Accessing Decaphenylmetallocenes of Ytterbium, Calcium, and Barium by Desolvation of Solvent-Separated Ion Pairs: Overcoming Adverse Solubility Properties[#]

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The redox-transmetalation ligand-exchange reaction of ytterbium or calcium metal with 2 equiv of pentaphenylcyclopentadiene (C_5Ph_5H) and 1 equiv of $HgPh_2$ in thf afforded the solvent-separated ion pairs (SSIPs) $[M(thf)_6][C_5Ph_5]_2$ (M = Yb, Ca), which were characterized by single-crystal X-ray analyses. Addition of toluene to the isolated SSIPs led to the precipitation of the homoleptic sandwich complexes $[M(C_5Ph_5)_2]$ (M = Yb, Ca). In the reaction of barium metal with C_5Ph_5H and $HgPh_2$ the corresponding SSIP was observed in situ, and only the sandwich complex $[Ba(C_5Ph_5)_2]$ could be isolated. Single-crystal X-ray analyses were carried out for $[M(C_5Ph_5)_2]$ (M = Yb, Ba), which confirmed the highly symmetric structure of these complexes with two parallel cyclopentadienyl ligands. Oxidation and metal-ligand exchange reactions were investigated for the divalent ytterbium complexes.

Introduction

The use of bulky polyalkyl- and polysilyl-substituted cyclopentadienyl ligands in the organometallic chemistry of alkaline earth and rare earth metals has recently allowed the rapid development of new classes of complexes, such as monocyclopentadienyl compounds and stable divalent lanthanoid complexes, even for the highly reducing lanthanum(II), thulium(II), and dysprosium(II) metals.[1–3] In addition, the very bulky pentaisopropylcyclopentadienyl ligand provided access to the first series of homoleptic parallel sandwich complexes for both rare earth (Eu)[4a] and alkaline earth (Ca, Sr, Ba)[4b] metals in contrast to less substituted cyclopentadienyl ligands, which mainly lead to bent complexes,[5] including bis(tetraisopropylcyclopentadienyl)europium(II).[4a] Despite their interesting steric and electronic properties, the use of polyarylcyclopentadienyl ligands with these metals is much less developed, and only a few examples have been reported so far.[6–8] The main reasons for this are (i) the reduced Lewis basicity of the ligands, which is due to the stabilization of the negative charge by the aryl groups; and (ii) the low solubility of the resulting complexes, especially in the case of the pentaphenylcyclopentadienyl ligand. Typical synthetic pathways such as salt me-

[#] Some aspects of this work have been previously presented at several conferences including the RACI Organometallic Conference, Gippsland, 2006 (OZOM 3), the RACI IC07, Hobart, 2007, and the XX. Tage der Seltenen Erden–Terrae Rarae, Bonn, 2007.

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(1) Mono-Cp AE complexes: (a) Sitzmann, H.; Weber, F.; Walter, M. D.; Wolmershäuser, G. *Organometallics* **2003**, *22*, 1931–1936. (b) Harvey, M. J.; Hanusa, T. P.; Young, V. G., Jr. *J. Organomet. Chem.* **2001**, *626*, 43–48. (c) Harvey, M. J.; Hanusa, T. P. *Organometallics* **2000**, *19*, 1556–1566. (d) Hanusa, T. P. *Chem. Rev.* **1993**, *93*, 1023–1036.

(2) Mono-Cp Ln complexes: (a) Walter, M. D.; Bentz, D.; Weber, F.; Schmitt, O.; Wolmershäuser, G.; Sitzmann, H. *New J. Chem.* **2007**, *31*, 305–318. (b) Zeimentz, P. M.; Arndt, S.; Elvidge, B. R.; Okuda, J. *Chem. Rev.* **2006**, *106*, 2404–2433. (c) Hou, Z.; Luo, Y.; Li, X. *J. Organomet. Chem.* **2006**, *691*, 3114–3121. (d) Shima, T.; Hou, Z. *J. Am. Chem. Soc.* **2006**, *128*, 8124–8125. (e) Giesbrecht, G. R.; Collis, G. E.; Gordon, J. C.; Clark, D. L.; Scott, B. L.; Hardman, N. J. *J. Organomet. Chem.* **2004**, *689*, 2177–2185. (f) Arndt, S.; Okuda, J. *Chem. Rev.* **2002**, *102*, 1953–1976. (g) Barbier-Baudry, D.; Heiner, S.; Kubicki, M. M.; Vigier, E.; Visseaux, M.; Hafid, A. *Organometallics* **2001**, *20*, 4207–4210. (h) Barbier-Baudry, D.; Blacque, O.; Hafid, A.; Nyassi, A.; Sitzmann, H.; Visseaux, M. *Eur. J. Inorg. Chem.* **2000**, 2333–2336.

(3) "New" divalent Ln complexes: (a) Hitchcock, P. B.; Lappert, M. F.; Maron, L.; Protchenko, A. V. *Angew. Chem., Int. Ed.* **2008**, *47*, 1–5. (b) Jaroschik, F.; Nief, F.; Ricard, L.; Le.Goff, X.-F. *Organometallics* **2007**, *26*, 1123–1125. (c) Jaroschik, F.; Nief, F.; Le.Goff, X.-F.; Ricard, L. *Organometallics* **2007**, *26*, 3552–3558. (d) Jaroschik, F.; Nief, F.; Ricard, L. *Chem. Commun.* **2006**, 426–428. (e) Evans, W. J.; Allen, N. T.; Ziller, J. W. *Angew. Chem., Int. Ed.* **2002**, *41*, 359–361. (f) Evans, W. J. *Inorg. Chem.* **2007**, *46*, 3435–3449. (g) Meyer, G. *Angew. Chem., Int. Ed.* **2008**, *47*, 4962–4964.
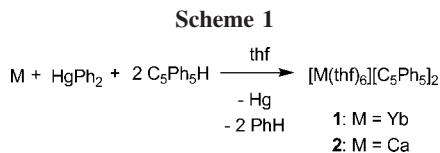
(4) (a) Sitzmann, H.; Dezember, T.; Schmitt, O.; Weber, F.; Wolmershäuser, G. *Z. Anorg. Allg. Chem.* **2000**, *626*, 2241–2244. (b) Sitzmann, H.; Dezember, T.; Ruck, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 3114–3116.

(5) (a) Harvey, M. J.; Quisenberry, K. T.; Hanusa, T. P. *Eur. J. Inorg. Chem.* **2003**, 3383–3390. (b) Weber, F.; Sitzmann, H.; Schultz, M.; Sofield, C. D.; Andersen, R. A. *Organometallics* **2002**, *21*, 3139–3146. (c) Schultz, M.; Burns, C. J.; Schwartz, D. J.; Andersen, R. A. *Organometallics* **2000**, *19*, 781–789. (d) Williams, R. A.; Tesh, K. F.; Hanusa, T. P. *J. Am. Chem. Soc.* **1991**, *113*, 4843–4851.

