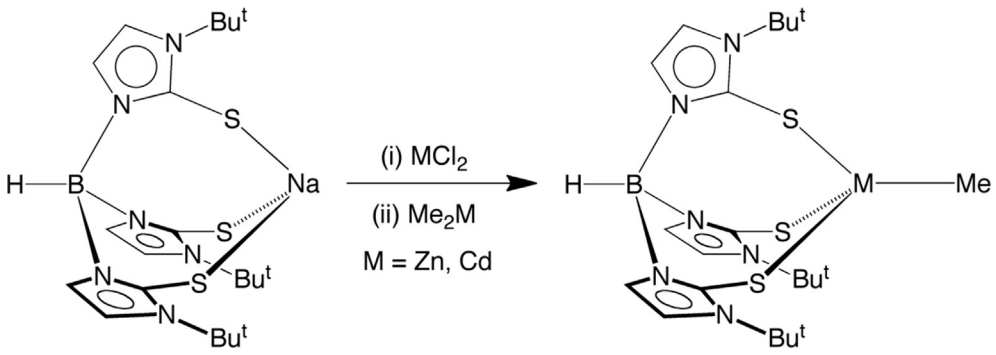
The formation of [TmBut]ZnMe and [TmBut]CdMe by these reactions provides a useful method of synthesis from the sodium complex because [TmBut]$_2$M may be generated *via* the reactions of [TmBut]Na [17,27] with MCl$_2$ (M = Zn, Cd), as illustrated in Scheme 2. Specifically, [TmBut]MMe can be obtained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



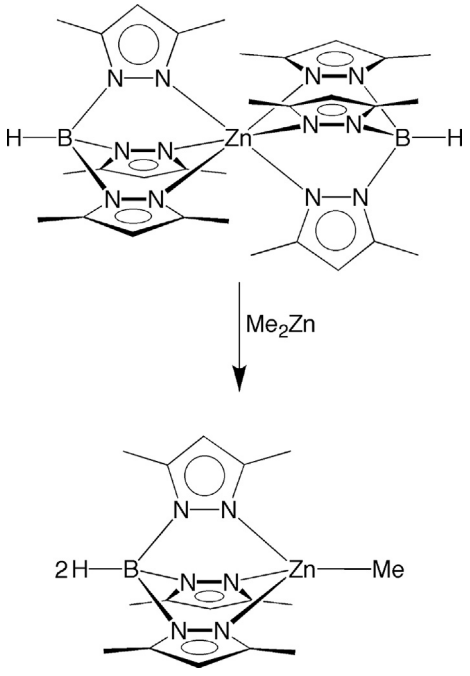
Scheme 1. Formation of [TmBut]MMe by treatment of [TmBut]$_2$M with Me$_2$M (M = Zn, Cd).



Scheme 2. Formation of [TmBut]$_2$M from MCl$_2$ (M = Zn, Cd) and [TmBut]Na.



Scheme 3. Synthesis of [TmBut]MMe from [TmBut]Na by sequential reaction with MCl$_2$ and Me$_2$M (M = Zn, Cd).



Scheme 4. Formation of [Tp^{Me_2}]ZnMe from [Tp^{Me_2}]$_2$Zn and Me_2Zn.

presented in Scheme 3 is more direct and does not require the use of a thallium reagent.

The Schlenk-type redistribution reaction illustrated in Scheme 1 is not restricted to the [Tm$^{Bu^t}$] ligand, and we have also observed it to occur with the tris(pyrazolyl)hydroborato ligand, [Tp^{Me_2}]. Specifically, [Tp^{Me_2}]$_2$Zn [28] reacts with Me_2Zn to form [Tp^{Me_2}]ZnMe [28], as illustrated in Scheme 4.

