

# Bulky Group 2 Octaphenylmetallocenes and Direct Access to Calcium and Ytterbium Pseudo-Grignard Complexes

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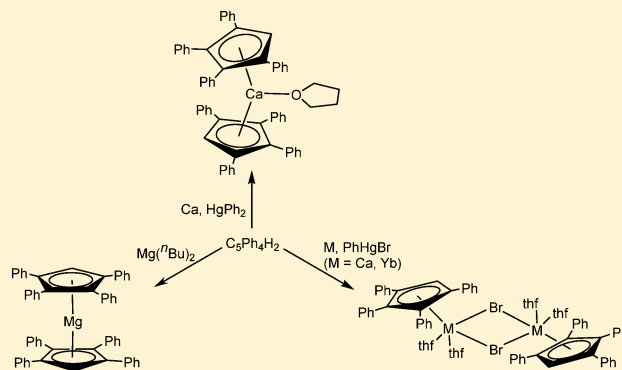
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## S Supporting Information

**ABSTRACT:** The reaction between  $\text{Mg}(\text{}^n\text{Bu})_2$  and  $\text{C}_5\text{Ph}_4\text{H}_2$  in toluene at 100–110 °C yielded octaphenylmagnesocene,  $[\text{Mg}(\text{C}_5\text{Ph}_4\text{H})_2]$ , which has two parallel Cp rings despite the steric bulk of the ligands. The redox-transmetalation/protolysis (RTP) reaction between calcium metal,  $\text{HgPh}_2$ , and  $\text{C}_5\text{Ph}_4\text{H}_2$  in thf afforded the bent calcium sandwich complex  $[\text{Ca}(\text{C}_5\text{Ph}_4\text{H})_2(\text{thf})]$ . Two rare calcium and ytterbium pseudo-Grignard complexes,  $[\text{M}(\text{C}_5\text{Ph}_4\text{H})(\mu\text{-Br})(\text{thf})_2]_2$ , were prepared from RTP reactions of the corresponding metal,  $\text{PhHgBr}$ , and  $\text{C}_5\text{Ph}_4\text{H}_2$  in thf. Reduction of the calcium bromide complex by  $\text{KC}_8$  in the presence of 18-crown-6 afforded the charge-separated potassium compound  $[\text{K}(18\text{-crown-6})(\text{thf})_2][\text{C}_5\text{Ph}_4\text{H}]$ , but no  $\text{Ca}^{\text{I}}$  species were detected.



## INTRODUCTION

Intriguing structural patterns have emerged from the study of alkaline-earth-metal cyclopentadienyl complexes, with pentamethylcyclopentadienyl ( $\text{Cp}^*$ ) complexes being the most studied.<sup>1</sup>  $[\text{Mg}(\text{Cp}^*)_2]$ , the structure of which was only reported in the past 10 years,<sup>1f</sup> exists with two parallel  $\text{Cp}^*$  ligands but the complexes of the heavier alkaline earths adopt bent structures.<sup>1a–e</sup> Various theories have been put forth to explain this seemingly counterintuitive behavior, but a consensus view has not yet been reached.<sup>2</sup> The first non-bent-sandwich complexes of the heavier alkaline earths,  $[\text{Ae}(\text{C}_5(\text{}^i\text{Pr})_5)_2]$  ( $\text{Ae} = \text{Ca}, \text{Sr}, \text{Ba}$ ), were prepared by Sitzmann et al. from reactions in liquid ammonia between calcium, strontium, or barium metal and the stable  $\text{C}_5(\text{}^i\text{Pr})_5^\bullet$  radical.<sup>3</sup> On the other hand, the related octaisopropyl derivatives exhibit slightly bent structures.<sup>4</sup> Surprisingly, the  $[\text{Ae}(\text{C}_5(\text{}^i\text{Pr})_5)_2]$  complexes are reported to be relatively robust toward air, in contrast to the case for most alkaline-earth organometallics, e.g.  $[\text{Ca}\{\text{C}_5\text{H}_3(\text{SiMe}_3)_2-1,3\}_2(\text{thf})]$ ,<sup>5</sup> which afforded the triplet biradical species  $[\text{Ca}\{\text{C}_5\text{H}_3(\text{SiMe}_3)_2-1,3\}\{\text{OC}_5\text{H}_3(\text{SiMe}_3)_2-2,4\}]_2$  after partial oxidation by oxygen.<sup>6</sup> It is clear that ligand design can result in interesting structural and reactivity features, and this continues to foster our interest in alkaline-earth cyclopentadienyl complexes.

In recent years, we have explored the use of the pentaphenylcyclopentadienyl ligand ( $\text{C}_5\text{Ph}_5$ ) in organolanthanoid and alkaline-earth-metal chemistry due to its different electronic and steric properties in comparison with alkyl- and silyl-substituted cyclopentadienyl ligands.<sup>7</sup> From a redox-transmetalation/protolysis (RTP) approach, we were able to

synthesize the decaphenylmetallocenes  $[\text{M}(\text{C}_5\text{Ph}_5)_2]$  ( $\text{M} = \text{Ca}, \text{Ba}, \text{Yb}$ ).<sup>7a</sup> These remarkable sandwich complexes display parallel  $\text{C}_5\text{Ph}_5$  rings that interact via cooperative  $\text{C}-\text{H}\cdots\text{C}(\pi)$  interactions between the ortho  $\text{C}-\text{H}$  atoms of one phenyl ring with the ortho  $\text{C}(\pi)$  atom of a phenyl ring on the other ligand. The net effect of 10 of these interactions is to bring the  $\text{C}_5\text{Ph}_5$  rings closer than would otherwise be expected (cf. sterically induced lengthening of the  $\text{Yb}-\text{C}(\text{C}_5\text{Ph}_5)$  bonds in  $[\text{Yb}(\text{C}_5\text{Ph}_5)(\mu\text{-CCPh})(\text{thf})_2]$ ).<sup>7b</sup> Unfortunately,  $[\text{M}(\text{C}_5\text{Ph}_5)_2]$  complexes are characterized by particularly low solubility in non-donor solvents. One method to circumvent these solubility issues is to add alkyl substituents on the phenyl rings. Harder and co-workers have exploited this to great effect in their syntheses of a range of  $[\text{M}(\text{Cp}^{\text{BIG}})_2]$  ( $\text{M} = \text{Ca}, \text{Sr}, \text{Ba}, \text{Sm}, \text{Eu}, \text{Yb}$ ;  $\text{Cp}^{\text{BIG}} = \text{C}_5(4\text{-}^n\text{BuC}_6\text{H}_4)_5$ ) complexes.<sup>8</sup> Another strategy to improve the solubility of such complexes is to have one less phenyl group: i.e., the tetraphenylcyclopentadienyl ligand ( $\text{C}_5\text{Ph}_4\text{H}$ ). We recently reported three ytterbium(II) complexes bearing the  $\text{C}_5\text{Ph}_4\text{H}$  ligand, and the sandwich complex  $[\text{Yb}(\text{C}_5\text{Ph}_4\text{H})_2(\text{thf})]$  displays much greater solubility in aromatic solvents than the corresponding  $[\text{M}(\text{C}_5\text{Ph}_5)_2]$  complexes.<sup>9</sup>

Low-valent alkaline-earth-metal chemistry has recently gained increasing interest with the synthesis of the first  $\text{Mg}^{\text{I}}$  and  $\text{Ca}^{\text{I}}$  complexes.<sup>10</sup> However, so far no cyclopentadienyl-

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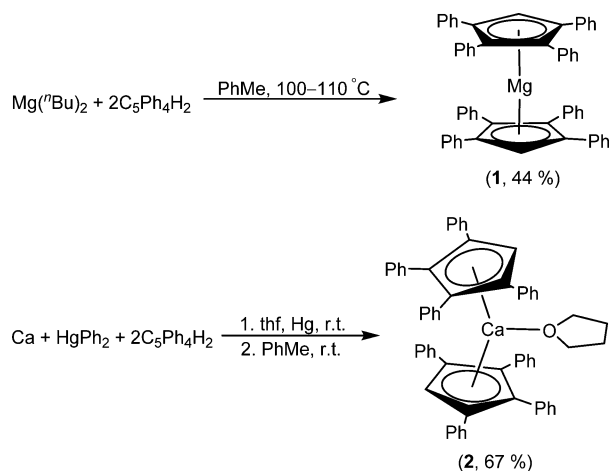


based complexes have been reported, even though theoretical studies have predicted their stability.<sup>11</sup> Polyarylcyclopentadienyl ligands might be good candidates, due to their steric and electronic properties. The characterization of the Ca and Ba sandwich complexes  $[M(C_5Ph_5)_2]$  by MALDI-TOF showed, in addition to the molecular ion peaks,  $[M(C_5Ph_5)_2]^+$ , peaks corresponding to  $[M_2(C_5Ph_5)_2]^+$ , which could be considered as low-valent Ca or Ba species.<sup>7a,12</sup> In the case of  $[Yb(C_5Ph_5)_2]$ , no such signal was observed. Unfortunately, the low solubility of the  $[M(C_5Ph_5)_2]$  complexes hindered attempts to reduce them. We have now turned our attention to the  $C_5Ph_4H$  ligand, which offers more soluble complexes.<sup>9,13</sup> Herein we report the syntheses and characterization of magnesium and calcium sandwich complexes bearing the  $C_5Ph_4H$  ligand. In addition, we present syntheses and structures of the half-sandwich pseudo-Grignard compounds  $[M(C_5Ph_4H)(\mu-Br)(thf)_2]_2$  ( $M = Ca, Yb$ ) and an attempt to access a  $Ca^I$  species stabilized by the  $C_5Ph_4H$  ligand. The only report of the use of the  $C_5Ph_4H$  ligand in alkaline-earth-metal chemistry is the synthesis of  $[Ba(C_5Ph_4H)_2(thf)]$  and  $[Ba(C_5Ph_4H)\{N(SiMe_3)_2\}(thf)_n]$ , the former being thermally unstable; solid-state structures were not reported for either complex.<sup>14</sup>