(6) $C_5Ph_3H_2$ complexes:(a) Barbier-Baudry, D.; Bouyer, F.; Bruno, A. S. M.; Visseaux, M. *Appl. Organomet. Chem.* **2006**, *20*, 24–31. (b) Bonnet, F.; Visseaux, M.; Barbier-Baudry, D. *J. Organomet. Chem.* **2004**, *689*, 264–269.

(7) C_5Ph_4H complexes:(a) Klimpel, M. G.; Görlitzer, H. W.; Tafipolsky, M.; Spiegler, M.; Scherer, W.; Anwander, R. *J. Organomet. Chem.* **2002**, *647*, 236–244. (b) Tanner, P. S.; Hanusa, T. P. *Polyhedron* **1994**, *13*, 2417–2420.

(8) C_5Ar_5 complexes:(a) Ruspic, C.; Moss, J. R.; Schürmann, M.; Harder, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 2121–2126. (b) Forsyth, C. M.; Deacon, G. B.; Field, L. D.; Jones, C.; Junk, P. C.; Kay, D. L.; Masters, A. F.; Richards, A. F. *Chem. Commun.* **2006**, 1003–1005. (c) Schumann, H.; Winterfeld, J.; Glanz, M.; Köhn, R. D.; Hemling, H. *J. Organomet. Chem.* **1994**, *481*, 275–82. (d) Zhang, R.; Tsutsui, M. *Youji Huaxue* **1982**, *6*, 435–37. (e) Note added in proof: Preparations and structures of the M = Sr, Ba complexes have now been achieved: Orzechowski, L.; Piezik, D. F.-J.; Ruspic, C.; Harder, S. *Dalton Trans.*, in press.

Scheme 1

$$M + HgPh_2 + 2\,C_5Ph_5H \xrightarrow[\substack{-Hg \\ -2\,PhH}]{\text{thf}} [M(thf)_6][C_5Ph_5]_2$$

1: M = Yb
2: M = Ca

tathesis or protolysis are often not suitable to access these complexes due to reactivity and purification problems.[7b] A recent report on para-alkyl-substituted pentaphenylcyclopentadienyl ligands showed one solution to circumvent the solubility problem. The penta(4-butylphenyl)cyclopentadienyl ligand (Cp^{BIG}) provided access to the first decaaryllanthanoid and alkaline earth complexes [M(Cp^{BIG})$_2$] (M = Yb, Sm, Ca).[8a,e]

In our ongoing studies on pentaphenylcyclopentadienyl lanthanoid complexes, we have found that the redox-transmetalation ligand-exchange approach is an alternative synthetic route.[8b] We recently reported that, when using the heteroleptic phenylethynylphenylmercury reagent, different divalent ytterbium products were observed depending on the solvent: either the ligand was bound to the metal or a solvent-separated ion pair (SSIP) was obtained (eq 1).[8b]
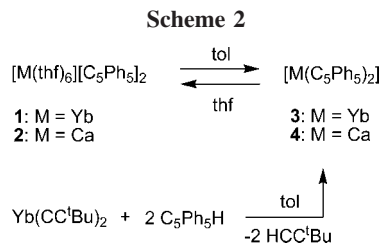
$$Yb + PhHg(CCPh) + C_5Ph_5H \xrightarrow[-PhH]{\text{thf}}$$

$$[Yb(C_5Ph_5)(\mu\text{-}CCPh)(thf)]_2 \xrightarrow[\text{dig = diglyme}]{\text{xs dig}}$$

$$[Yb(dig)_3][C_5Ph_5]_2 \quad (1)$$
$$\textbf{SSIP}$$
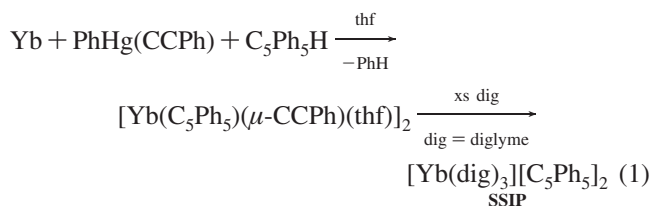
In developing this work, we now report the reaction outcome using the homoleptic organomercurial HgPh$_2$ with the aim to access the divalent sandwich complex [Yb(C$_5$Ph$_5$)$_2$]. This reaction proceeds via the solvent-separated ion pair [Yb(thf)$_6$][C$_5$Ph$_5$]$_2$, which can be completely desolvated to give the homoleptic sandwich compound. The same procedure has also been applied to obtain the corresponding homoleptic Ca and Ba complexes, the latter being previously considered inaccessible.[7b] This approach overcomes many of the problems posed by the low solubilities of these complexes. The reactivity of the divalent ytterbium complexes toward oxidizing agents and their use in ligand-exchange reactions is also considered.

Results

Synthesis of SSIPs [M(thf)$_6$][C$_5$Ph$_5$]$_2$ (M = Yb, Ca). The reaction of an excess of Yb metal with 2 equiv of the pentaphenylcyclopentadiene ligand and 1 equiv of diphenylmercury in thf at room temperature did not yield the sandwich complex [Yb(C$_5$Ph$_5$)$_2$], but after filtration of the solution from the remaining metal amalgam and evaporation of the solvent, the crystalline SSIP [Yb(thf)$_6$][C$_5$Ph$_5$]$_2$ (**1**) was obtained in moderate yield (Scheme 1). As the chemistries of Yb^{2+} and Ca^{2+} show many analogies,[9] we attempted the reaction under the same conditions using an excess of Ca metal in place of

Scheme 2

$$[M(thf)_6][C_5Ph_5]_2 \underset{\text{thf}}{\overset{\text{tol}}{\rightleftharpoons}} [M(C_5Ph_5)_2]$$

1: M = Yb
2: M = Ca

3: M = Yb
4: M = Ca

$$Yb(CC^tBu)_2 + 2\,C_5Ph_5H \xrightarrow[-2\,HCC^tBu]{\text{tol}}$$

Yb, resulting in the formation of the analogous SSIP [Ca(thf)$_6$][C$_5$Ph$_5$]$_2$ (**2**). **1** and **2** were characterized by ^{1}H and ^{13}C NMR and IR spectroscopy and elemental analysis. Furthermore, single crystals suitable for X-ray crystal structure analyses were obtained, but in the case of **2**, the data were poor and we were able to confirm only the connectivity of the molecule.

The NMR spectra of **1** and **2** are almost identical, and the resonances corresponding to the Cp and the phenyl rings in the ^{13}C spectra are in very good agreement with those of the already reported SSIP [Yb(dig)$_3$][C$_5$Ph$_5$]$_2$.[8b] The IR spectra of **1** and **2** show absorptions at 1498 and 1598 cm^{-1}, similar to the spectrum of [Yb(dig)$_3$][C$_5$Ph$_5$]$_2$,[8b] which indicate that the Cp ligand is not bound to the metal.

