# Divergent reactivity of $[(\kappa^3\text{-L})ThCl_2(dme)]$ with Grignard reagents: alkylation, ancillary ligand transfer to magnesium, and halide-exchange caught in the act ‡

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‡ *L represents the ancillary ligands 2,6-bis(2,6-diisopropylanilidomethyl)pyridine (BDPP) and 4,5-bis(2,6-diisopropylanilido)-2,7-di-tert-butyl-9,9-dimethylxanthene ($XA_2$).*

## ABSTRACT

Reaction of [(BDPP)ThCl$_2$(dme)] (**1**) with 2 equivalents of MeMgBr in OEt$_2$, followed by filtration and layering a toluene solution with hexanes at –30 °C yielded a single large crystal of [{(BDPP)ThX(μ-X)$_2$Mg(OEt$_2$)(μ-Me)}$_2$]·2 toluene (X = Br$_{0.73\text{-}0.87}$/Cl$_{0.13\text{-}0.27}$; **3**·2 toluene). This product is the result of halide exchange to form a partially brominated neutral thorium species, which is adducted with MeMgX(OEt$_2$). The complex is then tetrametallic as a result of Mg-Me-Mg bridges. The structure of complex **3** provides direct insight into the process by which halide exchange takes place between electrophilic metal halide complexes and Grignard reagents. This reactivity stands in stark contrast to the reactions of **1** and [(XA$_2$)ThCl$_2$(dme)] (**2**) with PhCH$_2$MgCl. In these cases the expected dialkyl products, [LTh(CH$_2$Ph)$_2$] [L = BDPP (**4**) and XA$_2$ (**5**)], were formed under most conditions. However, addition of a PhCH$_2$MgCl solution to **2** at –78 °C and warming to room temperature over a period of 1 hour gave [(XA$_2$)Mg(dme)] (**6**), the product of ancillary ligand transfer from thorium to magnesium, in 30-50 % yield.

## 1. Introduction

Much of early organometallic actinide chemistry has been dominated by carbocyclic ancillary ligand (*e.g.* $C_5R_5^-$ or $C_8R_8^{2-}$) complexes.[1] However, non-carbocyclic ligands have seen a flurry of recently activity in this area (Figure 1)[2-20] and offer a wide range of opportunities with respect to modification of metal complex geometry, coordination number, steric and electronic properties, and reactivity. Our research has focused on the rigid, planar and tridentate BDPP [2,6-bis(2,6-diisopropylanilidomethyl)pyridine][21] and $XA_2$ [4,5-bis(2,6-diisopropylanilido)-2,7-di-*tert*-butyl-9,9-dimethylxanthene][14] dianions (Figure 1),[22] and reaction of $Li_2$[BDPP], $Na_2[XA_2]$ or $K_2(dme)[XA_2]$ with $[ThCl_4(dme)_2]$[23] provided $[LThCl_2(dme)]$ [L = BDPP (**1**) or $XA_2$ (**2**)] in good yield. Subsequent reaction of **1** and **2** with $LiCH_2SiMe_3$ or $PhCH_2MgCl$ allowed access to $[LTh(CH_2SiMe_3)_2]$ (L = BDPP and $XA_2$),[14] and $[LTh(CH_2Ph)_2]$ [L = BDPP (**4**) and $XA_2$ (**5**)] from which the first examples of non-cyclopentadienyl thorium alkyl cations were prepared.[15, 18] However, caution is drawn to the expected outcome in reactions with $PhCH_2MgCl$ (*vide infra*).