## RESULTS AND DISCUSSION

**Syntheses of Octaphenylmetallocenes.** Octaphenylmagnesocene,  $[Mg(C_5Ph_4H)_2]$  (**1**), was isolated in moderate yield from the reaction between  $Mg(^nBu)_2$  and 2 equiv of  $C_5Ph_4H_2$  in toluene at 100–110 °C (Scheme 1). Starting

**Scheme 1.** Syntheses of  $[Mg(C_5Ph_4H)_2]$  (**1**) and  $[Ca(C_5Ph_4H)_2(thf)]$  (**2**)



material was recovered when the reaction was performed at room temperature. Notably, complex **1** is the first characterized arylcyclopentadienylmagnesium complex. Interestingly, when Harder et al. attempted an analogous reaction between  $Mg(^nBu)_2$  and  $Cp^{BIG}H$ , no reaction was observed, even under forcing conditions.<sup>8c</sup> Complex **1** is modestly soluble in aromatic solvents, but it is appreciably less soluble than the larger octaphenylytterbocene(II).<sup>9</sup>

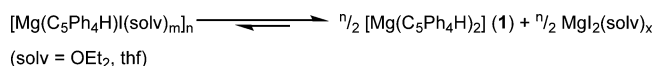
Octaphenylcalcium,  $[Ca(C_5Ph_4H)_2(thf)]$  (**2**), was prepared in reasonable yield from the redox-transmetalation/protolysis (RTP) reaction of Hg-activated calcium metal,  $HgPh_2$ , and 2 equiv of  $C_5Ph_4H_2$  in  $thf$  at room temperature (Scheme 1). This preparation mirrors that of the analogous ytterbium complex  $[Yb(C_5Ph_4H)_2(thf)]$ .<sup>9</sup> However, whereas

the ytterbium complex was recrystallized from hot toluene, attempts to heat solutions of **2** more than gently were accompanied by decomposition of the complex and the formation of dark orange solutions. Thermal instability of  $[Ba(C_5Ph_4H)_2(thf)]$  was reported by Hanusa and Tanner, and they suggested the poor nucleophilicity of the  $C_5Ph_4H$  ligand and open coordination sites on the metal as possible factors.<sup>14</sup> Given that  $Ca^{2+}$  and  $Yb^{2+}$  have very similar ionic radii,<sup>15</sup> the difference in thermal stability between  $[Yb(C_5Ph_4H)_2(thf)]$  and **2** is probably a result of more ionic bonding in the calcium complex and the greater oxophilicity of the  $Ca^{2+}$  ion.<sup>16</sup> Complex **2** displays good solubility in aromatic solvents.

**Attempted Syntheses of Magnesium Half-Sandwich Iodide Complexes.** Cyclopentadienyl  $Mg^I$ – $Mg^I$  complexes have been predicted to be accessible, but no reports on actual syntheses have been forthcoming.<sup>11</sup> Schnöckel et al. reported failed attempts to synthesize magnesium(I) complexes bearing the  $C_5Me_5$  ( $Cp^*$ ) ligand and they surmised that chelating ligands might in fact be necessary to isolate magnesium(I) complexes.<sup>17</sup> However, given the limited experimental work published to date in the area, we felt that the different steric and electronic properties of  $C_5Ph_4H$  in comparison with  $Cp^*$  made it worth investigating whether it could stabilize low-valent magnesium complexes. First, we attempted to synthesize some tetraphenylcyclopentadienylmagnesium iodide complexes as precursors for reduction. However, these syntheses failed, owing to a combination of low reactivity, decomposition, and ligand redistribution reactions, thereby precluding attempts to target  $Mg^I$  complexes.

Initially, we attempted to synthesize a complex of the type  $[Mg(C_5Ph_4H)I(OEt)_m]_n$  from the reaction between  $PhMgI$  (in  $Et_2O$ ) and  $C_5Ph_4H_2$  in toluene at room temperature, but no reaction was observed and  $C_5Ph_4H_2$  was recovered. If the reaction mixture was heated above approximately 70 °C, the solutions turned the familiar dark orange color indicative of decomposition, as when **2** was heated. When the reaction mixture was heated at lower temperatures, e.g. 60–70 °C, the reaction proceeded but ligand redistribution occurred and **1** was isolated and then characterized by X-ray crystallography. The other product is presumably  $MgI_2(OEt)_n$ . Stirring  $PhMgI$  (in  $Et_2O$ ) and  $C_5Ph_4H_2$  in  $thf$  at room temperature gave immediate precipitation of a light-colored solid, and the mixture was stirred overnight. Workup led to the isolation of single crystals of the known complex  $[Mg(thf)_6][I]_2$ .<sup>18</sup> The failure to isolate a complex of the form  $[Mg(C_5Ph_4H)I(solvent)_m]_n$  ( $solv = OEt_2, thf$ ) can be attributed to the relatively poor solubility of **1** and  $MgI_2$ , which could drive the Schlenk equilibrium to the right (Scheme 2). The comparatively poor donor ability of the

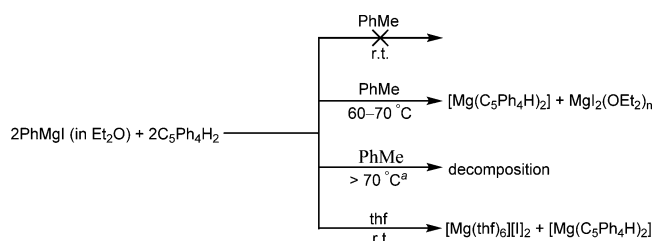
**Scheme 2.** Redistribution of  $[Mg(C_5Ph_4H)I(solvent)_m]_n$  ( $solv = OEt_2, thf$ ) by the Schlenk Equilibrium To Form **1** and  $MgI_2(solvent)_x$



$C_5Ph_4H$  ligand could also be a factor. The attempts to synthesize  $[Mg(C_5Ph_4H)I(solvent)_m]_n$  ( $solv = OEt_2, thf$ ) are summarized in Scheme 3.

**Syntheses of Calcium and Ytterbium Half-Sandwich Complexes from RTP Reactions.** Complexes of the type “ $CpCaX$ ” ( $X = \text{halide}$ ) are relatively rare due to facile ligand redistribution reactions, but bulky ligands can offer kinetic

**Scheme 3. Attempted Syntheses of  $[\text{Mg}(\text{C}_5\text{Ph}_4\text{H})\text{I}(\text{solv})_m]_n$  (solv =  $\text{OEt}_2$ , thf)**



<sup>a</sup>Heating above this approximate temperature consistently gave dark orange solutions.

stabilization.<sup>2</sup> Typical routes to such complexes involve either metathesis reactions between  $\text{CaX}_2$  and an appropriate alkali-metal cyclopentadienyl complex or a reaction between equimolar amounts of a calcium sandwich complex and  $\text{CaX}_2$ .<sup>2</sup> However, both of these methods suffer from the need to prepare air-sensitive precursors. Consequently, we sought a simple and convenient approach to “ $\text{CpCaX}$ ” complexes. Given our longstanding interest in RTP reactions, a heteroleptic organomercurial appeared to offer a simple route to heteroleptic metal halide complexes.  $\text{PhHgBr}$  is a commercially available and easily prepared air-stable compound that seemed suitable for some preliminary reactions. To the best of our knowledge, the use of  $\text{PhHgBr}$  in RTP reactions with alkaline-earth or lanthanoid metals has not been reported before, although redox-transmetalation reactions between magnesium or ytterbium metal and triazenidomercuric halides have been used to prepare triazenido–magnesium and –ytterbium halide complexes.<sup>19</sup> RTP syntheses should be more widely applicable than redox-transmetalation, as they can potentially be applied to a wide range of protic proligands more acidic than benzene.