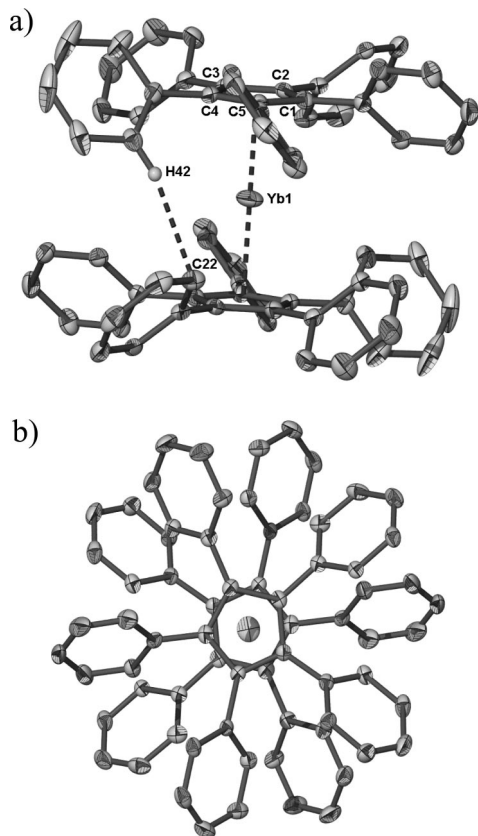**Synthesis of Sandwich Complexes [M(C$_5$Ph$_5$)$_2$] (M = Yb, Ca).** Addition of noncoordinating solvents such as benzene, toluene, or xylene to **1** led to the immediate formation of a green solid, **3**, which remained insoluble in any nonpolar solvent (Scheme 2). Sonication at 50 °C for 24 h increased the amount of green solid, which was isolated by filtration and washed with toluene. A similar procedure for **2** led to an off-white powder, **4**, in good yield. In both compounds, the absorptions of thf in the IR spectra were absent and a shift of the C$_5$Ph$_5$ absorptions to 1594 and 1500 cm^{-1}, similar to those of [Yb(C$_5$Ph$_5$)(μ-CCPh)(thf)]$_2$,[8b] was observed. The insolubility of the compounds in noncoordinating solvents did not allow the recording of any NMR spectra. It should be noted that addition of thf to **3** or **4** led to the conversion back to the corresponding SSIPs **1** and **2**. The amorphous nature of the solid materials prevented further investigation by crystallographic analysis. In order to confirm the proposed formulation of [M(C$_5$Ph$_5$)$_2$] (M = Yb (**3**), Ca (**4**)) for the new compounds, both species were examined by mass spectrometry. However, as many methods in mass spectrometry require soluble compounds and special arrangements for air- and moisture-sensitive compounds,[10] we investigated the possibility of using MALDI-TOF MS for our purpose. Indeed, using an inert C$_{60}$/C$_{70}$ matrix allowed the mass spectra of **3** and **4** to be obtained. These showed the relevant molecular ions with high intensity as well as the formation of several other related ions such as [M(C$_5$Ph$_5$)]$^+$, [M$_2$(C$_5$Ph$_5$)$_3$]$^+$, and [C$_5$Ph$_5$]$^{+}$.[11]

Among other synthetic routes to access **3**, we also investigated the ligand-exchange reaction between [Yb(CC^{t}Bu)$_2$] and C$_5$Ph$_5$H (Scheme 2). As shown previously, a similar reaction using [Yb(CCPh)$_2$] could be carried out only in thf due to the low solubility of this compound and led to the dimeric monocyclopentadienyl compound [Yb(C$_5$Ph$_5$)(μ-CCPh)(thf)]$_2$.[8b] The better solubility of [Yb(CC^{t}Bu)$_2$] allowed the reaction to be effected in toluene, and after heating the reaction mixture at 60 °C for 48 h a small crop of green crystals had formed, displaying the

(9) (a) Buch, F.; Harder, S. *Organometallics* **2007**, *26*, 5132–5135. (b) Ruspic, C.; Spielmann, J.; Harder, S. *Inorg. Chem.* **2007**, *46*, 5320–5326. (c) Panda, T. K.; Gamer, M. T.; Roesky, P. W. *Inorg. Chim. Acta* **2006**, *359*, 4765–4768. (d) Hitzbleck, J.; O'Brien, A. Y.; Deacon, G. B.; Ruhlandt-Senge, K. *Inorg. Chem.* **2006**, *45*, 10329–10337. (e) Walter, M. D.; Wolmershäuser, G.; Sitzmann, H. *J. Am. Chem. Soc.* **2005**, *127*, 17494–17503. (f) Harder, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2714–2718. (g) Fedushkin, I. L.; Kurskii, Y. A.; Balashova, T. V.; Bochkarev, M. N.; Dechert, S.; Muhle, S.; Schumann, H. *Russ. Chem. Bull.* **2003**, *52*, 1363–1371. (h) Hitchcock, P. B.; Khvostov, A. V.; Lappert, M. F. *J. Organomet. Chem.* **2002**, *663*, 263–268. (i) Izod, K.; Clegg, W.; Liddle, S. T. *Organometallics* **2000**, *19*, 3640–3643.

(10) (a) Evans, W. J.; Johnston, M. A.; Fujimoto, C. H.; Greaves, J. *Organometallics* **2000**, *19*, 4258–65. (b) May, M. A.; Marshall, A. G. *Rev. Sci. Instrum.* **1994**, *65*, 612–16. (c) Abdul-Sada, A. K.; Greenway, A. M.; Seddon, K. R. *J. Organomet. Chem.* **1989**, *375*, C17–19.

(11) A full account of the use of the MALDI-TOF MS method using the new C$_{60}$/C$_{70}$ matrix is in preparation.

Scheme 3

$$\text{Ba} + \text{HgPh}_2 + 2\,\text{C}_5\text{Ph}_5\text{H} \xrightarrow[\substack{-\text{Hg} \\ -2\,\text{PhH}}]{\text{thf}} \underset{\mathbf{5}}{[\text{Ba(thf)}_x][\text{C}_5\text{Ph}_5]_2} \xrightarrow{\text{hexane}} \underset{\mathbf{6}}{[\text{Ba(C}_5\text{Ph}_5)_2]}$$

same mass spectrum as the compound obtained by desolvation of the SSIP. The crystals were analyzed by X-ray crystallography, which confirmed the solvent-free, homoleptic sandwich structure of **3**. Due to the similarities in the IR spectra and physical and chemical behavior, we assume the same structure for the Ca analogue **4**. Attempts to obtain crystals of **4** by several methods have so far been unsuccessful.