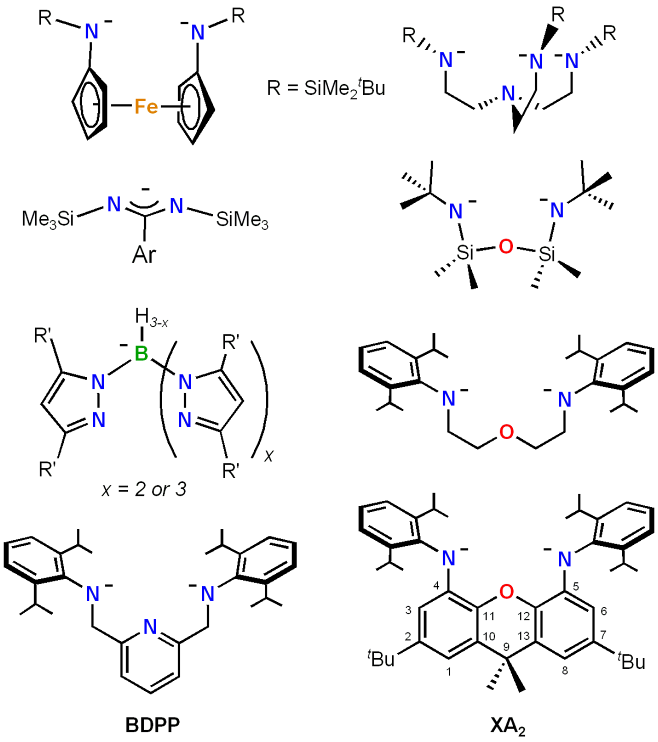


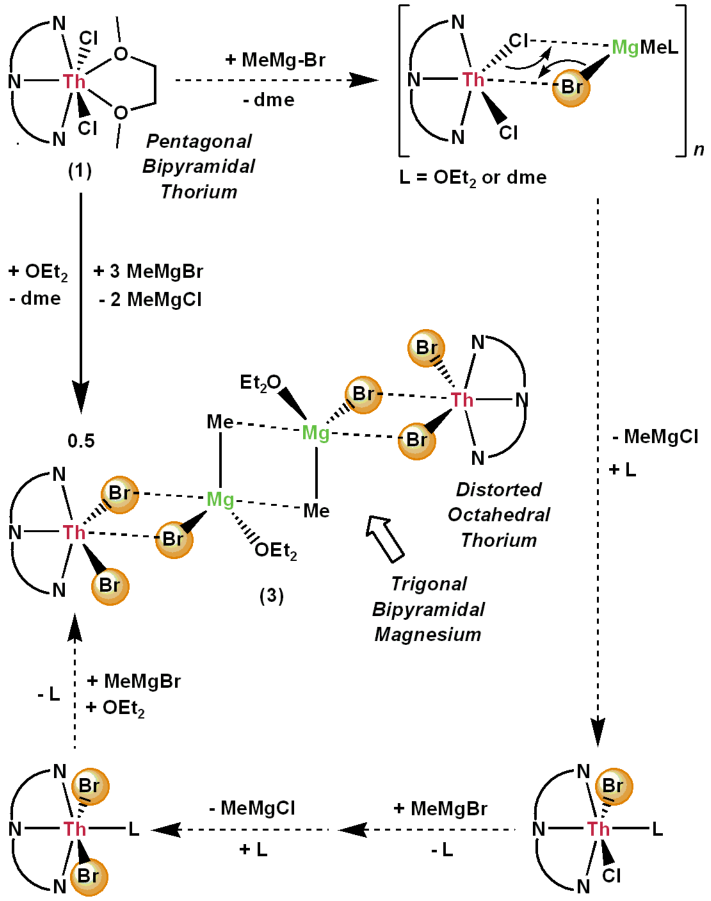
**Figure 1.** Selected Multidentate Non-Carbocyclic Ligands in Alkyl Actinide Chemistry: 1,1'-Bis(amido)ferrocene,[17, 19, 20] Amidinate,[2] Tris- or Tetrakis(pyrazolyl)borate,[3-8] 2,6-Bis(amidomethyl)pyridine (BDPP),[14-17] Tris(2-amidoethyl)amine,[9, 10], Bis(2-amidoethyl)ether, Bis(amidodimethylsilyl)ether,[11-13] and 4,5-Bis(amido)xanthene ($XA_2$)[14, 15, 18] ligands.

To explore the impact of alkyl group variation on complex stability and reactivity, the synthesis of *n*-butyl, methyl and benzyl complexes was undertaken. Thermally stable [(BDPP)Th$^n$Bu$_2$] proved readily accessible by reaction of **1** with $^n$BuLi, while reaction of **1** with MeLi was only useful as a direct route to the 'ate' complex [(BDPP)ThMe(μ-Me)$_2$Li(dme)] (the neutral dimethyl complex was subsequently prepared by reaction of [(BDPP)ThMe(μ-Me)$_2$Li(dme)] with 0.5 equiv. of **1**).[16] In this work, the reactions of [LThCl$_2$(dme)] [L = BDPP (**1**) or $XA_2$ (**2**)] with MeMgBr and PhCH$_2$MgCl[15, 18] are discussed, and the unexpected products $[\{(BDPP)ThX(\mu\text{-}X)_2Mg(OEt_2)(\mu\text{-}Me)\}_2]$ (X = $Br_{0.73\text{-}0.87}/Cl_{0.13\text{-}0.27}$; **3**) and $[(XA_2)Mg(dme)]$ (**6**) are reported. Grignard reagents are commonly employed for the alkylation of d- and f-block metal halide complexes, especially when there exists the potential for reduction or ate-complex formation with more aggressive alkylating agents (*e.g.* RLi).