A mixture of calcium metal,  $\text{PhHgBr}$ ,  $\text{C}_5\text{Ph}_4\text{H}_2$  and 1 drop of mercury in thf was sonicated at 40 °C for 5 days. After workup,  $[\text{Ca}(\text{C}_5\text{Ph}_4\text{H})(\mu\text{-Br})(\text{thf})_2]_2$  (**3**) was obtained in reasonable yield (Scheme 4). Complex **3** is a rare organocalcium bromide pseudo-Grignard complex, and its isolation shows the possible utility of the RTP approach with  $\text{PhHgBr}$  for the generation of “ $\text{LCaBr}$ ” ( $\text{L}$  = bulky ligand) complexes. Future development of the method will involve use of the less commercially accessible  $\text{PhHgI}$  in attempts to prepare  $\text{LCaI}$  analogues, as well as to examine extension to Sr and Ba complexes.

$\text{Ca}^{2+}$  and  $\text{Yb}^{2+}$  often display similar chemistry, but this is not always the case.<sup>20</sup> In order to see if the same RTP approach above could be used to synthesize an analogous ytterbium complex, the reaction was effected with ytterbium metal and gave  $[\text{Yb}(\text{C}_5\text{Ph}_4\text{H})(\mu\text{-Br})(\text{thf})_2]_2$  (**4**) (Scheme 4) in considerably lower yield in comparison to that for **3**. The reaction always also produced a poorly soluble yellow product of unknown composition. It does not appear that this solid is either  $\text{YbBr}_2(\text{thf})_2$ <sup>21</sup> or  $\text{YbBr}_3(\text{thf})_3$ ,<sup>22</sup> which have been

reported as light green and white (in the bulk product), respectively. It is quite possible that the redox properties of the in situ generated “ $\text{PhYb}^{\text{II}}\text{Br}$ ” species cause undesired side reactions.

**Reduction of  $[\text{Ca}(\text{C}_5\text{Ph}_4\text{H})(\mu\text{-Br})(\text{thf})_2]_2$ .** Recently, West-erhausen et al. published the first well-characterized case of a calcium(I) complex, the remarkable inverse sandwich complex  $[(\text{thf})_3\text{Ca}^{\text{I}}\{1,3,5\text{-Ph}_3\text{C}_6\text{H}_3\}\text{Ca}^{\text{I}}(\text{thf})_3]$ .<sup>10b</sup> However, no examples of  $\text{Ca}^{\text{I}}\text{--Ca}^{\text{I}}$ -bonded species have yet been reported.

A solution of **3** in toluene was treated with  $\text{KC}_8$  and 18-crown-6.  $[\text{K}(18\text{-crown-6})(\text{thf})_2][\text{C}_5\text{Ph}_4\text{H}]\cdot\text{thf}$  (**5**·thf) was isolated in modest yield after crystallization from thf (Scheme 5), but no  $\text{Ca}^{\text{I}}$  products were detected. This result is similar to the reduction of  $[\text{Ca}\{(\text{dippNC}(\text{tBu}))_2\text{CH}\}\text{I}(\text{thf})_2]_2$  by sodium, which led to the isolation of  $[\text{Na}\{(\text{dippNC}(\text{tBu}))_2\text{CH}\}]_2$ .<sup>23</sup> Complex **5** is a rare example of a charge-separated potassium cyclopentadienide complex.

**Characterization.** The identity of all complexes was established by single-crystal X-ray crystallography (vide infra).

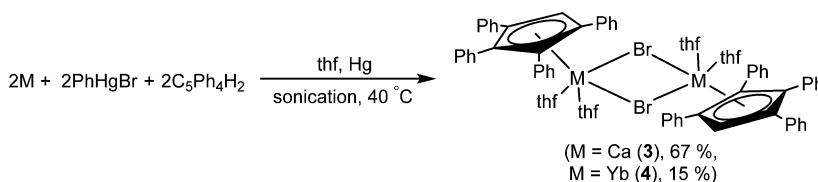
The  $^1\text{H}$  NMR spectra of all complexes support the solid-state descriptions, with the spectrum of **2** similar to those of  $[\text{Yb}(\text{C}_5\text{Ph}_4\text{H})_2(\text{thf})]$  and  $[\text{Ba}(\text{C}_5\text{Ph}_4\text{H})_2(\text{thf})]$ .<sup>9,14</sup> Only for **2** and **4** is the  $\text{C}_5\text{Ph}_4\text{H}$  ring proton observed as a resonance separate from those of phenyl groups. However, doublets for the ortho protons of the two different phenyl groups are clearly distinguishable in the spectra of **3–5** in the range 7.55–7.70 ppm. Integration of the resonances for **2–4** indicate that both coordinated thf and where present (**3**, **4**) thf of crystallization are retained in the bulk dried product. In contrast, the solvent of crystallization is lost from bulk **5** (see the Experimental Section), for which the methylene hydrogen atoms of the 18-crown-6 ligand appear as a singlet at 3.01 ppm.

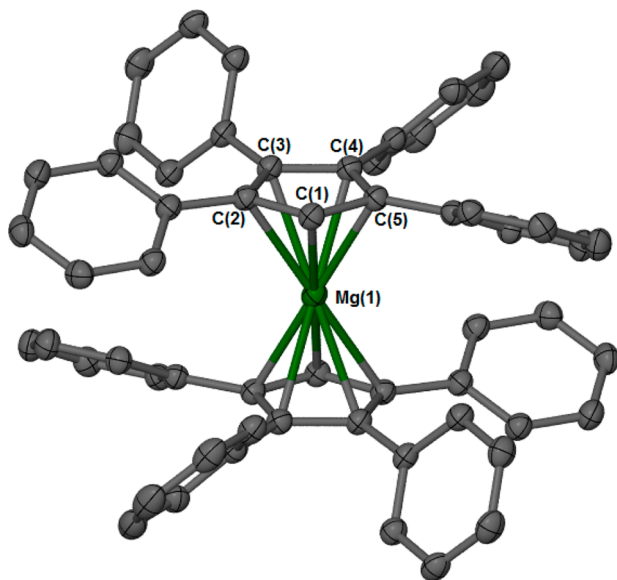
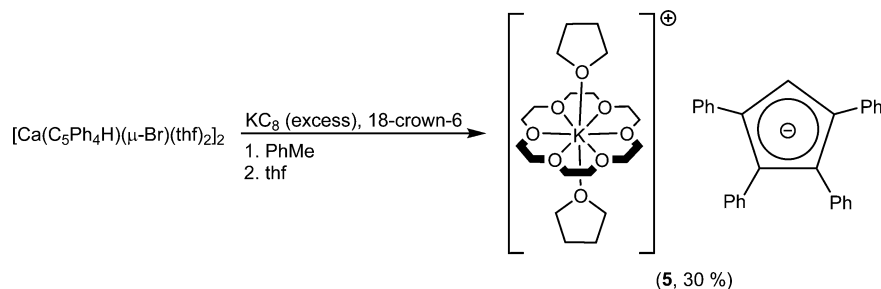
The IR spectra of compounds **1–4** are similar to each other and to those of the reported  $\text{Yb}(\text{C}_5\text{Ph}_4\text{H})$  complexes.<sup>9</sup> Characteristic absorptions corresponding to carbon–carbon stretching modes of the phenyl rings and those ( $\gamma(\text{CH})$  and ring modes) associated with monosubstituted benzene are observed in the expected regions for **1–5**. For compounds **2–4** coordinated thf is evident from bands at  $870\text{ cm}^{-1}$  ( $\pm 10\text{ cm}^{-1}$ ).

All complexes were characterized by microanalysis. The result for **1** was low in carbon, but this is a feature of many alkaline-earth and lanthanoid complexes with bulky cyclopentadienyl ligands.<sup>4b,5,24</sup> The result for **2** is slightly low in carbon, but in contrast the results for both **3** and **4** were in good agreement with the calculated values. Satisfactory results could not be obtained for **5**.