Synthesis of Ba-SSIP and [Ba(C₅Ph₅)₂] Sandwich. Having in hand a viable route to decaphenylmetallocenes, we then investigated whether this approach could be extended to decaphenylbarocene, as previous workers had shown that this compound could not be accessed by salt metathesis, protolysis, or oxidation of Rieke activated barium.[7b] The reaction to give the SSIP $[\text{Ba(thf)}_x][\text{C}_5\text{Ph}_5]_2$ (**5**) was carried out under the same conditions as for **1** and **2** using an excess of Ba metal (Scheme 3). However, the SSIP **5** could not be isolated, but after filtration and removal of the solvent, off-white decaphenylbarocene $[\text{Ba(C}_5\text{Ph}_5)_2]$ (**6**) was obtained, which was purified by washing with toluene. Two observations confirm that the SSIP **5** is an intermediate in this reaction: (i) the ^1H and ^{13}C NMR spectra of **6** dissolved in d_8-thf are almost identical to those of the SSIPs **1** and **2**, and (ii) a solution IR spectrum of **6** in thf showed noncoordinating C_5Ph_5 absorptions at 1588 and 1498 cm^{-1}, similar to those of **1** and **2**. Crystals of **6** suitable for X-ray analysis were obtained by slow diffusion of hexane into a thf solution of the in situ formed SSIP **5**. Using a similar diffusion procedure in an attempt to obtain crystals of **4** led to the crystallization of the SSIP **2**.

As in the case of **3** and **4**, the IR spectrum shows absorptions at 1595 and 1502 cm^{-1} for the coordinated C_5Ph_5 ligands, and no thf absorptions are present. In contrast to **3** and **4**, the MALDI-TOF mass spectrum of **6** shows only a very small intensity for the molecular ion with a peak for the cation $[\text{Ba(C}_5\text{Ph}_5)]^+$ being predominant (see Discussion below).

Crystal Structures of SSIPs. Crystals of **1** were obtained as the thf solvate $\{[\text{Yb(thf)}_6][\text{C}_5\text{Ph}_5]_2\}_2 \cdot 7(\text{thf})$ and crystals of **2** as a thf/toluene solvate $\{[\text{Ca(thf)}_6][\text{C}_5\text{Ph}_5]_2\}_2 \cdot 2(\text{thf}) \cdot (\text{toluene})$. The facile loss of lattice solvent molecules during handling and X-ray data collection led to poor quality data. As both compounds are isostructural, we base our discussion on the higher quality structure **1** (Figure 1).

1 and **2** crystallize in the centrosymmetric triclinic space group $P\bar{1}$, and the cation contains a divalent metal ion surrounded by six thf ligands in a distorted octahedral arrangement. The Yb–O distances are in the range from 2.375(3) to 2.419(3) Å and compare well with other $[\text{Yb(thf)}_6]^{2+}$ cations in the literature,[12] such as $[\text{Yb(thf)}_6][\text{BPh}_4]_2$ (average 2.377 Å).[12c] The noncoordinated pentaphenylcyclopentadienyl anions are situated with their centroids approximately 6.98 Å from the closest metal center. Four pentaphenylcyclopentadienyl anions pack around each $[\text{M(thf)}_6]^{2+}$ cation, with an angle of 86.6°

(12) (a) Poplaukhin, P. V.; Chen, X.; Meyers, E. A.; Shore, S. G. *Inorg. Chem.* **2006**, *45*, 10115–10125. (b) Chen, X.; Lim, S.; Pleènik, C. E.; Liu, S.; Du, B.; Meyers, E. A.; Shore, S. G. *Inorg. Chem.* **2004**, *43*, 692–698. (c) Evans, W. J.; Johnston, M. A.; Greci, M. A.; Gummersheimer, T. S.; Ziller, J. W. *Polyhedron* **2003**, *22*, 119–126. (d) Kornienko, A.; Huebner, L.; Freedman, D.; Emge, T. J.; Brennan, J. G. *Inorg. Chem.* **2003**, *42*, 8476–8480. (e) Bochkarev, L. N.; Molosnova, N. E.; Zakharov, L. N.; Fukin, G. K.; Yanovsky, A. I.; Struchkov, Y. T. *J. Organomet. Chem.* **1995**, *485*, 101–107.

a)

b)

Figure 1. (a) Molecular structure of the SSIP **1** with 50% probability ellipsoids. Lattice thf molecules are omitted for clarity. H atoms are omitted except for those with C–H···C π-interactions. Selected interatomic distances (Å) and angles (deg): Yb1–O1 = 2.393(3), Yb1–O2 = 2.420(3), Yb1–O3 = 2.393(3), Yb1–O4 = 2.375(3), Yb1–O5 = 2.386(3), Yb1–O6 = 2.389(3), C3–H61E = 2.609, C12–H41B = 2.739, C73–H51C = 2.820, C10–H41C = 2.761, C9–H41E = 2.789, O5–Yb1–O6 = 177.02(9), O4–Yb1–O3 = 176.33(10), O1–Yb1–O2 = 178.44(10). (b) Cation-in-a-box crystal structure of **1**. Lattice thf molecules are omitted.

formed between the cyclopentadienyl ring planes of adjacent anionic units. The near-orthogonal nature of this arrangement as well as nonclassical C–H···C interactions between thf protons and carbon atoms on the ligand (see Figure 1) results in the well-ordered "cation-in-a-box" structure, similar to the reported $[\text{Ca(thf)}_6][\text{Me}_3\text{Si(fluorenyl)}]_2$ complex.[13] The lattice thf molecules occupy the vertices of the box.

Crystal Structures of Sandwich Complexes. Compounds **3** and **6** were obtained as solvent-free crystals in the monoclinic space groups $P2_1/n$ and $P2_1/c$, respectively (Figures 2 and 3). In both cases, the phenyl groups on the ligand all tilt in the same direction, generating a propeller-like ligand. The metal resides on an inversion center, thereby generating the second ligand with opposite chirality. The Yb–C distances range from 2.652(2) to 2.680(2) Å and compare well with those of the recently reported $[\text{Yb(Cp}^{\text{BIG}})_2]$ (average 2.673 Å).[8a] Despite the steric bulk of the pentaarylcyclopentadienyl ligands, the Yb–C distances are not significantly longer than in other homoleptic Yb sandwiches with less substituted ligands, such as

(13) Harder, S.; Feil, F.; Repo, T *Chem.−Eur. J.* **2002**, *8*, 1992–1999.