## 2. Results and Discussion

### *2.1 Reactions of [(BDPP)ThCl$_2$(dme)] with MeMgBr.*

Reaction of $[(BDPP)ThCl_2(dme)]$ (**1**) with 2 or 3 equivalents of MeMgBr (3.0 M in $OEt_2$) in $OEt_2$ or toluene yielded $^1$H NMR spectra similar to those of the starting materials, but substantially broadened. Attempts to isolate an organometallic complex from these mixtures were in most instances unsuccessful. However, on one occasion, reaction of **1** with MeMgBr (2 equiv.) in diethylether, filtration, and layering a toluene solution with hexanes at –30 °C yielded a single large (~4x4x2mm) X-ray quality crystal. The solid state structure of this product, $[\{(BDPP)ThX(\mu\text{-}X)_2Mg(OEt_2)(\mu\text{-}Me)\}_2]\cdot 2$ toluene (X = $Br_{0.73\text{-}0.87}/Cl_{0.13\text{-}0.27}$; **3**·2 toluene; Scheme 1, Figure 2), revealed that alkylation had not taken place; instead, halide exchange and adduct formation between the resulting $[(BDPP)ThX_2]$ moiety and $XMgMe(OEt_2)$ had occurred. The product is then tetrametallic as a result of Mg–Me–Mg bridges. Generation of the fully brominated analogue of **3** would require reaction of **1** with three equivalents of MeMgBr, releasing two equivalents of MeMgCl per thorium centre (Scheme 1). It is of note that the formation of $[(BDPP)ThMe_2]$ must not occur to any significant extent given that the thorium dimethyl complex decomposes rapidly at room temperature in solution to form a mixture of products,[16] none of which were observed in reactions of **1** and MeMgBr.



**Scheme 1.** Reaction of **1** with MeMgBr to form the fully brominated analogue of complex **3**.

Although the reaction of **1** with MeMgBr did not provide reproducible access to complex **3**, this product presents substantial insight into the type of intermediates involved in halide exchange reactivity between metal halide precursors and Grignard reagents. Such reactivity is relatively common for f-element complexes, and is generally observed as an undesirable outcome in attempted alkylation, allylation or arylation reactions. For example, reaction of $[\{O(SiMe_2N^tBu)_2\}UCl_2]_2$ with MeMgBr resulted in the formation of $[\{O(SiMe_2N^tBu)_2\}UBr_{1.46}Cl_{0.54}]_2$ rather than the expected methyl uranium complex. By contrast, $[\{O(SiMe_2N^tBu)_2\}UCl_2]_2$ reacted with $(C_3H_5)MgBr$ to give the expected diallyl complex, and closely related $[\{O(SiMe_2N^tBu)_2\}UCl(Cp^*)]$ reacted with MeMgBr to give the anticipated methyl complex.[11] These reactions illustrate the extent to which Grignard reactivity (alkylation versus halide exchange) is influenced by subtle changes in the nature of the Grignard reagent and the metal halide complex. Another example of halide exchange in actinide chemistry is the reaction of $[Cp^*_2ThCl(\eta^2\text{-}^tBuNSPh)]$ with MeMgBr to form $[Cp^*_2ThBr(\eta^2\text{-}^tBuNSPh)]$.[24] Halide redistribution reactivity has also been reported for a range of lanthanide and group 3 complexes. For example, $[(P_2N_2)YCl]_2$ [$P_2N_2$ = $Ph_2P(CH_2SiMe_2NSiMe_2CH_2)_2PPh_2$] reacted with PhMgBr, *p*-tolylMgBr or *p*-biphenylMgBr to afford exactly the same mixture of products: the dinuclear dichloride, the mixed chloride/bromide and the dibromide.[25],[26]