**Molecular Structure of  $[\text{Mg}(\text{C}_5\text{Ph}_4\text{H})_2]$ .** Complex **1** crystallized from toluene in the triclinic space group  $\text{P}\bar{1}$ . The molecular structure is shown in Figure 1, and selected bond lengths and angles are given in Table 1. The complex is a genuine sandwich complex with two parallel  $\text{C}_5\text{Ph}_4\text{H}$  ligands, and the structure is reminiscent of the decaphenylmetallocenes,  $[\text{M}(\text{C}_5\text{Ph}_5)_2]$  ( $\text{M} = \text{Ba}, \text{Yb}$ ).<sup>7a</sup> Despite the parallel nature of the

**Scheme 4. Syntheses of  $[\text{M}(\text{C}_5\text{Ph}_4\text{H}_2)(\mu\text{-Br})(\text{thf})_2]_2$  ( $\text{M} = \text{Ca}$  (**3**),  $\text{Yb}$  (**4**))**



Scheme 5. Reduction of **4** by  $\text{KC}_8$  To Give  $[\text{K}(\text{18-crown-6})(\text{thf})_2][\text{C}_5\text{Ph}_4\text{H}]$  (**5**)

**Figure 1.** Molecular structure of  $[\text{Mg}(\text{C}_5\text{Ph}_4\text{H})_2]$  (**1**) shown with 50% probability thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

ligands, there is considerable deviation in the  $\text{Mg}-\text{C}$  bond lengths ( $\text{Mg}-\text{C}(\text{range}) = 2.291(2) - 2.422(2) \text{ \AA}$ ). However, the  $\text{Mg}-\text{Cn}$  ( $\text{Cn} = \text{centroid}$ ) distance of **1** ( $2.016 \text{ \AA}$ ) is not much longer than that of  $[\text{Mg}(\text{C}_5\text{H}_5)_2]$  ( $1.98(1) \text{ \AA}$ ).<sup>25</sup> On the other

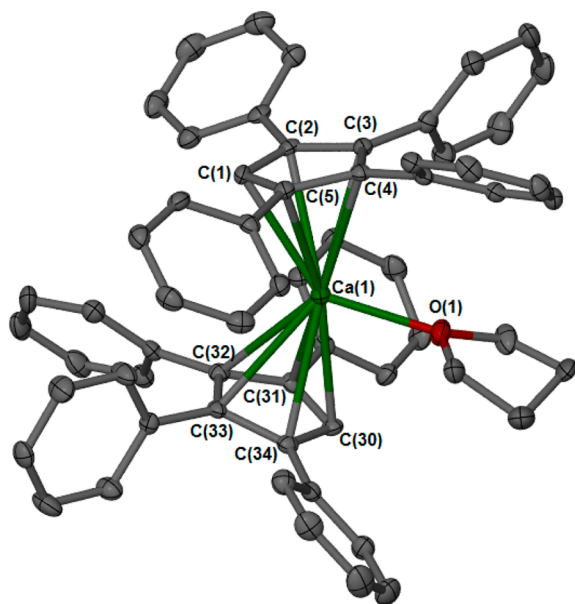
hand, the bulky nonsymmetrical magnesocene  $[\text{Mg}(1,2,4\text{-}(t\text{Bu})_3\text{C}_5\text{H}_2)_2]$  has  $\text{Mg}-\text{Cn}$  distances of  $2.058$  and  $2.063 \text{ \AA}$ .<sup>26</sup> The comparatively short  $\text{Mg}-\text{Cn}$  distances in **1** are potentially due to the presence of close  $\text{C}-\text{H}_{\text{ortho}} \cdots \text{C}_{\text{ortho}}(\pi)$  interactions between the phenyl rings of the two  $\text{C}_5\text{Ph}_4\text{H}$  ligands, as observed in  $[\text{M}(\text{C}_5\text{Ar}_5)_2]$  complexes.<sup>7a,8</sup> Furthermore, there are short *intermolecular*  $\text{C}-\text{H} \cdots \text{C}(\pi)$  interactions between the phenyl rings of discrete  $[\text{Mg}(\text{C}_5\text{Ph}_4\text{H})_2]$  units (refer to the CIF file in the Supporting Information).

**Molecular Structure of  $[\text{Ca}(\text{C}_5\text{Ph}_4\text{H})_2(\text{thf})]$ .** Complex **2** crystallized from toluene in the monoclinic space group  $P2_1/n$ , and it is isomorphous with  $[\text{Yb}(\text{C}_5\text{Ph}_4\text{H})_2(\text{thf})]$ .<sup>9</sup> Unsurprisingly, **2** has bond lengths and angles very similar to those of the ytterbium complex. The molecular structure of **2** is shown in Figure 2, and selected bond lengths and angles are given in Table 1, along with those of the ytterbium complex for comparison. As with  $[\text{Yb}(\text{C}_5\text{Ph}_4\text{H})_2(\text{thf})]$ , **2** displays marked variation in the  $\text{M}-\text{C}$  bond lengths ( $2.620(3) - 2.788(3) \text{ \AA}$ ). The structure of the slightly bent metallocene  $[\text{Ca}(\text{C}_5(\text{Pr})_4\text{H})_2]$  shows less variation in its  $\text{Ca}-\text{C}$  bond lengths ( $2.594(4) - 2.682(4) \text{ \AA}$ ),<sup>4a</sup> and this can be accounted for by the lack of coordinating solvent. The structure of  $[\text{Ca}(\text{Cp}^{\text{BIG}})_2]$  shows even less variation in its  $\text{Ca}-\text{C}$  bond lengths ( $2.643(1) - 2.661(1) \text{ \AA}$ ),<sup>8b</sup> and this can be attributed to the very high symmetry of this complex. In **2**, as in **1**, there is evidence of  $\text{C}-\text{H}_{\text{ortho}} \cdots \text{C}_{\text{ortho}}(\pi)$  interactions, but they do not appear to play as large a role as the analogous interactions in symmetrical polyarylmatalocenes such as **1** and  $[\text{M}(\text{C}_5\text{Ph}_5)_2]$ .<sup>7a</sup> Similarly to

**Table 1.** Selected Bond Lengths ( $\text{\AA}$ ) and Angles ( $^\circ$ ) for  $[\text{Mg}(\text{C}_5\text{Ph}_4\text{H})_2]$  (**1**),  $[\text{Ca}(\text{C}_5\text{Ph}_4\text{H})_2(\text{thf})]$  (**2**), and  $[\text{Yb}(\text{C}_5\text{Ph}_4\text{H})_2(\text{thf})]$ <sup>9</sup>

	<b>1</b>	<b>2</b>	$[\text{Yb}(\text{C}_5\text{Ph}_4\text{H})_2(\text{thf})]$
$\text{M}-\text{C}(1)$	2.291(2)	2.655(3)	2.681(6)
$\text{M}-\text{C}(2)$	2.392(2)	2.750(3)	2.677(6)
$\text{M}-\text{C}(3)$	2.422(2)	2.769(3)	2.750(6)
$\text{M}-\text{C}(4)$	2.368(2)	2.734(3)	2.778(6)
$\text{M}-\text{C}(5)$	2.301(2)	2.652(3)	2.772(6)
$\text{M}-\text{C}(30)$		2.638(3)	2.663(6)
$\text{M}-\text{C}(31)$		2.620(3)	2.770(5)
$\text{M}-\text{C}(32)$		2.735(3)	2.806(6)
$\text{M}-\text{C}(33)$		2.788(3)	2.745(6)
$\text{M}-\text{C}(34)$		2.751(3)	2.627(5)
$\text{M}-\text{C}(\text{range})$	2.291(2)–2.422(2)	2.620(3)–2.788(3)	2.627(5)–2.806(6)
$\text{M}-\text{Cn}(1)$	2.016	2.429	2.448
$\text{M}-\text{Cn}(2)$	2.016	2.423	2.440
$\text{M}-\text{O}(1)$		2.330(2)	2.369(4)
$\text{Cn}(1)-\text{M}-\text{Cn}(2)$	180	150.88	150.84
$\text{Cn}(1)-\text{M}-\text{O}(1)$		102.11	107.19
$\text{Cn}(2)-\text{M}-\text{O}(1)$		106.98	101.86

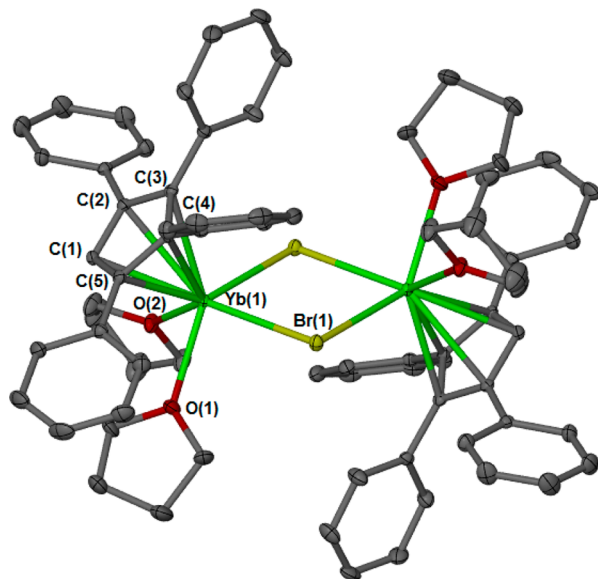




**Figure 2.** Molecular structure of  $[\text{Ca}(\text{C}_5\text{Ph}_4\text{H})_2(\text{thf})]$  (**2**) shown with 50% probability thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

**1**, complex **2** also exhibits numerous *intermolecular*  $\text{C}-\text{H}\cdots\text{C}(\pi)$  interactions between the phenyl rings of discrete  $[\text{Ca}(\text{C}_5\text{Ph}_4\text{H})_2(\text{thf})]$  units (refer to the CIF file in the Supporting Information).