Figure 2. (a) Molecular structure of **3** with 50% probability ellipsoids (side view). H atoms are omitted, except H42, which is representative of all ortho-hydrogens involved in C−H···C π-interactions. Selected interatomic distances (Å) and angles (deg): Yb1−C1 = 2.680(2), Yb1−C2 = 2.668(2), Yb1−C3 = 2.652(2), Yb1−C4 = 2.652(2), Yb1−C5 = 2.672(2), C22−H42 = 2.692, Cp−Yb−Cp = 180. (b) Molecular structure of **3** with 50% probability ellipsoids (top view).
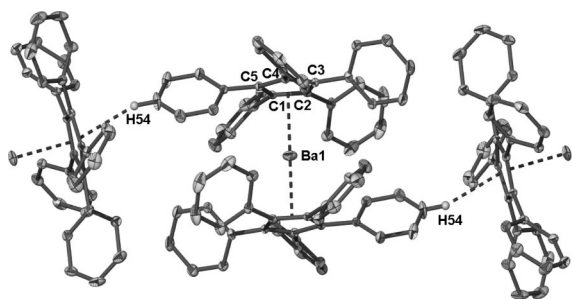
Figure 3. Molecular structure of **6** with 50% probability ellipsoids. H atoms are omitted, except for H54, which shows the π-stacking interaction between the para-hydrogen and the centroid of the C_5Ph_5 ligand. Selected interatomic distances (Å) and angles (deg): Ba1−C1 = 2.910(2), Ba1−C2 = 2.924(2), Ba1−C3 = 2.951(2), Ba1−C4 = 2.943(2), Ba1−C5 = 2.925(2), Cp(centroid)−H54 = 2.740, Cp−Ba−Cp = 180.

$[Yb(C_5Me_5)_2]$, $[Yb(C_5(^tBu)_2H_3)_2]$ (average 2.66 Å in both) or $[Yb(C_5(^tBu)_3H_2)_2]$ (average 2.68 Å).[5b,c] The larger barium ion leads to longer Ba−C distances in the range 2.910(2) to 2.951(2) Å, which are significantly longer than the largest reported metal carbon distances in decaarylmetallocenes, i.e., Sm−C in [Sm-(Cp^{BIG})$_2$] (average 2.782 Å).[8a] However, the Ba−centroid distance of 2.670 Å is surprisingly much shorter, by over 0.1 Å, compared with the only other reported flat Ba sandwich complex [Ba(C$_5^i$Pr$_5$)$_2$] (2.7848 Å),[4b] suggesting a lower steric

bulk of the phenyl groups compared with the ^iPr groups. The Ba−centroid distance is also shorter than in nonplanar [Ba(C$_5$(SiMe$_3$)$_3$H$_2$)$_2$] (2.75 Å) and similar to that in [Ba(C$_5^i$Pr$_4$H)$_2$] (2.68 Å).[5a,d] The recent investigation of deca(4-butylphenyl)metallocenes has shown that interplanar, nonclassical C−H···C interactions may contribute to the stabilization of these compounds and hence reduce the metal−centroid distance.[8a] In **3**, these interactions between an ortho-H of one ligand and an ortho-C of the other ligand are comparable (2.79 Å average) to the corresponding [Yb(Cp^{BIG})$_2$] (average 2.74 Å).[8a] However, in **6** these interactions are much less pronounced, with an average of 3.00 Å,[14] which is 0.1 Å greater than the sum of the van der Waals radii for C and H (2.90 Å). In contrast to **3**, the Ba complex **6** also displays *intermolecular* interactions: the para-hydrogen atom H54 of one phenyl group shows an orthogonal π-stacking interaction with another Cp ring (H−Cp-(Centroid) distance of 2.74 Å). As observed in the [M(Cp^{BIG})$_2$] complexes (M = Yb, Sm, Ca),[8a] the metals in **3** and **6** exhibit larger thermal parameters in the plane parallel to the Cp planes than in the perpendicular plane, leading to the elongation of the ellipsoids. This "flattening" of the metal, which is usually not observed in bent complexes, may arise from electronic strain imposed by the planar negatively charged Cp rings.

Reactivity Studies of Compounds 1−6. All SSIP and sandwich complexes are extremely air- and moisture-sensitive. Contact with traces of oxygen leads immediately to the formation of the stable, violet C_5Ph_5 radical.[15] Examination of the IR spectra of compounds **1−6** after short exposure to air shows a typical OH absorption at 3300 cm^{-1}, indicating the formation of metal hydroxide complexes. This result is surprising in the case of **4** and **6**, as the analogous [M(C$_5^i$Pr$_5$)$_2$] (M = Ca, Ba) complexes have been reported to be air-stable,[4b] and the Ba derivative has longer Ba−C bonds than **6** (see above).

No trivalent bis(pentaphenyl)cyclopentadienyl lanthanoid compounds have been crystallographically identified previously, even though the synthesis of [Lu(C$_5$Ph$_5$)$_2$Cl][8d] was described in the 1980s and a bis(pentaarylcyclopentadienyl)aminobenzyl intermediate has been proposed in the recent synthesis of [Yb(Cp^{BIG})$_2$] and [Sm(Cp^{BIG})$_2$].[8a] In order to shed some light on the possible structure of such a trivalent complex, we examined the oxidation of the divalent Yb sandwich **3** with different oxidizing agents to attempt to obtain similar [Yb(C$_5$Ph$_5$)$_2$X] complexes (X = halide). Two different results were found depending on the strength of the oxidizing reagent. Oxidants as powerful as oxygen, e.g., PhICl$_2$ or I$_2$, led to the formation of C$_5$Ph$_5$ radicals and YbX$_3$. Weaker oxidants, such as C$_2$Cl$_6$, did not react with **3**, even in boiling toluene. By contrast, all oxidants reacted readily with the SSIP **1** to give the C$_5$Ph$_5$ radical and YbX$_3$. Attempts to use an excess of **1** or **3** led predominantly to unreacted starting material and no [Yb(C$_5$Ph$_5$)$_2$X] or [Yb(C$_5$Ph$_5$)X$_2$] species could be identified.

The first reports on organolanthanoid complexes showed that triscyclopentadienyllanthanoid complexes could be used in salt metathesis reactions, for example to produce ferrocene.[16] We therefore were interested to explore whether our complexes could be suitable precursors to access decaphenylmetallocenes. Due to the solubility problems of **3**, we examined the SSIP **1** in the reaction with FeBr$_2$ (Scheme 4). An immediate color

(14) This elongation is in agreement with the size difference of 0.33Å for a six-coordinated Ba^{2+} cation compared to a six-coordinated Yb^{2+} cation.
(15) Ziegler, K.; Schnell, B. *Justus Liebigs Ann. Chem.* **1925**, *445*, 266–282.
(16) Birmingham, J. M.; Wilkinson, G. *J. Am. Chem. Soc.* **1956**, *78*, 42–44.

Scheme 4

$$\textbf{1} + FeBr_2 \xrightarrow[-YbBr_2]{thf} [Fe(\eta^6\text{-}Ph(C_5Ph_4))(C_5Ph_5)]$$

$$\textbf{7}$$
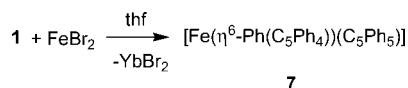
change to blue indicated the formation of the linkage isomer $[Fe(\eta^6\text{-}Ph(C_5Ph_4))(C_5Ph_5)]$ (**7**),[17] which was isolated in good yield, and its identity was confirmed by NMR, IR, and MALDI-TOF MS studies.