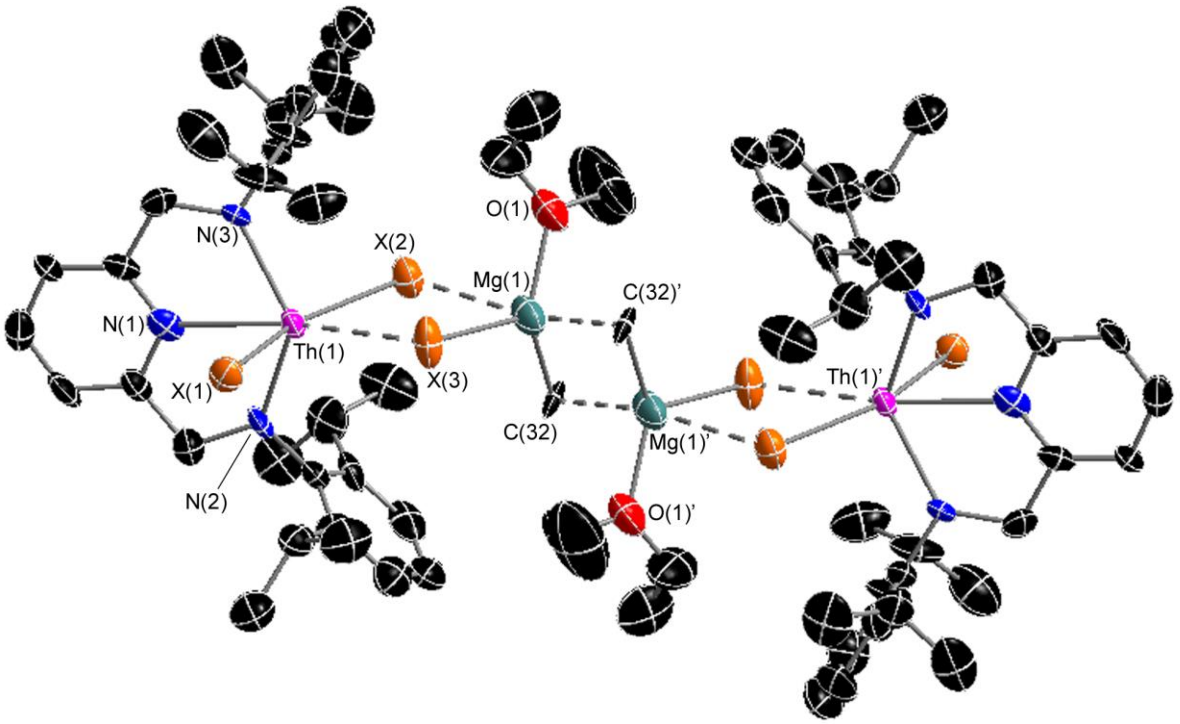


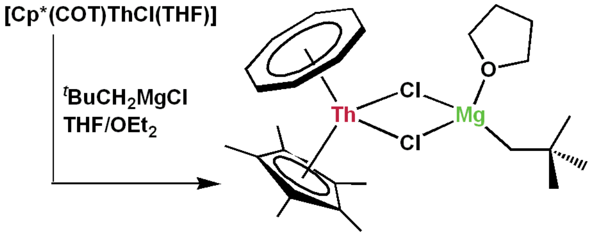
**Figure 2.** Solid state structure of **3**•2toluene with thermal ellipsoids at 50 %. Lattice solvent and hydrogen atoms are omitted for clarity. X(1) = $Br_{0.865(8)}/Cl_{0.135(8)}$; X(2) = $Br_{0.735(8)}/Cl_{0.265(8)}$; X(3) = $Br_{0.814(9)}/Cl_{0.186(9)}$. Selected bond lengths (Å) and angles (°): Th–N(1) 2.501(10), Th–N(2) 2.259(8), Th–N(3) 2.250(9), Th–X(1) 2.856(2), Th–X(2) 2.887(2), Th–X(3) 3.007(2), Mg(1)–O(1) 1.995(11), Mg(1)–C(32) 2.177(10), Mg(1)–C(32)' 2.355(12), Mg(1)–X(2) 2.913(6), Mg(1)–X(3) 2.538(5), N(1)–Th–X(3) 164.9(2), N(2)–Th–N(3) 127.1(4), X(1)–Th–X(2) 158.36(5), X(3)–Mg(1)–O(1) 114.8(4), C(32)–Mg(1)–O(1) 124.1(5), C(32)–Mg(1)–X(3) 117.5(4), C(32)'–Mg(1)–X(2) 169.9(3), Th–X(3)–Mg(1) 102.83(13), Th–X(2)–Mg(1) 97.00(11), Mg(1)–C(32)–Mg(1)' 77.5(4).

In the X-ray crystal structure of complex **3**, thorium adopts a distorted octahedral geometry, while magnesium is trigonal bipyramidal. Of the three Th–X bond lengths, Th–X(1) and Th-X(2) are very similar [2.856(2) and 2.887(2) Å, respectively], even though X(1) is terminal while X(2) bridges between thorium and magnesium. These bond distances fall in the usual range for thorium bromide complexes (2.8–2.9 Å).[27-34] However, at 3.007(2) Å, Th–X(3) is significantly longer than Th–X(1) and Th–X(2). Further, on magnesium, the Mg–X and Mg–C bond distances in the trigonal plane [Mg–X(3) = 2.538(5) Å; Mg–C(32) = 2.177(10) Å] are much shorter than those in the apical sites [Mg–X(2) = 2.913(6) Å; Mg–C(32') = 2.355(12) Å]. Based on these bond lengths, the structure can be viewed as two molecules of (BDPP)Th$X_2$ interacting with a central Grignard core, itself composed of two trigonal planar MeMgX($OEt_2$) units linked by Mg–C–Mg bridges.

The Mg-C-Mg angles in **3** are acute [77.5(4)°], but are typical for sterically uncluttered complexes containing a Mg(μ-alkyl)$_2$Mg core, for example [{Mg(μ-Me)$_2$}$_n$] [75°],[35] [({Mg(μ-Np)$_2$}$_3$Mg(μ-Br)$_2$)$_n$] [74.1 and 74.9°],[36] [{$Br_2$Mg(μ-Me)}$_2$]$^{2-}$ [73.7°][37] and [{(κ$^3$-MeN{($CH_2$)$_2$N$Me_2$}$_2$)Mg(μ-Me)}$_2$]$^{2+}$ [80.8 and 80.3°].[38] The asymmetry of the Mg(μ-Me)$_2$Mg core in **3** [Mg–C = 2.177(10) and 2.355(12) Å] is also not uncommon; while [{Mg(μ-Me)$_2$}$_n$] and [{$Br_2$Mg(μ-Me)}$_2$]$^{2-}$ adopt much more symmetrical structures [Mg–C = 2.24 Å in the former; Mg–C = 2.26 and 2.28 Å in the latter],[35, 37] Mg–C bond distances from 2.23 to 2.34 Å were observed in [{(κ$^3$-MeN{($CH_2$)$_2$N$Me_2$}$_2$)Mg(μ-Me)}$_2$]$^{2+}$,[38] and Mg–C distances from 2.20 to 2.42 Å were observed in [({Mg(μ-Np)$_2$}$_3$Mg(μ-Br)$_2$)$_n$].[36] The long Mg–C distances and acute Mg–C–Mg angle in **3** are consistent with a 3-centre 2-electron interaction, and confirm that the atoms bridging between Mg(1) and Mg(1') are carbon, not oxygen. For comparison, Mg–O distances and Mg–O–Mg angles are 1.94-1.99 Å and 103–106°, respectively, in the three crystallographically characterized μ$_2$-hydroxy magnesium complexes; [{(κ$^3$-Tp$^{Ar,Me}$)Mg(μ-OH)}$_2$], [{(nacnac)Mg(THF)(μ-OH)}$_2$] and [$Mg_4$(THF)$_4$(OMes)$_6$(μ-OH)(μ$_4$-OH)].[39-41]