**Molecular Structures of  $[\text{Ca}(\text{C}_5\text{Ph}_4\text{H})(\mu\text{-Br})(\text{thf})_2]_2$  and  $[\text{Yb}(\text{C}_5\text{Ph}_4\text{H})(\mu\text{-Br})(\text{thf})_2]_2$ .** The dimeric calcium complex **3**·3thf crystallized from thf in the triclinic space group  $P\bar{1}$ , as did the isomorphous ytterbium complex **4**·3thf. When **4** was crystallized from toluene, the toluene solvate **4**·4PhMe was obtained. The representative structure of **4**·3thf is shown in Figure 3, and selected bond lengths and angles for all of the complexes are given in Table 2. Complexes **3** and **4** are rare



**Figure 3.** Molecular structure of  $[\text{Yb}(\text{C}_5\text{Ph}_4\text{H})(\mu\text{-Br})(\text{thf})_2]_2 \cdot 3\text{thf}$  (**4**·3thf) shown with 50% probability thermal ellipsoids. Hydrogen atoms and lattice solvent have been omitted for clarity. Note: complex **4**·3thf is isostructural with **3**·3thf.

metal–organic calcium and ytterbium bromide pseudo-Grignard complexes, respectively. As expected, the structures of both **3** and **4** display striking similarities. They each have a dimeric  $\text{M}_2\text{Br}_2$  core, and each metal is also bound to two thf molecules and one  $\text{C}_5\text{Ph}_4\text{H}$  ligand. The structures are similar to that of  $[\text{Yb}(\text{C}_5\text{Ph}_4\text{H})(\mu\text{-F})(\text{thf})_2]_2$ .<sup>9</sup> In contrast to the sandwich complexes **2** and  $[\text{Yb}(\text{C}_5\text{Ph}_4\text{H})_2(\text{thf})]$ , both **3** and **4** feature somewhat narrower  $\text{M}-\text{C}(\text{range})$  values (2.6935(19)–2.826(2) Å for **3**; 2.704(2)–2.820(2) Å for **4**·3thf), but they are still considerably wider than the corresponding  $\text{Yb}-\text{C}(\text{range})$  observed in  $[\text{Yb}(\text{C}_5\text{Ph}_4\text{H})(\mu\text{-F})(\text{thf})_2]_2$  (2.773(3)–2.806(3) Å). This could be a result of decreasing steric congestion in the order  $[\text{M}(\text{C}_5\text{Ph}_4\text{H})_2(\text{thf})] > [\text{M}(\text{C}_5\text{Ph}_4\text{H})(\mu\text{-Br})(\text{thf})_2]_2 > [\text{Yb}(\text{C}_5\text{Ph}_4\text{H})(\mu\text{-F})(\text{thf})_2]_2$ . The  $\text{Ca}-\text{Br}$  bond lengths of **3** (2.8779(4) and 2.9160(5) Å) are shorter than those of the six-coordinate complex  $[\text{Ca}(\text{naphthyl})(\mu\text{-Br})(\text{thf})_3]_2$  (2.9341(8) and 2.9457(8) Å),<sup>27</sup> while the  $\text{Yb}-\text{Br}$  bond lengths of **4**·3thf (2.8932(2) and 2.9216(3) Å) are comparable in length to those of the six-coordinate ytterbium complex  $[\text{Yb}(\text{dpp-Bian})(\mu\text{-Br})(\text{dme})_2]$  (dpp-Bian = 1,2-bis{(2,6-diisopropylphenyl)imino}acenaphthene; 2.8673(9) and 2.9325(9) Å).<sup>28</sup> Once again, *intermolecular*  $\text{C}-\text{H}\cdots\text{C}(\pi)$  interactions between neighboring phenyl rings are present in the structures (refer to the CIF files in the Supporting Information).

#### Molecular Structure of $[\text{K}(\text{18-crown-6})(\text{thf})_2][\text{C}_5\text{Ph}_4\text{H}]$ .

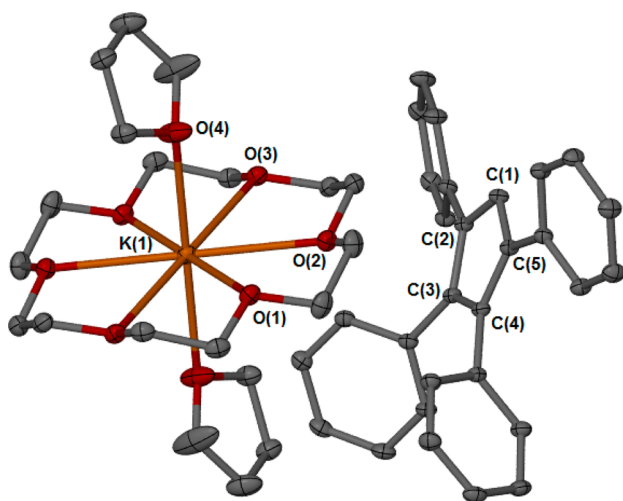
The charge-separated potassium cyclopentadienide complex  $[\text{K}(\text{18-crown-6})(\text{thf})_2][\text{C}_5\text{Ph}_4\text{H}] \cdot \text{thf}$  (**5**·thf) crystallized from thf in the triclinic space group  $P\bar{1}$ . The structure features two similar but crystallographically unique  $[\text{K}(\text{18-crown-6})(\text{thf})_2]^+$  units, but only one is used to describe the structure. The molecular structure is shown in Figure 4, and selected bond lengths are given in the caption. The majority of crystallographically characterized potassium cyclopentadienyl compounds in the literature show interactions between the potassium ions and the cyclopentadienyl ligands. However, in **5** each of the crystallographically independent potassium ions is encapsulated by coordination of one 18-crown-6 ligand and two thf molecules. This prevents interactions with the  $\text{C}_5\text{Ph}_4\text{H}$  anions, leading to so-called “naked” tetraphenylcyclopentadienide ions permeating the structure, reminiscent of  $[\text{K}(\text{15-crown-5})_2][\text{Cp}]$ .<sup>29</sup> The most glaring effect of this is that the ranges for the  $\text{K}-\text{O}(\text{crown})$  bonds of **5** (2.718(2)–2.8130(17) Å for  $\text{K}(1)$ ; 2.7266(19)–2.8313(17) Å for  $\text{K}(2)$ ) show considerably less variation in bond lengths than other potassium cyclopentadienide complexes: e.g.,  $[\text{K}(\text{18-crown-6})][\text{Cp}]$  (2.787(4)–2.983(4) Å)<sup>30</sup> and  $[\text{K}(\text{18-crown-6})][\text{Cp}^*]$  (2.853(2)–3.056(2) Å).<sup>30</sup> The  $\text{K}-\text{O}(\text{thf})$  bond lengths of **5** (2.730(2) Å for  $\text{K}(1)$ ; 2.718(3) Å for  $\text{K}(2)$ ) are shorter than the  $\text{K}-\text{O}(\text{crown})$  bond lengths, and the  $\text{C}-\text{C}(\text{range})$  for the ring carbon atoms of the  $\text{C}_5\text{Ph}_4\text{H}$  ligands (1.404(4)–1.432(4) Å) is consistent with a delocalized system.

## CONCLUSION

In summary, we have prepared and characterized the octaphenylmetallocenes  $[\text{Mg}(\text{C}_5\text{Ph}_4\text{H})_2]$  (**1**) and  $[\text{Ca}(\text{C}_5\text{Ph}_4\text{H})_2(\text{thf})]$  (**2**). Complex **1** is the first fully characterized (polyaryl)cyclopentadienylmagnesium complex, and it is a symmetrical metallocene. Complex **2** is structurally similar to the ytterbium analogue, but **2** displays much lower thermal stability. Redox-transmetalation/protolysis (RTP) reactions of either calcium or ytterbium metal,  $\text{PhHgBr}$ , and  $\text{C}_5\text{Ph}_4\text{H}_2$  yielded the rare calcium and ytterbium heteroleptic bromide

**Table 2.** Selected Bond Lengths (Å) and Angles (deg) for  $[\text{Ca}(\text{C}_5\text{Ph}_4\text{H})(\mu\text{-Br})(\text{thf})_2]_2 \cdot 3\text{thf}$  (3·3thf),  $[\text{Yb}(\text{C}_5\text{Ph}_4\text{H})(\mu\text{-Br})(\text{thf})_2]_2 \cdot 3\text{thf}$  (4·3thf), and  $[\text{Yb}(\text{C}_5\text{Ph}_4\text{H})(\mu\text{-Br})(\text{thf})_2]_2 \cdot 4\text{PhMe}$  (4·4PhMe)