In addition to examining Schlenk-type equilibria involving [Tm$^{Bu^t}$]MMe complexes, we have also investigated alkyl exchange between two different metals. For example, treatment of the zinc methyl compound, [Tm$^{Bu^t}$]ZnMe, with Me_2Cd results in the rapid formation of [Tm$^{Bu^t}$]CdMe and Me_2Zn. However, the reaction does not proceed to completion, but rather results in the generation of an equilibrium mixture, which has been confirmed by examining the reverse reaction between [Tm$^{Bu^t}$]CdMe and Me_2Zn (Scheme 5). The equilibrium constant for the reaction between [Tm$^{Bu^t}$]ZnMe and Me_2Cd, as determined by ^{1}H NMR spectroscopy, is $7.0(5) \times 10^{-2}$ at 300 K [ΔG = 1.6(1) kcal mol^{-1}]. Furthermore, measurement of the temperature dependence of the equilibrium constant (Fig. 2) allows determination of ΔH [1.82(7) kcal mol^{-1}] and ΔS [0.9(3) e.u.]. The latter value is close to zero, which is to be expected for the entropy change associated with a redistribution reaction of this type [29].

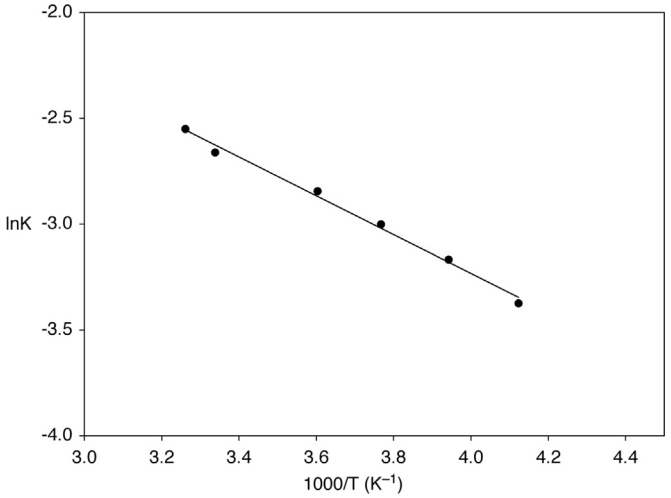


Fig. 2. van't Hoff plot for the reaction of [Tm$^{Bu^t}$]ZnMe with Me_2Cd.

The above thermodynamic data indicate that there is a phenomenological preference for the [Tm$^{Bu^t}$] ligand to coordinate to zinc rather than to cadmium in this system. However, this observation does not, *per se*, mean that the Zn–[Tm$^{Bu^t}$] bond dissociation energy (BDE, D) is greater than the Cd–[Tm$^{Bu^t}$] BDE because it is also necessary to take into account the M–Me BDEs in [Tm$^{Bu^t}$]MMe and Me_2M.

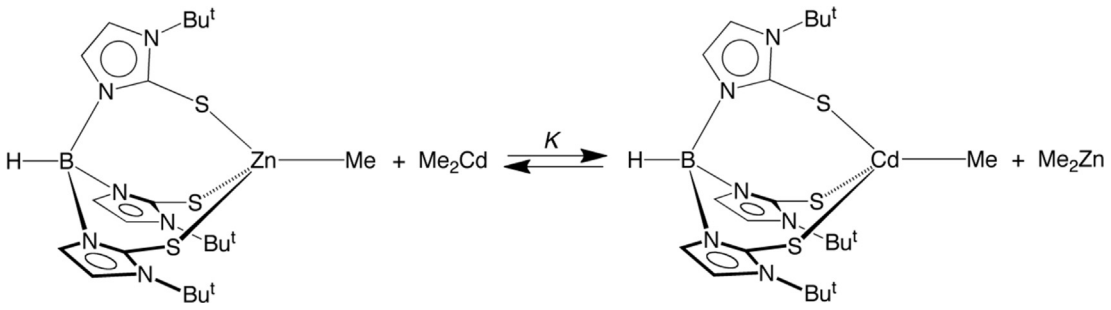
Specifically, ΔH for the reaction may be expressed by Equation (1), where L = [Tm$^{Bu^t}$]:

$$\Delta H = \left[2D(\mathrm{Cd-Me})_{\mathrm{Me_2Cd}} + D(\mathrm{Zn-Me})_{\mathrm{LZnMe}} + D(\mathrm{Zn-}L)_{\mathrm{LZnMe}}\right] - \left[2D(\mathrm{Zn-Me})_{\mathrm{Me_2Zn}} + \mathrm{D(Cd-Me)}_{\mathrm{LCdMe}} + D(\mathrm{Cd-L})_{\mathrm{LCdMe}}\right] \quad (1)$$