The Mg-X(3) distance in **3** [2.538(5) Å][34] is similar to those observed in dinuclear [{LMgEt(μ-Br)}$_2$] complexes (2.56 Å for L = $NEt_3$ and 2.58 Å for L = $O^{i}Pr_2$)[42, 43] and in [(THF){$(Me_3Si)_3C$}Mg(μ-Br)$_2$Li(THF)$_2$] (2.52 and 2.55 Å).[44] By contrast, at 2.913(6) Å, Mg-X(2) is extremely long.[34] A similar bonding situation was observed in the weakly bound dimer [{($^{t}$BuCN){$(Me_3Si)_2HC$}Mg(μ-Br)}$_2$], with Mg-Br distances of 2.56 and 2.93 Å.[45]

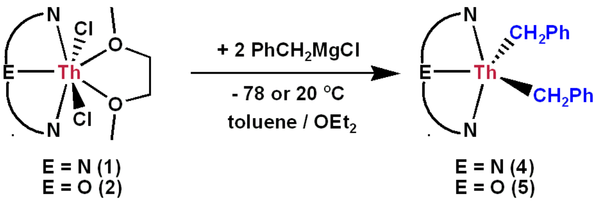
Complex **3** is a rare example of an adduct between a d- or f-block metal complex and a Grignard reagent, and is the first example of such a complex containing a terminal halide ligand (on the d- or f-block metal). The only other well-characterized d- or f-element Grignard adduct (containing an M–X–Mg–R linkage) is [Cp*(COT)Th(μ-Cl)$_2$Mg($CH_2{}^{t}Bu$)(THF)], formed via the reaction of [Cp*(COT)ThCl(THF)] with $^{t}BuCH_2MgCl$ (Scheme 2).[46] However, adduct formation *and* halide exchange has to the best of our knowledge only been observed in **3**. As such, complex **3** provides direct insight into the type of intermediates responsible for halide exchange. Complex **3** also highlights the potential compatibility of magnesium alkyls with metal halides; both bridging and terminal. A proposed reaction pathway for the conversion of **1** to the fully brominated analogue of **3** is provided in Scheme 1.[47] A related pathway was previously proposed by Cooper *et al.* to explain the formation of [Cp{$\eta^5$-$C_5H_4(CH_2CH=CH_2)$}WHBr] in the reaction of [$Cp_2WCl_2$] with $H_2C=CHCH_2MgBr$.[48]



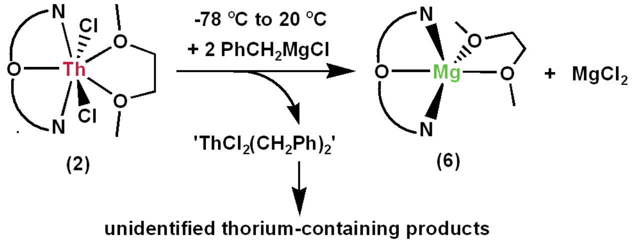
**Scheme 2.** Synthesis of [Cp*(COT)Th(μ-Cl)$_2$Mg(CH$_2$$^t$Bu)(THF)].[46]

*2.2. Reactions of [LThCl$_2$(dme)] with PhCH$_2$MgCl.*

The reactivity of **1** and **2** with PhCH$_2$MgCl stands in stark contrast to the reactivity of **1** with MeMgBr; with PhCH$_2$MgCl (2 equiv. in toluene), the expected dialkyl products, [LTh(CH$_2$Ph)$_2$] [L = BDPP (**4**) and XA$_2$ (**5**); previously reported] were obtained in high yield (Scheme 3).[15, 18] However, the reaction to form **5** is best performed: (a) with addition of PhCH$_2$MgCl at 20 °C, or (b) with addition of PhCH$_2$MgCl at –78 °C, followed by stirring at 0 °C for 3 hours. If the addition of PhCH$_2$MgCl to **2** was performed at –78 °C, and the reaction was allowed to warm to room temperature over 1 hour, a substantial amount (30-50 %) of a new product, [(XA$_2$)Mg(dme)] (**6**), was formed in addition to complex **5** (Scheme 4).[49] This product is a result of ancillary ligand transfer from thorium to magnesium, and was characterized by $^1$H and $^{13}$C NMR spectroscopy, elemental analysis and X-ray crystallography. Interestingly, [(XA$_2$)Th(CH$_2$Ph)$_2$] (**5**) does not react with MgCl$_2$ or PhCH$_2$MgCl at room temperature in toluene or OEt$_2$, so the reaction pathway responsible for formation of **6** must involve either complex **2**, or a mixed benzyl/chloride thorium intermediate.