	3·3thf	4·3thf	4·4PhMe
M–C(1)	2.6935(19)	2.704(2)	2.7045(19)
M–C(2)	2.7266(19)	2.735(2)	2.7417(19)
M–C(3)	2.8034(19)	2.797(2)	2.7807(19)
M–C(4)	2.826(2)	2.820(2)	2.7943(19)
M–C(5)	2.7608(19)	2.757(2)	2.7534(19)
M–C(range)	2.6935(19)–2.826(2)	2.704(2)–2.820(2)	2.7045(19)–2.7943(19)
M–Cn	2.484	2.484	2.476
M–O(1)	2.4093(14)	2.4302(17)	2.4336(15)
M–O(2)	2.3957(15)	2.4440(17)	2.4184(14)
M–Br(1)	2.8779(4)	2.8932(2)	2.9233(2)
M–Br(1) <sup>#</sup>	2.9160(5)	2.9216(3)	2.8995(2)
Cn–M–X(1)	117.28	120.32	117.04
Cn–M–X(1) <sup>#</sup>	120.06	117.81	119.86
X(1)–M(1)–X(1) <sup>#</sup>	78.675(12)	79.261(8)	79.654(7)

**Figure 4.** Molecular structure of  $[\text{K}(18\text{-crown-6})(\text{thf})_2][\text{C}_5\text{Ph}_4\text{H}] \cdot \text{thf}$  (5·thf) shown with 30% probability thermal ellipsoids. Hydrogen atoms and lattice solvent have been omitted for clarity. Only one of the crystallographically unique potassium ions is shown, and half of its structure is generated by symmetry. Only one orientation of the disordered thf molecules is shown. Selected bond lengths (Å): K(1)–O(1) = 2.7937(16), K(1)–O(2) = 2.7655(16), K(1)–O(3) = 2.8130(17), K(1)–O(4) = 2.718(2), K(2)–O(5) = 2.8088(16), K(2)–O(6) = 2.8313(17), K(2)–O(7) = 2.7776(17), K(2)–O(8) = 2.7266(19), C(1)–C(2) = 1.407(2), C(1)–C(5) = 1.413(2), C(2)–C(3) = 1.434(2), C(3)–C(4) = 1.414(2), C(4)–C(5) = 1.425(2).

complexes  $[\text{Ca}(\text{C}_5\text{Ph}_4\text{H})(\mu\text{-Br})(\text{thf})_2]_2$  ( $\text{M} = \text{Ca}$ , 3;  $\text{M} = \text{Yb}$ , 4). This novel route could greatly expand the range of accessible pseudo-Grignard complexes. Attempted reduction of 3 using  $\text{KC}_8$  led to the isolation of the charge-separated potassium complex  $[\text{K}(18\text{-crown-6})(\text{thf})_2][\text{C}_5\text{Ph}_4\text{H}]$  (5), without evidence for a  $\text{Ca}^{\text{I}}$  species.

## EXPERIMENTAL SECTION

The compounds described herein are extremely air- and moisture-sensitive, and they were prepared and handled using conventional glovebox and Schlenk line techniques under an atmosphere of nitrogen. IR spectra were recorded as Nujol mulls between NaCl plates using a PerkinElmer Spectrum RX 1 FTIR spectrometer across the range 4000–650  $\text{cm}^{-1}$ . Multinuclear NMR spectra were recorded on a Bruker DPX 300 spectrometer. Chemical shifts were referenced to the residual resonances of the deuterated solvents. Melting points

were determined in sealed glass capillaries under nitrogen and are not calibrated. Microanalyses were determined by the Elemental Analysis Service, London Metropolitan University, London, U.K., or by the elemental analysis service at the Université de Reims, Reims, France. Hexane and thf were predried over sodium metal and distilled over sodium benzophenone ketyl (solubilized with tetraglyme in the still used for hexane) before being stored under an atmosphere of nitrogen. Toluene and  $\text{C}_6\text{D}_6$  were predried over sodium and then distilled under nitrogen from sodium metal before being stored under an atmosphere of nitrogen.  $\text{Mg}(\text{tBu})_2$ , calcium metal, and ytterbium metal were commercial samples and were used as received.  $\text{PhMgI}$  was made by the reaction between magnesium turnings (activated with a small amount of  $\text{I}_2$ ) and iodobenzene in  $\text{Et}_2\text{O}$ , and it was standardized using salicylaldehyde phenylhydrazine before use.  $\text{PhHgBr}$  was made by stirring equimolar amounts of  $\text{HgPh}_2$  and  $\text{HgBr}_2$  in thf followed by drying under vacuum. Note:  $\text{PhHgBr}$  is very toxic, and suitable precautions (e.g., personal protective equipment and a well-ventilated fume cupboard) should be taken for all manipulations involving it.  $\text{C}_5\text{Ph}_4\text{H}_2^{13\text{b}}$  and  $\text{KC}_8^{31}$  were made by reported methods.

All characterization, with the exception of X-ray crystallography, was carried out on bulk dried (under vacuum at room temperature) samples.

**Synthesis of  $[\text{Mg}(\text{C}_5\text{Ph}_4\text{H})_2]$  (1).** A solution of  $\text{Mg}(\text{tBu})_2$  (0.45 mL, 1.0 M in heptane, 0.45 mmol) was added by syringe to a stirred solution of  $\text{C}_5\text{Ph}_4\text{H}_2$  (0.31 g, 0.84 mmol) in toluene (10 mL). The solution was heated to 100–110  $^\circ\text{C}$ , and a white precipitate formed overnight. The mixture was heated for a further 2 days, and then the solvent was removed under vacuum, giving an off-white solid. The solid was washed with hexane and then dried under vacuum once more to afford 1 (0.15 g, 44%). Single crystals were grown by slow cooling of a hot, saturated toluene solution. Mp: 150  $^\circ\text{C}$  dec. IR (Nujol,  $\text{cm}^{-1}$ ): 1595s, 1576m, 1496m, 1328m, 1276w, 1189w, 1176w, 1109w, 1085m, 1072m, 1059w, 1026s, 1001w, 966w, 933w, 910s, 841w, 811s, 788s, 758vs, 734s, 694vs, 672w, 634s.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 300 MHz, 303 K):  $\delta$  6.84–7.23 (overlapping signals, 42H, ArH).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 75.47 MHz, 303 K): 104.82, 123.01, 123.42, 126.85, 127.07, 128.88, 129.30, 129.37, 132.48, 136.10, 136.48. Anal. Calcd for  $\text{C}_{58}\text{H}_{42}\text{Mg}$  (763.26): C, 91.27; H, 5.55. Found: C, 89.11; H, 5.43.

**Attempted Syntheses of  $[\text{Mg}(\text{C}_5\text{Ph}_4\text{H})(\text{sol})_m]_n$  ( $\text{sol} = \text{Et}_2\text{O}$ , thf).** **Method 1.** A solution of  $\text{PhMgI}$  (1.6 mL, 0.72 M in  $\text{Et}_2\text{O}$ , 1.2 mmol) was added by syringe to a stirred solution of  $\text{C}_5\text{Ph}_4\text{H}_2$  (0.41 g, 1.1 mmol) in toluene (10 mL). The solution was stirred at room temperature for approximately 2 days. The mixture was then filtered, and the solvent was removed under vacuum. The  $^1\text{H}$  NMR spectrum of the product indicated  $\text{C}_5\text{Ph}_4\text{H}_2$  and none, or very little, of the desired product.

**Method 2.** A solution of  $\text{PhMgI}$  (1.4 mL, 0.72 M in  $\text{Et}_2\text{O}$ , 1.0 mmol) was added by syringe to a stirred solution of  $\text{C}_5\text{Ph}_4\text{H}_2$  (0.36 g,

0.97 mmol) in toluene (10 mL). The solution was heated to 60–70 °C, and a white precipitate formed after 4 days. The mixture was heated for another 2 days, and then the solid was dissolved with increased heating. The solution was slowly cooled to room temperature, affording colorless crystals. These were found by X-ray crystallography to be **1**. Unit cell data: space group  $P\bar{1}$ ;  $a = 8.2040(16)$  Å,  $b = 10.755(2)$  Å,  $c = 12.969(3)$  Å;  $\alpha = 66.47(3)^\circ$ ,  $\beta = 76.50(3)^\circ$ ,  $\gamma = 87.23(3)^\circ$ ;  $V = 1018.9(4)$  Å<sup>3</sup>.

**Method 3.** A solution of PhMgI (1.4 mL, 0.72 M in Et<sub>2</sub>O, 1.0 mmol) was added by syringe to a stirred solution of C<sub>5</sub>Ph<sub>4</sub>H<sub>2</sub> (0.36 g, 0.97 mmol) in thf (10 mL), and a yellow suspension formed almost immediately. The mixture was stirred overnight, and after being allowed to stand, there was a yellow solution and a white precipitate. More thf (5 mL) was added, and the mixture was gently heated, giving a yellow solution. After the solution was cooled to room temperature, colorless crystals emerged. These were found by X-ray crystallography to be the known compound [Mg(thf)<sub>6</sub>][I]<sub>2</sub>. Unit cell data: space group  $Pn\bar{3}$ ;  $a = b = c = 14.2592(9)$  Å;  $\alpha = \beta = \gamma = 90^\circ$ ;  $V = 2899.25(18)$  Å<sup>3</sup>. Literature unit cell data: space group  $Pn\bar{3}$ ;  $a = b = c = 14.279(2)$  Å;  $\alpha = \beta = \gamma = 90^\circ$ ;  $V = 2911.343$  Å<sup>3</sup>.