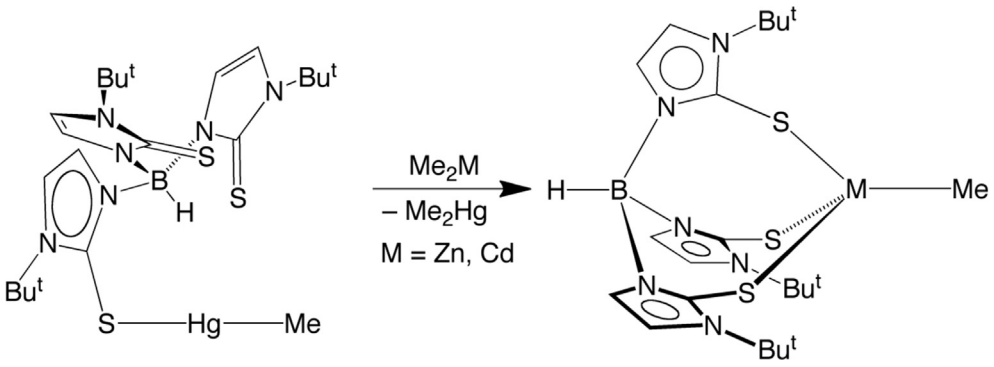
Alternatively, ΔH may be expressed in the form shown in Equation (2):

$$\Delta H = \left[D(\mathrm{Zn-L})_{\mathrm{LZnMe}} - D(\mathrm{Cd-L})_{\mathrm{LCdMe}}\right] + \left[2D(\mathrm{Cd-Me})_{\mathrm{Me_2Cd}} - D(\mathrm{Cd-Me})_{\mathrm{LCdMe}}\right] - \left[2D(\mathrm{Zn-Me})_{\mathrm{Me_2Zn}} - D(\mathrm{Zn-Me})_{\mathrm{LZnMe}}\right] \quad (2)$$

Thus, ΔH will only correspond to the difference in Zn–[Tm$^{Bu^t}$] and Cd–[Tm$^{Bu^t}$] BDEs if the combined term {[$2D$(Cd–Me)$_{Me_2Cd}$ – D(Cd–Me)$_{LCdMe}$] – [$2D$(Zn–Me)$_{Me_2Zn}$ – D(Zn–Me)$_{LZnMe}$]} is



Scheme 5. [Tm$^{Bu^t}$] Ligand transfer between zinc and cadmium.



Scheme 6. [Tm$^{Bu^t}$] Ligand transfer from mercury to zinc or cadmium.

coincidentally zero, *i.e.* 2[D(Zn–Me)$_{Me_2Zn}$ – D(Cd–Me)$_{Me_2Cd}$] = [D(Zn–Me)$_{LZnMe}$ – D(Cd–Me)$_{LCdMe}$].

Employing the literature values for the average M–Me BDEs of Me_2Zn (42.0 kcal mol^{-1}) and Me_2Cd (33.3 kcal mol^{-1}) [30,31] and the experimental value of 1.8 kcal mol^{-1} determined for ΔH, the difference in Zn–[Tm$^{Bu^t}$] and Cd–[Tm$^{Bu^t}$] BDEs may be expressed in the form shown in Equation (3), which clearly indicates how determination of its value is linked to the difference in Zn–Me and Cd–Me BDEs.