Discussion

The redox-transmetalation ligand-exchange approach toward metal−organic complexes of lanthanoid and alkaline earth metals has been reported for several different classes of ligands, including pyrazoles, phenols, and formamidines,[18a−c] whereas cyclopentadienes have only been sporadically investigated.[8b,18d,e] Employing the bulky pentaphenylcyclopentadienyl ligand in this synthetic route enabled us to isolate two different classes of compounds, the divalent SSIPs **1** and **2** and the divalent homoleptic sandwich complexes **3**, **4**, and **6**. Hence, this synthetic route has provided a way of overcoming the synthetic problems imposed by the extremely low solubility of decaphenylmetallocenes. The latter complexes were isolated in pure form in reasonable yields, and this has not been possible using common salt metathesis reactions for alkaline earth derivatives.[7b]

The formation of SSIPs for Yb and Ca has been well established using both organic and inorganic counterions.[8b,9f,12,13] Their formation is proposed to occur due to the high oxophilicity of these elements in combination with the stability of the anionic ligands. Additional interactions between solvent and ligand molecules, as observed in **1** and **2**, may further enhance the stability of these complexes. In the case of Ba however, SSIPs are rarely observed, even in solution, due to the larger cation size and the lower oxophilicity of the metal.[19d] In the solid state the isolation of SSIPs is limited to multidentate ligands, such as tetraglyme or crown-ethers,[19a,c] or strongly coordinating solvents, such as HMPA.[19b] In our case, the ready formation of **5** in solution has been proven by NMR and IR studies, but the thf ligands are not sufficiently strong donors to stabilize the SSIP in the solid state. Bidentate or tridentate ligands, such as DME or diglyme, may provide the necessary stability.

The complete desolvation of solvent-separated ion pairs to the corresponding sandwich complexes has not been observed before, with partial desolvation being the most usual reaction outcome.[12a] One of the driving forces for the formation of **3**, **4**, and **6** may be the possibility of nonclassical C−H···C interactions. These interactions are also held partially responsible for the spontaneous reduction of the suggested trivalent $[Ln(Cp^{BIG})_2(o\text{-}$dimethylaminobenzyl)]$ species to the divalent $[Ln(Cp^{BIG})_2]$ (Ln = Yb, Sm) complexes.[8a]

Further confirmation of these intramolecular interactions was obtained from the MALDI-TOF MS spectra. As expected, these forces are much stronger in the case of the Yb and Ca complexes **3** and **4** than for the bigger Ba complex **6**. This result is consistent with the observation of the molecular ions in high intensities for **3** and **4**, whereas the corresponding ion is of low intensity in the case of **6**, where the mono-C_5Ph_5 species dominates. The formation of the Ba sandwich was surprising, as several unsuccessful synthetic pathways had been described to access this complex.[7b] The high thermal stability of this sandwich complex (mp >360 °C) is also in contrast to the observed degradation of $[Ba(C_5Ph_4H)_2(thf)]$ at room temperature.[7b] Again, the interplanar C−H bondings could contribute to this stability.

The failure to oxidize the divalent Yb species to Yb^{III} can also be related to these interactions, which make the metal center sterically inaccessible to attack. If the oxidizing power is sufficient, the ligand is oxidized to the radical; otherwise no reaction is observed. The reactivity is further influenced by the poor electron-donating nature of the C_5Ph_5 ligand, arising from the delocalization of the negative charge, which contributes to the stabilization of the divalent species and hence lowers its reactivity. The C_5Ph_5 ligand therefore appears very suitable for further investigation with the more reducing Sm^{II}, Tm^{II}, Dy^{II}, and Nd^{II}.

Conclusion

We have shown that the redox-transmetalation ligand-exchange reaction is a good alternative to salt metathesis reactions in the synthesis of pentaphenylcyclopentadienyl lanthanoid and alkaline earth complexes. The use of the homoleptic organomercurial $HgPh_2$ has allowed the synthesis of the SSIPs $[M(thf)_x][C_5Ph_5]_2$ (M = Yb, Ca, Ba), which can be fully desolvated to give the highly symmetric sandwich complexes $[M(C_5Ph_5)_2]$ (M = Yb, Ca, Ba). Attempts to oxidize the divalent ytterbium complexes have not led to the isolation of trivalent complexes due to the ease of oxidation of the pentaphenylcyclopentadienyl ligand. However, the utility of the ytterbium sandwich in the ligand-exchange reaction with $FeBr_2$ to yield the linkage isomer $[Fe(\eta^6\text{-}Ph(C_5Ph_4))(C_5Ph_5)]$ has been shown. Further work will concentrate on expanding this synthetic approach to other divalent lanthanoids and on examining the reactivity of these complexes.

Experimental Section

General Procedures. All manipulations were carried out under an inert atmosphere using standard Schlenk, vacuum line, and drybox techniques. Solvents were dried from the appropriate drying agent and degassed by distillation under nitrogen. Bulk ytterbium, calcium, and barium were freshly filed prior to use. $FeBr_2$ and diphenylmercury were purchased from Aldrich and used without further purification. The ligand C_5Ph_5H[20] and $[Yb(CC^tBu)_2]$[21] were prepared according to literature methods. Microanalyses were performed by the Campbell Microanalytical Laboratories, University of Otago, New Zealand, on samples sealed under argon. IR spectra are for Nujol mulls on NaCl plates using a Perkin-Elmer 1600 FTIR instrument. ^{1}H and ^{13}C NMR spectra were obtained using a Bruker DPX 300 MHz spectrometer. d_8-thf was dried and distilled from Na/K alloy under nitrogen prior to use. MALDI-TOF mass spectra

(17) Field, L. D.; Hambley, T. W.; Humphrey, P. A.; Masters, A. F.; Turner, P. *Inorg. Chem.* **2002**, *41*, 4618–4620.

(18) For example: (a) Cole, M. L.; Deacon, G. B.; Forsyth, C. M.; Junk, P. C.; Konstas, K.; Wang, J. *Chem.−Eur. J.* **2007**, *13*, 8092–8110. (b) Hitzbleck, J.; Deacon, G. B.; Ruhlandt-Senge, K. *Eur. J. Inorg. Chem.* **2007**, 592–601. (c) Deacon, G. B.; Fallon, G. D.; Forsyth, C. M.; Harris, S. C.; Junk, P. C.; Skelton, B. W.; White, A. H. *Dalton Trans.* **2006**, 802–812. (d) Deacon, G. B.; Forsyth, C. M.; Nickel, S. *J. Organomet. Chem.* **2002**, *647*, 50–60. (e) Deacon, G. B.; Forsyth, C. M.; Patalinghug, W. C.; White, A. H.; Dietrich, A.; Schumann, H. *Aust. J. Chem.* **1992**, *45*, 567–582.