**Synthesis of [Ca(C<sub>5</sub>Ph<sub>4</sub>H)<sub>2</sub>(thf)] (2).** thf (10 mL) was added to a Schlenk flask charged with calcium metal pieces (0.11 g, 2.7 mmol), HgPh<sub>2</sub> (0.24 g, 0.68 mmol), C<sub>5</sub>Ph<sub>4</sub>H<sub>2</sub> (0.51 g, 1.4 mmol), and 1 drop of mercury, and the suspension was stirred for 4 days, giving a dark yellow solution. The solution was filtered into another Schlenk flask, and the solvent was removed under vacuum. The fluffy yellow residue was dissolved in a mixture of toluene and thf with gentle heating. Overnight, colorless crystals of **2** deposited. The solution was filtered and concentrated, yielding a further crop of crystals (combined yield 0.39 g, 67%). Mp: 116 °C dec. IR (Nujol, cm<sup>-1</sup>): 1594vs, 1575w, 1504s, 1495vs, 1191m, 1072m, 1014m, 927w, 910m, 864m, 806w, 789m, 783m, 758vs, 740m, 698vs, 670w, 661w. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz, 303 K):  $\delta$  1.14 (s, 4H,  $\beta$ -H C<sub>4</sub>H<sub>8</sub>O), 3.20 (s, 4H;  $\alpha$ -H C<sub>4</sub>H<sub>8</sub>O), 6.75 (s, 2H, C<sub>5</sub>Ph<sub>4</sub>H), 6.88–7.36 (overlapping signals, 40 H; ArH). Anal. Calcd for C<sub>62</sub>H<sub>50</sub>CaO (851.14): C, 87.49; H, 5.92. Found: C, 86.71; H, 5.89.

**Synthesis of [Ca(C<sub>5</sub>Ph<sub>4</sub>H)( $\mu$ -Br)(thf)<sub>2</sub>·3thf (3·3thf).** thf (10 mL) was added to a Schlenk flask charged with calcium metal pieces (0.18 g, 4.5 mmol), HgPhBr (0.44 g, 1.2 mmol), C<sub>5</sub>Ph<sub>4</sub>H<sub>2</sub> (0.46 g, 1.2 mmol), and 1 drop of mercury, and the suspension was sonicated at 40 °C for 5 days, giving a yellow solution and a small amount of white precipitate. The solution was filtered and concentrated under vacuum to afford colorless crystals. The solvent was decanted, and the crystals were dried under vacuum to yield 3·3thf (0.57 g, 67%). Mp: 114 °C dec. IR (Nujol, cm<sup>-1</sup>): 1594vs, 1510s, 1505m, 1494s, 1296vw, 1260vw, 1196m, 1176w, 1152vw, 1072m, 1028s, 998w, 930w, 914w, 905w, 874m, 792m, 770sh, 761vs, 744w, 731s, 695vs, 666w, 660w. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz, 303 K):  $\delta$  1.32 (br s, 28H,  $\beta$ -H C<sub>4</sub>H<sub>8</sub>O), 3.50 (br s, 28H,  $\alpha$ -H C<sub>4</sub>H<sub>8</sub>O), 6.74–7.37 (overlapping signals, 26H, ArH), 7.52 (d, 8H, <sup>3</sup>J<sub>H,H</sub> = 7.2 Hz, *o*-H C<sub>6</sub>H<sub>5</sub>), 7.60 (d, 8H, <sup>3</sup>J<sub>H,H</sub> = 7.5 Hz, *o*-H C<sub>6</sub>H<sub>5</sub>). Anal. Calcd for C<sub>86</sub>H<sub>98</sub>Br<sub>2</sub>Ca<sub>2</sub>O<sub>7</sub> (1483.69) (retention of lattice thf): C, 69.62; H, 6.66. Found: C, 69.27; H, 6.20.

**Synthesis of [Yb(C<sub>5</sub>Ph<sub>4</sub>H)( $\mu$ -Br)(thf)<sub>2</sub>] (4; Crystallized as 4·3thf and 4·4PhMe).** thf (10 mL) was added to a Schlenk flask charged with ytterbium pieces (0.25 g, 1.4 mmol), HgPhBr (0.16 g, 0.45 mmol), and C<sub>5</sub>Ph<sub>4</sub>H<sub>2</sub> (0.17 g, 0.46 mmol), and the suspension was sonicated at 40 °C for 4 days, giving a dark orange solution. The solution was filtered and concentrated under vacuum. Overnight, yellow crystals of 4·3thf formed (0.050 g, 15%). Orange single crystals of 4·4PhMe were grown from storage of a concentrated toluene solution at –30 °C, while single crystals of 4·3thf were grown from storage of a concentrated thf solution at –30 °C. All characterization was performed on 4·3thf, other than microanalysis (4·4PhMe). Mp: 168 °C dec. IR (Nujol, cm<sup>-1</sup>): 1594s, 1574w, 1538w, 1505m, 1496s, 1309vw, 1261w, 1189m, 1065vs, 1027vs, 906m, 870s, 791m, 766s, 754vs, 735m, 696vs, 658 w. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz, 303 K):  $\delta$  1.39 (vbr s, 28H;  $\beta$ -H thf), 3.59 (vbr s, 28H;  $\alpha$ -H thf), 6.69 (s, 2H, C<sub>5</sub>Ph<sub>4</sub>H), 6.95–7.26 (overlapping signals, 32H, ArH), 7.60 (d, <sup>3</sup>J<sub>H,H</sub> = 6 Hz, 4H, *o*-H C<sub>6</sub>H<sub>5</sub>), 7.67 (d, <sup>3</sup>J<sub>H,H</sub> = 6.9 Hz, 4H, *o*-H C<sub>6</sub>H<sub>5</sub>). Anal.

Calcd for C<sub>88</sub>H<sub>90</sub>Br<sub>2</sub>O<sub>4</sub>Yb<sub>2</sub> (1717.60) (loss of two PhMe molecules of crystallization): C, 61.54; H, 5.28. Found: C, 61.38; H, 5.16.

**Reduction of [Ca(C<sub>5</sub>Ph<sub>4</sub>H)( $\mu$ -Br)(thf)<sub>2</sub>] by KC<sub>8</sub> Giving [K(18-crown-6)(thf)<sub>2</sub>][C<sub>5</sub>Ph<sub>4</sub>H]·thf (5·thf).** Complex 3·3thf (0.25 g, 0.20 mmol) was added to a suspension of KC<sub>8</sub> (0.32 g, 2.4 mmol) and 18-crown-6 (0.11 g, 0.42 mmol) in toluene (7 mL). The suspension was stirred for 2 days. Initially, there was a brownish color to the suspension, but after 2 days the color had disappeared. thf (5 mL) was added to the mixture, and then it was filtered into another Schlenk flask. The solvent was removed under vacuum, and thf (10 mL) was added to the residue. The solution was concentrated under vacuum, and single crystals of 5·thf deposited. The solution was decanted, and the single crystals were dried under vacuum, giving **5** as an orange solid (0.097 g, 30%) (no thf of crystallization). IR (Nujol, cm<sup>-1</sup>): 1589s, 1496s, 1397w, 1349s, 1282m, 1261s, 1234s, 1192s, 1176sh, 1104brs, 1058brs, 1028sh, 995m, 962s, 900m, 836m, 809sh, 791s, 776sh, 762s, 742s, 701s, 668w. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz, 298 K):  $\delta$  1.42 (m, 8H,  $\beta$ -H C<sub>4</sub>H<sub>8</sub>O), 3.01 (s, 24H, CH<sub>2</sub> 18-crown-6), 3.57 (m, 8H,  $\alpha$ -H C<sub>4</sub>H<sub>8</sub>O), 6.86–7.22 (overlapping multiplets, 13H, ArH), 7.58 (d, 4H, <sup>3</sup>J<sub>H,H</sub> = 7.5 Hz, *o*-H C<sub>6</sub>H<sub>5</sub>), 7.67 (d, 4H, <sup>3</sup>J<sub>H,H</sub> = 7.8 Hz, *o*-H C<sub>6</sub>H<sub>5</sub>). Satisfactory microanalyses could not be obtained.