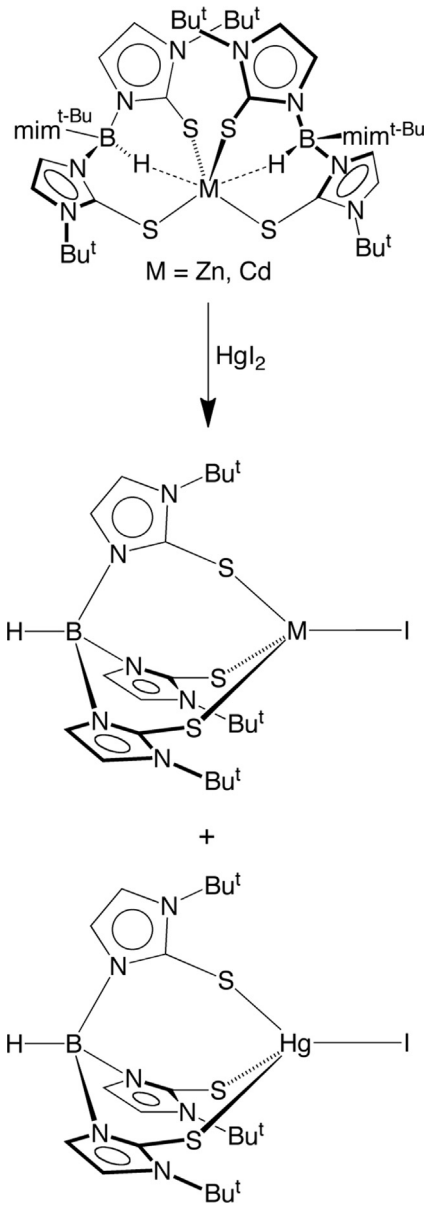
$$\left[D(\mathrm{Zn-L})_{\mathrm{LZnMe}} - D(\mathrm{Cd-L})_{\mathrm{LCdMe}}\right] = 19.2 - \left[D(\mathrm{Zn-Me})_{\mathrm{LZnMe}} - D(\mathrm{Cd-Me})_{\mathrm{LCdMe}}\right] \quad (3)$$

Thus, a difference of less than 19.2 kcal mol^{-1} between the Zn–Me and Cd–Me BDEs corresponds to a Zn–[Tm$^{Bu^t}$] interaction that is stronger than the Cd–[Tm$^{Bu^t}$] interaction, whereas a greater difference corresponds to a Cd–[Tm$^{Bu^t}$] interaction that is stronger than the Zn–[Tm$^{Bu^t}$] interaction[1]. For reference, we are aware of few comparisons between Zn–X and Cd–X BDEs, but note that the Zn–N BDE of Zn[N(SiMe$_3$)$_2$]$_2$ is 15.6 kcal mol^{-1} stronger than the corresponding Cd–N bond in Cd[N(SiMe$_3$)$_2$]$_2$ [32], while the Zn–C BDE of Me_2Zn is 8.7 kcal mol^{-1} stronger than the corresponding Cd–C bond in Me_2Cd [30]. Thus, if the difference in Zn–Me and Cd–Me BDEs of [Tm$^{Bu^t}$]MMe were to be of a comparable value to the above Zn–X and Cd–X BDEs, the Zn–[Tm$^{Bu^t}$] interaction would be predicted to be stronger than the Cd–[Tm$^{Bu^t}$] interaction.

In addition to observing transfer of the [Tm$^{Bu^t}$] ligand from cadmium to zinc, we have also observed the analogous transfer from mercury to both cadmium and zinc. Thus, [Tm$^{Bu^t}$]HgMe [24a] reacts with Me_2Zn and Me_2Cd to give, respectively, [Tm$^{Bu^t}$]ZnMe and [Tm$^{Bu^t}$]CdMe (Scheme 6).

While the transfer of the [Tm$^{Bu^t}$] ligand from mercury to zinc and cadmium may seem unexpected in terms of the often discussed thiophilicity of mercury [8–10], it is important to emphasize that, as discussed above, the thermodynamics of the exchange reactions require due consideration to be given to *all* M–X bonds. As such, a contributing factor to the observed exchange reaction is that the mercury methyl compound [Tm$^{Bu^t}$]HgMe exhibits κ^1-coordination of the [Tm$^{Bu^t}$] ligand [24a], whereas both the zinc and cadmium counterparts exhibit κ^3-coordination.