(19) (a) Mishra, S.; Hubert-Pfalzgraf, L. G.; Jeanneau, E. *Polyhedron* **2007**, *26*, 66–72. (b) Teng, W.; Englich, U.; Ruhlandt-Senge, K. *Angew. Chem., Int. Ed.* **2003**, *42*, 3661–3664. (c) Pantenburg, I.; Hohn, F.; Tebbe, K.-F. *Z. Anorg. Allg. Chem.* **2002**, *628*, 383–388. (d) Drake, S. R.; Otway, D. J. *Polyhedron* **1992**, *11*, 745–758.

(20) Field, L. D.; Ho, K. M.; Lindall, C. M.; Masters, A. F.; Webb, A. G. *Aust. J. Chem.* **1990**, *39*, 281–291.

(21) Deacon, G. B.; Koplick, A. J.; Tuong, T. D. *Aust. J. Chem.* **1982**, *35*, 941–949.

were recorded on a Micromass-TOF Spec 2E spectrometer with a 337 nm dinitrogen UV laser. A continuous acceleration voltage of 20 kV was used in positive-ion mode.

General Procedure 1 for the Synthesis of SSIPs 1 and 2. A mixture of freshly filed metal (excess), C_5Ph_5H (2.0 equiv), and $HgPh_2$ (1.0 equiv) were combined in a 50 mL Schlenk flask, and thf (20 mL) was added via cannula. The reaction mixture was stirred at room temperature for 72 h, after which the solution was separated from remaining solids by filtration through Celite. The solvent was partly evaporated under vacuum and the solution allowed to stand at room temperature. The resulting crystalline product was isolated and dried under vacuum.

Synthesis of $[Yb(thf)_6][C_5Ph_5]_2$ (1). According to the general procedure 1, ytterbium metal (0.87 g, 5.00 mmol), C_5Ph_5H (0.893 g, 2.00 mmol), and $HgPh_2$ (0.355 g, 1.00 mmol) were reacted to give pale orange $[Yb(thf)_6][C_5Ph_5]_2$ in 53% yield (0.800 g, 0.53 mmol). ^1H NMR (300 MHz, d_8-thf): δ 7.01−6.78 (m, Ph−H), 3.62 (m, thf OCH_2CH$_2$), 1.76 (m, thf OCH$_2$CH_2). $^{13}C\{^1H\}$ NMR (75 MHz, d_8-thf): δ 143.4, 132.1, 126.1, 120.7 (all phenyl), 120.6 (C_5-ring), 67.5 (thf), 25.6 (thf). Anal. Calcd for $C_{94}H_{98}Yb$: C, 75.43; H, 6.60. Found: C, 73.68; H, 5.52. IR (Nujol, cm^{-1}): $\tilde{\nu}$ 1589vs, 1498vs, 1142m, 1072m, 1015s, 997w, 859m (br), 802m, 776s, 739m, 702vs.

Single crystals of **1** with the composition {[Yb(thf)$_6$][C$_5$-Ph$_5$]$_2$}$_2$·7(thf) suitable for X-ray diffraction studies were grown from a concentrated thf solution.

Synthesis of $[Ca(thf)_6][C_5Ph_5]_2$ (2). According to the general procedure 1, calcium metal (0.112 g, 2.79 mmol), C_5Ph_5H (0.500 g, 1.12 mmol), and $HgPh_2$ (0.200 g, 0.564 mmol) were reacted to give pure yellow $[Ca(thf)_6][C_5Ph_5]_2$ in 47% yield (0.366 g, 0.265 mmol). ^1H NMR (300 MHz, d_8-thf): δ 7.10−6.88 (m, Ph−H), 3.62 (m, thf OCH_2CH$_2$), 1.78 (m, thf OCH$_2$CH_2). $^{13}C\{^1H\}$ NMR (75 MHz, d_8-thf): δ 143.4, 132.2, 126.1, 120.7 (all phenyl), 120.6 (C_5-ring), 67.5 (thf), 25.7 (thf). Anal. Calcd for $C_{94}H_{98}Ca$: C, 82.78; H, 7.24. Found: C, 82.86; H, 6.90. IR (Nujol, cm^{-1}): $\tilde{\nu}$ 1588s, 1498vs, 1418w, 1172w, 1142m, 1071m, 1012m, 996w, 908w (br), 861m (br), 802w, 776m, 737m, 704s (sh), 700vs.

Single crystals of **2** with the composition {[Ca(thf)$_6$][C$_5$-Ph$_5$]$_2$}$_2$·2(thf)·(toluene) suitable for X-ray diffraction studies were grown from slow diffusion of toluene into a thf solution.

General Procedure 2 for the Synthesis of Metallocenes 3, 4, and 6. A mixture of freshly filed metal (excess), C_5Ph_5H (2.0 equiv), and $HgPh_2$ (1.0 equiv) were combined in a 50 mL Schlenk flask, and thf (20 mL) was added via cannula. The reaction mixture was stirred at room temperature for 72 h, after which the solution was separated from remaining solids by filtration through Celite. The solvent was evaporated under vacuum, and toluene was added onto the residue. Sonication of the solution led to the precipitation of the insoluble metallocenes, which were isolated by filtration or centrifugation.

Synthesis of $[Yb(C_5Ph_5)_2]$ (3). (a) According to the general procedure 2, ytterbium metal (0.870 g, 5.00 mmol), C_5Ph_5H (0.893 g, 2.00 mmol), and $HgPh_2$ (0.355 g, 1.00 mmol) were reacted to give pale green $[Yb(C_5Ph_5)_2]$ in 76% yield (0.806 g, 0.76 mmol). Addition of thf led to the conversion back to **1**. IR (Nujol, cm^{-1}): ν 1595m, 1501s, 1261m, 1076m, 1024m (br), 839vw, 800m, 777m, 738m, 700s. Anal. Calcd for $C_{70}H_{50}Yb$: C, 79.00; H, 4.74. Found: C, 77.13; H, 4.86. MALDI-TOF MS (*m/z* (%)): 2095.4 (13), 1683.9 (18, $[Yb_2(C_5Ph_5)_3]^+$), 1064.8 (80, $[Yb(C_5Ph_5)_2]^+$), 619.0 (55, $[Yb(C_5Ph_5)]^+$), 461.7 (33, $[C_5Ph_5 + O]^+$), 446.9 (100, $[C_5Ph_5H]^+$), 445.7 (100, $[C_5Ph_5]^+$), 368.6 (50, $[C_5Ph_4]^+$).