**Scheme 3.** Reactions of complexes **1** and **2** with PhCH$_2$MgCl to form **4** and **5**.



**Scheme 4.** Reaction of complex **2** with $PhCH_2MgCl$ (–78 °C for 5 minutes, then stirring at room temperature for 1 hour) to form **6**.

In the solid state structure of **6**·hexane (Figure 3), the geometry at magnesium is intermediate between square pyramidal and trigonal bipyramidal [N(1)-Mg-N(2) = 138.8(1)°; N(1)-Mg-O(3) = 112.9(1)°; N(2)-Mg-O(3) = 104.2(1)°], which requires significant bending of the xanthene backbone of the $XA_2$ ligand; pln1–pln2 = 41° (pln1 = plane through C1-C4, C10 and C11; pln2 = plane through C1-C4, C12 and C13). For comparison, in the chemistry of thorium, the backbone of the $XA_2$ ligand is invariably more planar (*e.g.* pln1–pln2 = 12° and 19° for the two independent molecules in the X-ray crystal structure of **5**).[18] Surprisingly, given the large binding pocket of the $XA_2$ ligand, the Mg-N bond distances of 2.054(2) Å in **6** also lie within the expected range (cf. 2.055(2) Å in $[(Ph_2N)_2Mg(hmpa)_2]$ and 2.013(3) Å in $[(Ph_2N)_2Mg(THF)_2]$).[50, 51] This is achieved through appreciable distortion of the ligand framework to bring the two amido donors closer to one another [C(1)···C(8) = 4.87 Å, C(4)···C(5) = 4.40 Å and N(1)···N(2) = 3.85 Å]. The Mg–O distances in **6** [2.047(2)–2.096(2) Å] also fall in the usual range (cf. Mg–O distances of 2.047(5) Å in $[Mg\{P(SiMe_3)_2\}_2(dme)]$,[52] 2.124(4) Å in $[Mg(SiMe_3)_2(dme)]$,[53] 2.084(7) and 2.096(6) Å in $[Mg(^tBuNSiMe_2(C_6H_4)OMe\text{-}o\}_2]$,[54] and 2.052(2) and 2.087(2) Å in $[(diglyme)Mg(BH_4)_2]$[55]), although due to constraints imposed by the rigid $XA_2$ ligand, Mg–

O(1) is somewhat shorter than might be expected for coordination to a diarylether ligand; other crystallographically characterized Mg–diarylether complexes are not available for comparison.

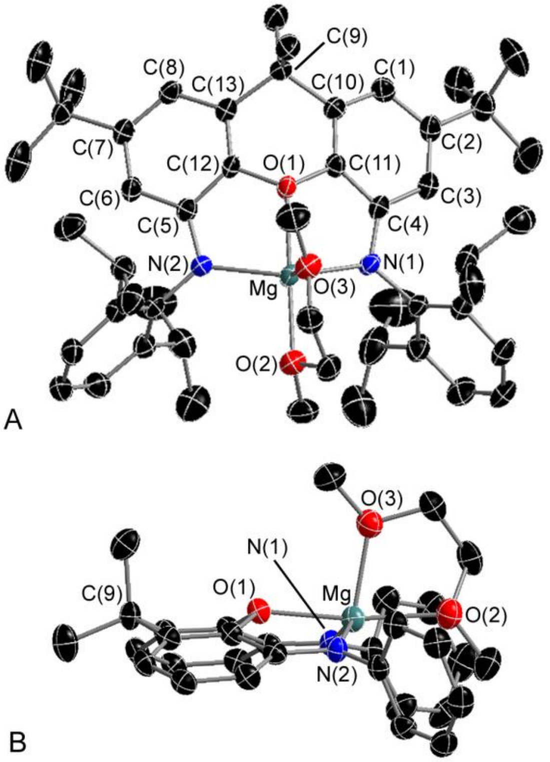


**Figure 3.** The solid state structure of **6**·hexane with thermal ellipsoids at 50 % probability. Lattice solvent and hydrogen atoms are omitted for clarity. In view B, isopropyl and *tert*-butyl groups are also omitted for clarity. Selected bond lengths (Å) and angles (°): Mg–N(1) 2.054(2), Mg–N(2) 2.054(2), Mg–O(1) 2.047(2), Mg–O(2) 2.084(2), Mg–O(3) 2.096(2), O(1)–Mg–O(2) 172.07(7), N(1)–Mg–N(2) 138.79(8), N(1)–Mg–O(3) 112.92(7), N(2)–Mg–O(3) 104.18(7).