In this regard, it is noteworthy that we have also observed transfer of the [Tm$^{Bu^t}$] ligand from zinc to mercury and from cadmium to mercury upon treatment of [Tm$^{Bu^t}$]$_2$M(M = Zn, Cd) with HgI_2 to afford [Tm$^{Bu^t}$]MI (M = Zn [20a], Cd [23]) and [Tm$^{Bu^t}$]HgI [24a], as illustrated in Scheme 7. Thus, it is evident that the thermodynamics of ligand exchange reactions in this system depend strongly on the nature of co-ligands.



Scheme 7. [Tm$^{Bu^t}$] Ligand transfer from zinc or cadmium to mercury.

[1] Adopting a value of 44.5 kcal mol^{-1} for the average BDE of Me_2Zn (reference 31), the threshold difference is 24.2 kcal mol^{-1} rather than 19.2 kcal mol^{-1}.

Summary

In summary, a variety of ligand exchange reactions between zinc, cadmium and mercury centers has been investigated for compounds of the type $[Tm^{Bu^t}]MX(M = Zn, Cd, Hg)$. For example, ligand redistribution is facile between $[Tm^{Bu^t}]_2M$ and Me_2M to afford $[Tm^{Bu^t}]MMe$ (M = Zn, Cd). Ligand exchange is also observed between different metal centers. Thus, $[Tm^{Bu^t}]CdMe$ reacts with Me_2Zn to afford $[Tm^{Bu^t}]ZnMe$ and Me_2Cd, while the corresponding reaction between $[Tm^{Bu^t}]HgMe$ and Me_2Zn affords $[Tm^{Bu^t}]ZnMe$ and Me_2Hg. In contrast to the transfer of the $[Tm^{Bu^t}]$ ligand from mercury to zinc in the methyl system, $[Tm^{Bu^t}]HgMe/Me_2Zn$, transfer from zinc to mercury is observed upon treatment of $[Tm^{Bu^t}]_2Zn$ with HgI_2 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 mercury or zinc is strongly influenced by the nature of the co-ligands, which is a reflection of the fact that all metal–ligand bond energies need to be considered when predicting exchange reactions of this type.

Experimental section

General considerations

All manipulations were performed using a combination of glovebox, high-vacuum, and Schlenk techniques under a nitrogen or argon atmosphere [33], except where otherwise stated. Solvents were purified and degassed by standard procedures. NMR solvents were purchased from Cambridge Isotope Labs and stored over 3 Å molecular sieves. NMR spectra were measured on Bruker 300 DPX, Bruker 400 Avance III, Bruker 400 Cyber-enabled Avance III, and Bruker 500 DMX spectrometers. ^1H NMR chemical shifts are reported in ppm relative to $SiMe_4$ ($\delta = 0$) and were referenced internally with respect to the protio solvent impurity ($\delta = 7.16$ for C_6D_6, 2.08 for C_7D_8, and 1.94 for CD_3CN) [34]. Me_2Cd and Me_2Zn were obtained from Strem, while $[Tm^{Bu^t}]Na$ [17][2], $[Tm^{Bu^t}]_2Zn$ [22], $[Tm^{Bu^t}]_2Cd$ [23], $[Tp^{Me_2}]_2Zn$ [28] and $[Tm^{Bu^t}]HgMe$ [24a] were prepared by literature methods. *CAUTION: Mercury and cadmium compounds are toxic, and appropriate safety precautions must be taken in handling these compounds.*

Formation of $[Tm^{Bu^t}]_2Zn$ upon treatment of $[Tm^{Bu^t}]Na$ with $ZnCl_2$

A mixture of $[Tm^{Bu^t}]Na$ (31 mg, 0.0619 mmol) and $ZnCl_2$ (4.0 mg, 0.0293 mmol) in C_6D_6 (1.5 mL) in an NMR tube equipped with a J. Young valve was heated at 80 °C for 20 h and monitored by ^1H NMR spectroscopy, thereby demonstrating the formation of, *inter alia*, $[Tm^{Bu^t}]_2Zn$.