**X-ray Diffraction Structure Determinations.** Single crystals coated with viscous hydrocarbon oil were mounted on loops. Data were obtained at –150 °C (123 K) on a Bruker X8 APEX II CCD diffractometer (2, 3·3thf, 4·3thf, and 4·4PhMe) equipped with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) or at –173 °C (100 K) on the MX1: Macromolecular Crystallography beamline (1) or the MX2: Macromolecular Crystallography beamline (5·thf) at the Australian Synchrotron, Victoria, Australia. Data collected on the Bruker X8 APEX II CCD diffractometer were empirically corrected for absorption (SADABS)<sup>32</sup> and then merged. Data collection and integration on the MX1: Macromolecular Crystallography beamline were initially processed using Blu-Ice<sup>33</sup> and the XDS software package.<sup>34</sup> The structures were solved using SHELXS or SHELXT<sup>35</sup> and refined by full-matrix least squares on all  $F^2$  data using SHELX-2014,<sup>35</sup> in conjunction with the Olex2 graphical user interface.<sup>36</sup> All hydrogen atoms were placed in calculated positions using the riding model. CCDC-1032411 (1), CCDC-1032412 (2), CCDC-1032413 (3·3thf), CCDC-1032414 (4·3thf), CCDC-1032415 (4·4PhMe), and CCDC-1032416 (5·thf) contain supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). CIF files are available as Supporting Information.

**Variata.** Complex **1** was collected on the MX1: Macromolecular Crystallography beamline at the Australian Synchrotron, Victoria, Australia, which at the time was only equipped to perform  $\psi$  scans. After the first data set was collected, the crystal was manually rotated approximately 90°, another data set was collected, and the two data sets were then merged. In addition, the crystal was twinned and Platon<sup>37</sup> was used to generate an HKLF 5 file, which was then used for further refinements. The BASF value was refined to approximately 0.443.

Complex 5·thf was collected on the MX2: Macromolecular Crystallography beamline at the Australian Synchrotron, Victoria, Australia, which at the time was only equipped to perform  $\psi$  scans. In order to address the low completeness of the data (92%), attempts were made to manually rotate the crystal in the same manner as **1**. However, all attempts to do so led to degradation of the crystal (due to the sensitivity of compound **5** to air and moisture), thereby preventing the collection of a good second data set.

**Crystal data for 1:** C<sub>88</sub>H<sub>92</sub>Mg ( $M_r = 763.22$  g/mol), triclinic, space group  $P\bar{1}$  (No. 2),  $a = 8.2040(16)$  Å,  $b = 10.755(2)$  Å,  $c = 12.969(3)$  Å,  $\alpha = 66.47(3)^\circ$ ,  $\beta = 76.50(3)^\circ$ ,  $\gamma = 87.23(3)^\circ$ ,  $V = 1018.9(4)$  Å<sup>3</sup>,  $Z = 1$ ,  $T = 100.0$  K,  $\mu$ (synchrotron) = 0.084 mm<sup>-1</sup>,  $D_{\text{calc}} = 1.244$  g/cm<sup>3</sup>, 34097 reflections measured ( $3.522^\circ \leq 2\theta \leq 57.592^\circ$ ), 5085 unique reflections ( $R_{\text{int}} = 0.1058$ ,  $R_\sigma = 0.0490$ ), which were used in all calculations. The final R1 value was 0.0695 ( $I > 2\sigma(I)$ ), and the wR2 value was 0.2096 (all data).



**Crystal data for 2:**  $C_{62}H_{50}CaO$  ( $M_r = 851.10$  g/mol), monoclinic, space group  $P2_1/n$  (No. 14),  $a = 10.2420(5)$  Å,  $b = 40.367(2)$  Å,  $c = 11.1505(5)$  Å,  $\beta = 105.518(2)^\circ$ ,  $V = 4442.0(4)$  Å<sup>3</sup>,  $Z = 4$ ,  $T = 123$  K,  $\mu(\text{Mo K}\alpha) = 0.186$  mm<sup>-1</sup>,  $D_{\text{calc}} = 1.273$  g/cm<sup>3</sup>, 38402 reflections measured ( $5.538^\circ \leq 2\theta \leq 56.896^\circ$ ), 10786 unique reflections ( $R_{\text{int}} = 0.1177$ ,  $R_\sigma = 0.1618$ ), which were used in all calculations. The final  $R_1$  value was 0.0682 ( $I > 2\sigma(I)$ ), and the  $wR_2$  value was 0.1502 (all data).

**Crystal data for 3-3thf:**  $C_{86}H_{98}O_7Ca_2Br_2$  ( $M_r = 1483.62$  g/mol), triclinic, space group  $P\bar{1}$  (No. 2),  $a = 11.3598(6)$  Å,  $b = 12.5296(9)$  Å,  $c = 14.3526(7)$  Å,  $\alpha = 92.999(3)^\circ$ ,  $\beta = 90.558(2)^\circ$ ,  $\gamma = 115.076(2)^\circ$ ,  $V = 1846.63(19)$  Å<sup>3</sup>,  $Z = 1$ ,  $T = 123.15$  K,  $\mu(\text{Mo K}\alpha) = 1.292$  mm<sup>-1</sup>,  $D_{\text{calc}} = 1.334$  g/cm<sup>3</sup>, 20718 reflections measured ( $6.84^\circ \leq 2\theta \leq 54.994^\circ$ ), 8439 unique reflections ( $R_{\text{int}} = 0.0249$ ,  $R_\sigma = 0.0432$ ), which were used in all calculations. The final  $R_1$  value was 0.0368 ( $I > 2\sigma(I)$ ), and the  $wR_2$  value was 0.0891 (all data).

**Crystal data for 4-3thf:**  $C_{86}H_{98}Br_2O_7Yb_2$  ( $M_r = 1733.41$  g/mol), triclinic, space group  $P\bar{1}$  (No. 2),  $a = 11.3758(4)$  Å,  $b = 12.5225(5)$  Å,  $c = 14.3701(5)$  Å,  $\alpha = 93.069(2)^\circ$ ,  $\beta = 90.738(2)^\circ$ ,  $\gamma = 115.190(2)^\circ$ ,  $V = 1848.30(12)$  Å<sup>3</sup>,  $Z = 1$ ,  $T = 123$  K,  $\mu(\text{Mo K}\alpha) = 3.650$  mm<sup>-1</sup>,  $D_{\text{calc}} = 1.557$  g/cm<sup>3</sup>, 21750 reflections measured ( $6.528^\circ \leq 2\theta \leq 57.136^\circ$ ), 9095 unique reflections ( $R_{\text{int}} = 0.0205$ ,  $R_\sigma = 0.0305$ ), which were used in all calculations. The final  $R_1$  value was 0.0229 ( $I > 2\sigma(I)$ ), and the  $wR_2$  value was 0.0555 (all data).

**Crystal data for 4-4PhMe:**  $C_{102}H_{106}Br_2O_4Yb_2$  ( $M_r = 1901.76$  g/mol), triclinic, space group  $P\bar{1}$  (No. 2),  $a = 11.8774(4)$  Å,  $b = 12.5527(4)$  Å,  $c = 15.7359(5)$  Å,  $\alpha = 66.7020(10)^\circ$ ,  $\beta = 81.237(2)^\circ$ ,  $\gamma = 83.161(2)^\circ$ ,  $V = 2125.19(12)$  Å<sup>3</sup>,  $Z = 1$ ,  $T = 123$  K,  $\mu(\text{Mo K}\alpha) = 3.179$  mm<sup>-1</sup>,  $D_{\text{calc}} = 1.486$  g/cm<sup>3</sup>, 35431 reflections measured ( $6.956^\circ \leq 2\theta \leq 56.8^\circ$ ), 10513 unique reflections ( $R_{\text{int}} = 0.0212$ ,  $R_\sigma = 0.0241$ ), which were used in all calculations. The final  $R_1$  value was 0.0212 ( $I > 2\sigma(I)$ ), and the  $wR_2$  value was 0.0512 (all data).

**Crystal data for 5-thf:**  $C_{53}H_{69}KO_9$  ( $M_r = 889.18$  g/mol): triclinic, space group  $P\bar{1}$  (No. 2),  $a = 10.123(2)$  Å,  $b = 12.975(3)$  Å,  $c = 19.538(4)$  Å,  $\alpha = 78.32(3)^\circ$ ,  $\beta = 89.11(3)^\circ$ ,  $\gamma = 73.78(3)^\circ$ ,  $V = 2410.8(9)$  Å<sup>3</sup>,  $Z = 2$ ,  $T = 100$  K,  $\mu(\text{synchrotron}) = 0.166$  mm<sup>-1</sup>,  $D_{\text{calc}} = 1.225$  g/cm<sup>3</sup>, 33659 reflections measured ( $2.13^\circ \leq 2\theta \leq 66.32^\circ$ ), 14279 unique reflections ( $R_{\text{int}} = 0.0745$ ,  $R_\sigma = 0.0831$ ), which were used in all calculations. The final  $R_1$  value was 0.0658 ( $I > 2\sigma(I)$ ), and the  $wR_2$  value was 0.1890 (all data).

## ■ ASSOCIATED CONTENT

### Supporting Information

CIF files giving crystallographic data for **1**, **2**, **3-3thf**, **4-3thf**, **4-4PhMe**, and **5-thf**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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## ■ DEDICATION

Dedicated to Professor Michael Lappert FRS, a leader in creative synthetic inorganic and organometallic chemistry across the whole periodic table.

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