Several examples of ancillary ligand transfer from a rare earth element to magnesium have previously been reported. For example, [(nacnac)LaBr$_2$(THF)$_2$] or [(nacnac)La(THF)(μ-

$Cl)_3LaCl(nacnac)]$ [nacnac = *N*,*N*-bis(2,6-diisopropylphenyl)-β-diketiminate] reacted with RMgCl (R = Me or allyl) to form [(nacnac)MgR(THF)] and $[LaX_3(THF)_n]$ (X = Cl or Br).[40, 56] Similarly, the yttrium complex $[(PNP)_2Y(\mu\text{-}Cl)]_2$ $[PNP = N(SiMe_2CH_2PMe_2)_2]$ yielded $[(PNP)Y(C_3H_5)(\mu\text{-}Cl)]_2$ and $[Mg(PNP)_2]$ when treated with either $(C_3H_5)MgCl$ or $Mg(C_3H_5)_2$(dioxane).[57],[58] The temperature sensitivity of the reactions of **2** with $PhCH_2MgCl$ is remarkable, and the absence of ancillary ligand transfer to magnesium in reactions of similarly ligated **1** with $PhCH_2MgCl$ highlights the extent to which this reaction manifold is sensitive to the specific steric and electronic properties of the ligands involved.

## 3. Summary and Conclusions

The formation of $[\{(BDPP)ThX(\mu\text{-}X)_2Mg(OEt_2)(\mu\text{-}Me)\}_2]$ ($X = Br_{0.73\text{-}0.87}/Cl_{0.13\text{-}0.27}$; **3**) from $[(BDPP)ThCl_2(dme)]$ (**1**) involves both halide exchange (Cl for Br) and adduct formation with MeMgX. As such, complex **3** can be considered to provide a snapshot of the process responsible for halide exchange between highly electrophilic metal halide complexes and Grignard reagents. The composition of **3** also highlights the compatibility of magnesium alkyls with certain metal halides; both bridging and terminal. In contrast to the reaction of **1** with MeMgBr, reactions of **1** and $[(XA_2)ThCl_2(dme)]$ (**2**) with $PhCH_2MgCl$ provided the expected dibenzyl complexes, $[LTh(CH_2Ph)_2]$ [L = BDPP (**4**) and $XA_2$ (**5**); previously reported] under most reaction conditions.[15, 18] However, addition of $PhCH_2MgCl$ to **1** at –78 °C and warming to room temperature after 5 minutes yielded a significant amount of $[(XA_2)Mg(dme)]$ (**6**), the product of ancillary ligand transfer from thorium to magnesium. This reaction outcome further highlights the diversity of behaviour accessible in the reactions of f-element halides with Grignard reagents.

## 4. Experimental

**General Details**. An argon-filled MBraun UNIlab glove box was employed for the manipulation and storage of all oxygen and moisture sensitive compounds, and all compounds were stored in a -30 °C freezer within the glove box. Commonly utilized specialty glassware includes double manifold high vacuum lines, swivel frit assemblies, J-Young NMR tubes, and thick walled flasks equipped with Teflon stopcocks (Chemglass and Toonen Glassblowing).[59] Any residual oxygen and moisture was removed from the argon stream by passage through an Oxisorb-W scrubber from Matheson Gas Products.

Hexanes and toluene were initially distilled under nitrogen from $CaH_2$ and sodium, respectively, prior to storage under vacuum over $Na/Ph_2CO$ (toluene) or $Na/Ph_2CO$/tetraglyme (hexanes). $C_6D_6$ was purchased from ACP chemicals and dried over $Na/Ph_2CO$. All solvents were introduced into reactions or storage flasks by vacuum transfer with condensation at –78 °C. MeMgBr (3.0 M in $OEt_2$), $PhCH_2MgCl$ (1.0 M in $OEt_2$), were purchased from Aldrich. [(BDPP)$ThCl_2$(dme)] (**1**) and [($XA_2$)$ThCl_2$(dme)] (**2**) were prepared as previously reported.[14]

Combustion elemental analyses were performed on a Thermo EA1112 CHNS/O analyzer. X-ray crystallography was performed on suitable crystals coated in Paratone oil and mounted on either: (a) a P4 diffractometer with a Bruker Mo rotating-anode generator and a SMART1K CCD area detector, or (b) a SMART APEX II diffractometer with a 3 kW Sealed tube Mo generator in the McMaster Analytical X-Ray (MAX) Diffraction Facility.

NMR spectroscopy [$^1H$, $^{13}C\{^1H\}$, DEPT-135, COSY, HSQC, HMBC] was performed on a Bruker AV-600 spectrometer. All $^1H$ NMR and $^{13}C$ NMR spectra were referenced to $SiMe_4$ through a resonance of the deuterated solvent or proteo impurity of the solvent ($C_6D_6$):

δ 7.15 ppm for $^{1}$H NMR, and δ 128.0 ppm for $^{13}$C NMR. Herein, *Ar* = 2,6-diisopropylphenyl. The numbering scheme for the $XA_2$ ligand backbone is shown in Figure 1.