Formation of $[Tm^{Bu^t}]_2Cd$ upon treatment of $[Tm^{Bu^t}]Na$ with $CdCl_2$

A mixture of $[Tm^{Bu^t}]Na$ (19 mg, 0.0380 mmol) and $CdCl_2$ (3.3 mg, 0.0180 mmol) in C_6D_6 (1.5 mL) in an NMR tube equipped with a J. Young valve was heated at 80 °C for 20 h and monitored by ^1H NMR spectroscopy, thereby demonstrating the formation of, *inter alia*, $[Tm^{Bu^t}]_2Cd$.

[2] $[Tm^{Bu^t}]Na$ may be obtained in both solvated and non-solvated forms (see reference 17). The non-solvated form was used herein. The molecular structure of non-solvated $[Tm^{Bu^t}]Na$ has not been determined by X-ray diffraction and the monomeric κ^3-coordination geometry shown in Schemes 2 and 3 is only intended to be illustrative.

Reaction of $[Tm^{Bu^t}]_2Zn$ with Me_2Zn

A solution of $[Tm^{Bu^t}]_2Zn$ (2.7 mg, 0.0026 mmol) in C_6D_6 (0.7 mL) in an NMR tube equipped with a J. Young valve was treated with Me_2Zn (150 μL of a 0.082 M solution in C_6D_6, 0.0123 mmol) The reaction was monitored by ^1H NMR spectroscopy, which demonstrated the immediate formation of $[Tm^{Bu^t}]ZnMe$ [20a].

Reaction of $[Tm^{Bu^t}]_2Cd$ with Me_2Cd

A solution of $[Tm^{Bu^t}]_2Cd$ (2.4 mg, 0.0022 mmol) in C_6D_6 (1 mL) in an NMR tube equipped with a J. Young valve was treated with excess Me_2Cd (60 μL of a 0.111 M solution in C_6D_6, 0.0067 mmol). The reaction was monitored by ^1H NMR spectroscopy, which demonstrated the immediate formation of $[Tm^{Bu^t}]CdMe$ [23].

Reaction of $[Tp^{Me_2}]_2Zn$ with Me_2Zn

A solution of $[Tp^{Me_2}]_2Zn$ (4 mg, 0.006 mmol) in C_6D_6 (1 mL) in an NMR tube equipped with a J. Young valve was treated with excess Me_2Zn. The reaction was monitored by ^1H NMR spectroscopy, which demonstrated the immediate formation of $[Tp^{Me_2}]ZnMe$ [28]. The sample was lyophilized to remove solvent and excess Me_2Zn and the residue was dissolved in benzene. The solution was allowed to crystallize by slow evaporation at room temperature to afford $[Tp^{Me_2}]ZnMe$ as a white solid (3.2 mg, yield 71%).

Reaction of $[Tm^{Bu^t}]ZnMe$ with Me_2Cd

(a) A solution of $[Tm^{Bu^t}]ZnMe$ (5.8 mg, 0.0104 mmol) in C_6D_6 (0.7 mL) in an NMR tube equipped with a J. Young valve was treated with Me_2Cd (50 μL of a 0.111 M solution in C_6D_6, 0.0056 mmol). The reaction was monitored by ^1H NMR spectroscopy, which demonstrated the immediate formation of an equilibrium mixture with $[Tm^{Bu^t}]CdMe$ [23] and Me_2Zn.

(b) A solution of $[Tm^{Bu^t}]ZnMe$ (3.8 mg, 0.0068 mmol) in C_7D_8 (1 mL) in an NMR tube equipped with a J. Young valve was treated with Me_2Cd (50 μL of a 0.111 M solution in C_6D_6, 0.0056 mmol). The reaction was monitored by ^1H NMR spectroscopy, which demonstrated the immediate formation of an equilibrium mixture with $[Tm^{Bu^t}]CdMe$ [23] and Me_2Zn. The equilibrium constant was measured as a function of temperature, thereby allowing determination of ΔH and ΔS.

Reaction of $[Tm^{Bu^t}]CdMe$ with Me_2Zn

A solution of Me_2Zn (1 mL of a 0.0143 M solution in C_6D_6, 0.0143 mmol) was added to an NMR tube equipped with a J. Young valve that contained $[Tm^{Bu^t}]CdMe$ (6.1 mg, 0.0101 mmol). The reaction was monitored by ^1H NMR spectroscopy, which demonstrated the immediate formation of $[Tm^{Bu^t}]ZnMe$ [20a] and Me_2Cd.