**[{(BDPP)ThX(μ-X)$_2$Mg(OEt$_2$)(μ-Me)}$_2$]·2 toluene (X = Br$_{0.73\text{-}0.87}$/Cl$_{0.13\text{-}0.27}$; 3·2 toluene):** A 3.0 M solution of MeMgBr in $Et_2O$ (0.157 mL, 0.47 mmol) was added dropwise to a slurry of [($XA_2$)Th$Cl_2$(dme)] (0.200 g, 0.24 mmol) in $OEt_2$ (20 mL) at –78 °C. The solution was then warmed to room temperature, stirred for 3 hours, filtered to remove insoluble salts, and the filtrate was evaporated to dryness *in vacuo*. Sonication in hexanes and filtration provided 0.128g of an off-white solid which was dissolved in toluene and layered with hexanes at –30 °C to yield a single large (~4x4x2 mm) colourless X-ray quality crystal of **3**.2 toluene.

**Improved conditions for the preparation of [($XA_2$)Th($CH_2Ph$)$_2$] (5):** The preparation of complex **5** in ref. 18 yielded a mixture of **5** (major product) and **6** (minor product).[49] By contrast, addition of a 1.0 M solution of $PhCH_2MgCl$ in $Et_2O$ (30 μL, 30 μmol) to a solution of [($XA_2$)Th$Cl_2$(dme)] (15 mg, 14 μmol) in d$_8$-toluene (1.0 mL) or $C_6D_6$ (1.0 mL) at room temperature and stirring for between 1 and 24 hours yielded only complex **5** by $^{1}$H NMR spectroscopy.

**[($XA_2$)Mg(dme)] (6):** 1.0 M $PhCH_2MgCl$ in $Et_2O$ (0.570 mL, 0.57 mmol) was added dropwise to a solution of [($XA_2$)Th$Cl_2$(dme)] (0.280 g, 0.28 mmol) in toluene (30 mL) at –78 °C. After 5 minutes, the solution was warmed to room temperature and stirred for 1 hour, filtered, and the filtrate was evaporated to dryness *in vacuo*. Recrystallization from toluene/hexanes (complex **5** is substantially more soluble in hexanes, so remains in solution) and drying *in vacuo* gave **6** as a yellow solid (0.091 g, 0.11 mmol) in 41 % yield. X-ray quality crystals of **6**·hexane were obtained from toluene/hexane at –30 °C. **$^{1}$H ($C_6D_6$, 600 MHz):** δ 7.27 (d, 4H, $^{3}J_{\text{H-H}}$ 7.4 Hz, Ar-$H_{\text{meta}}$), 7.20 (t, 2H, $^{3}J_{\text{H-H}}$ 7.4 Hz, Ar-$H_{\text{para}}$), 6.62 (d, 2H, $^{4}J_{\text{H-H}}$ 1.7 Hz, C$H^{3}$), 6.24 (d, 2H, $^{4}J_{\text{H-H}}$ 1.7 Hz, C$H^{1}$), 3.55 (sept, 4H, $^{3}J_{\text{H-H}}$ 6.7 Hz, C*H*$Me_2$), 2.79 (s, 6H, O*Me*), 2.58 (s, 4H, OC$H_2$), 1.70 (s, 6H, C$Me_2$), 1.27, 1.12 (d, 2 x 12H, $^{3}J_{\text{H-H}}$ 6.7 Hz, CH$Me_2$). **$^{13}$C{$^{1}$H} NMR ($C_6D_6$, 125 MHz):** δ 148.8 (Ar-$CH_{\text{ortho}}$), 148.2, 147.0, 132.1 (Xanth-*Q*), 146.1 (Ar-$C_{\text{ipso}}$), 123.5 (Ar-$CH_{\text{para}}$), 123.8 (Ar-$CH_{\text{meta}}$), 109.1 ($CH^{1}$), 103.0($CH^{3}$), 69.4 (O$CH_2$), 59.9 (O*Me*), 36.5 ($CMe_2$), 35.1 ($CMe_3$), 28.8 (C$Me_2$), 32.0 (C$Me_3$), 28.2 ($CHMe_2$), 26.0, 24.4 (CH$Me_2$). **Anal. Calcd. for: $C_{51}H_{72}MgN_2O_3$:** C, 77.99; H, 9.24; N, 3.57. Found: C, 78.43; H, 9.71; N, 3.48.

**Acknowledgements.** D. J. H. E. thanks NSERC of Canada for a Discovery Grant, and Canada Foundation for Innovation (CFI) and Ontario Innovation Trust (OIT) for New Opportunities Grants. C. A. C. thanks the Government of Ontario for an Ontario Graduate Scholarship (OGS) and NSERC of Canada for a PGS-D scholarship.

**Supporting Information Available:** Supplementary data associated with this article (X-ray crystallographic data in PDF format) can be found in the online version at doi:xxxxxxxx.

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