Reaction of $[Tm^{Bu^t}]HgMe$ with Me_2Zn

A solution of $[Tm^{Bu^t}]HgMe$ (2.4 mg, 0.0035 mmol) in C_6D_6 (0.7 mL) in an NMR tube equipped with a J. Young valve was treated with Me_2Zn (100 μL of a 0.082 M solution in C_6D_6, 0.0082 mmol). The reaction was monitored by ^1H NMR spectroscopy, which demonstrated the immediate formation of $[Tm^{Bu^t}]ZnMe$ [20a] and Me_2Hg.

Reaction of $[Tm^{Bu^t}]HgMe$ with Me_2Cd

A solution of $[Tm^{Bu^t}]HgMe$ (2.7 mg, 0.0039 mmol) in C_6D_6 (0.7 mL) in an NMR tube equipped with a J. Young valve was treated

with Me_2Cd (85 μL of a 0.111 M solution in C_6D_6, 0.0094 mmol). The reaction was monitored by ^1H NMR spectroscopy, which demonstrated the immediate formation of [Tm^{But}]CdMe [23] and Me_2Hg.

Reaction of [Tm^{But}]$_2$Zn with HgI_2

A solution of [Tm^{But}]$_2$Zn (1.5 mg, 0.0015 mmol) in CD_3CN (1 mL) was added to HgI_2 (0.7 mg, 0.0015 mmol) and the solution was transferred to an NMR tube equipped with a J. Young valve. The reaction was monitored by ^1H NMR spectroscopy, which demonstrated the immediate formation of a 1:1 mixture of [Tm^{But}]HgI [24a] and [Tm^{But}]ZnI [20a].

Reaction of [Tm^{But}]$_2$Cd with HgI_2

A solution of [Tm^{But}]$_2$Cd (4.4 mg, 0.0041 mmol) in CD_3CN (1 mL) was added to HgI_2 (1.8 mg, 0.0040 mmol) and the solution was transferred to an NMR tube equipped with a J. Young valve. The reaction was monitored by ^1H NMR spectroscopy, which demonstrated the immediate formation of a *ca.* 1:1 mixture of [Tm^{But}]HgI [24a] and [Tm^{But}]CdI [23].

Synthesis of [Tm^{But}]CdMe

A suspension of [Tm^{But}]Na (1.110 g, 2.22 mmol) in benzene (*ca.* 30 mL) was treated with $CdCl_2$ (193.5 mg, 1.06 mmol) and heated at 125 °C with stirring in a pressure vessel for 19 h. After this period, the reaction mixture was allowed to cool to room temperature, thereby depositing a white precipitate. Me_2Cd (120 μL, 1.67 mmol) was added and the mixture was stirred at room temperature for 1 h and filtered. The white precipitate was extracted with benzene (*ca.* 2 × 5 mL), and the extracts were combined with the filtrate from the reaction. A white precipitate started to form and was redissolved by addition of benzene (*ca.* 10 mL). The solution was transferred to a Schlenk flask and the volatile components removed *in vacuo* to yield [Tm^{But}]CdMe as a white solid (984 mg, 77%) which was identified by ^1H NMR spectroscopy [23].

Synthesis of [Tm^{But}]ZnMe

A suspension of [Tm^{But}]Na (384.5 mg, 0.768 mmol) in benzene (*ca.* 10 mL) was treated with $ZnCl_2$ (51.2 mg, 0.376 mmol) and stirred vigorously at room temperature for 2 days, resulting in the formation of a thick white suspension. Me_2Zn (157.8 mg, 1.65 mmol) was added and the mixture was stirred at room temperature for 1 day. After this period, the reaction mixture was centrifuged and the mother liquor was filtered. The solid isolated from the centrifugation was extracted with benzene (8 mL) and the extract was combined with the above filtrate. The volatile components were removed *in vacuo* to yield [Tm^{But}]ZnMe as a white solid (235.0 mg, 56%), which was identified by ^1H NMR spectroscopy [20a].

Acknowledgments

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