(b) $[Yb(CC^tBu)_2]$ (0.410 g, 1.20 mmol) and C_5Ph_5H (0.530 g, 1.20 mmol) were combined in a Schlenk tube, and toluene was introduced via cannula. The reaction mixture was heated without stirring at 65 °C for 20 h and filtered while hot, affording a small crop of dark green crystals of $[Yb(C_5Ph_5)_2]$, which showed the same MALDI-TOF MS spectrum as under (a) and which were suitable for X-ray diffraction studies

Synthesis of $[Ca(C_5Ph_5)_2]$ (4). According to the general procedure 2, calcium metal (0.056 g, 1.40 mmol), C_5Ph_5H (0.250 g, 0.56 mmol), and $HgPh_2$ (0.100 g, 0.28 mmol) were reacted to give off-white $[Ca(C_5Ph_5)_2]$ in 58% yield (0.150 g, 0.16 mmol). Addition of thf led to the conversion back to **2**. IR (Nujol, cm^{-1}): ν 1595m, 1501vs, 1260w, 1076m, 1024m, 801m, 778s, 738s, 707vs. Anal. Calcd for $C_{70}H_{50}Ca$: C, 90.28; H, 5.41. Found: C, 88.87; H, 5.65. MALDI-TOF MS (*m/z* (%)): 1415.1 (50, $[Ca_2(C_5Ph_5)_3]^+$), 1001.4 (20), 970.3 (19, $[Ca_2(C_5Ph_5)_2]^+$), 931.3 (100, $[Ca(C_5Ph_5)_2 + H]^+$), 930.2 (89, $[Ca(C_5Ph_5)_2]^+$), 485.3 (8, $[Ca(C_5Ph_5)]^+$), 461.3 (6, $[C_5Ph_5 + O]^+$), 446.3 (43, $[C_5Ph_5H]^+$), 445.3 (5, $[C_5Ph_5]^+$).

Synthesis of $[Ba(thf)_x][C_5Ph_5]_2$ (5) and $[Ba(C_5Ph_5)_2]$ (6). According to the general procedure 2, barium metal (0.192 g, 1.40 mmol), C_5Ph_5H (0.250 g, 0.56 mmol), and $HgPh_2$ (0.100 g, 0.28 mmol) were reacted to give white $[Ba(C_5Ph_5)_2]$ in 66% yield (0.184 g, 0.18 mmol). IR (Nujol, cm^{-1}): ν 1594s, 1501s, 1261m, 1076m, 1024m, 802m, 777m, 738m, 704s. Anal. Calcd for $C_{70}H_{50}Ba$: C, 81.74; H, 4.90. Found: C, 80.76; H, 5.02. MALDI-TOF MS (*m/z* (%)): 1611.3 (5, $[Ba_2(C_5Ph_5)_3]^+$), 1166.1 (5, $[Ba_2(C_5Ph_5)_2]^+$), 1028.2 (3, $[Ba(C_5Ph_5)_2]^+$), 583.1 (100, $[Ba(C_5Ph_5)]^+$), 507.0 (15, $[BaC_5Ph_4H]^+$), 446.3 (8, $[C_5Ph_5H]^+$), 445.3 (5, $[C_5Ph_5]^+$).

Single crystals of **6** suitable for X-ray diffraction studies were grown from slow diffusion of hexane into a thf-solution. Dissolving the sandwich complex **6** in d_8-thf or thf allowed the characterization of the SSIP $[Ba(thf)_x][C_5Ph_5]_2$ (**5**) by NMR and IR studies. ^1H NMR (300 MHz, d_8-thf): δ 6.98−6.74 (m, Ph−H), 3.62 (m, thf OCH_2CH$_2$), 1.78 (m, thf OCH$_2$CH_2). $^{13}C\{^1H\}$ NMR (75 MHz, d_8-thf): δ 141.5, 131.9, 126.6 (all phenyl), 122.1 (br, phenyl + C_5-ring). IR (thf solution, cm^{-1}): ν 1588s, 1498vs (other absorptions could not be observed due to the presence of strong thf absorptions).

Synthesis of $[Fe(\eta^6\text{-}Ph(C_5Ph_4))(C_5Ph_5)]$ (7). Anhydrous $FeBr_2$ (0.022 g, 0.10 mmol) was added to a suspension of $[Yb(C_5Ph_5)_2]$ (0.107 g, 0.10 mmol) in thf (10 mL), resulting in an immediate darkening of the solution. After stirring for 5 min, the resultant dark blue solution was filtered to remove an insoluble gray-black solid, and removal of solvent afforded a dark blue solid identified as the linkage isomer of decaphenylferrocene, $[Fe(\eta^6\text{-}Ph(C_5Ph_4))(C_5Ph_5)]$, in 98% yield (0.095 g, 0.098 mmol). The ^1H NMR data are in accordance with the literature.[17] $^{13}C\{^1H\}$ NMR (75 MHz, d_8-thf): δ 143.0, 133.5, 132.6, 132.2, 131.8, 130.7, 130.3, 129.0, 128.6, 128.3, 127.8, 127.6, 127.0, 124.3, 91.7. IR (Nujol, cm^{-1}): ν 1595w (br), 1261w, 1167w, 1155w, 1074m, 1028m (br), 966w (br), 932w, 916w, 889w, 800w, 770w, 696m. MALDI-TOF MS (*m/z* (%)): 1449.2 (20, $[Fe_2(C_5Ph_5)_3]^+$), 947.8 (100, $[Fe(C_5Ph_5)_2 + H]^+$), 946.7 (85, $[Fe(C_5Ph_5)_2]^+$), 501.4 (10, $[Fe(C_5Ph_5)]^+$), 461.3 (75, $[C_5Ph_5 + O]^+$), 446.4 (88, $[C_5Ph_5H]^+$), 445.3 (65, $[C_5Ph_5]^+$).

X-ray Diffraction Structure Determination. Crystals were mounted in an inert atmosphere under viscous oil onto a glass fiber. Low-temperature (123 K) data were collected on an Enraf-Nonius CCD diffractometer with Mo Kα radiation, λ 0.71073 Å, frames comprising 1.0° increments in ϕ or ω yielding a sphere of data. Each data set was empirically corrected for absorption using SORTAV,[22] then merged (R_{int} as quoted) to N unique reflections. The structures were solved by conventional methods and refined with anisotropic thermal parameter forms for the non-hydrogen atoms by full-matrix least-squares on all F^2 data using SHELX 97.[23] Hydrogen atoms were included in calculated positions and allowed to ride on the parent carbon atom. For {[Yb-(thf)$_6$][C$_5$Ph$_5$]$_2$}$_2$·7(thf), lattice thf molecules O(9), C(911−914), O(92), and C(921−924) were modeled as disordered. Each unique thf was partially occupied (set at 0.5 after trial refinement) and refined with a common thermal parameter, the symmetry-related molecule being the second disorder component of the other thf

(22) Blessing, R. H. *J. Appl. Crystallogr.* **1997**, *30*, 421–426.
(23) Sheldrick, G. M. *SHELXL-97*; University of Göttingen: Germany, 1997.

molecule. The molecule O(10), C(110−114) was modeled as disordered over a symmetry site.

Crystal Data. {[Yb(thf)$_6$][C$_5$Ph$_5$]$_2$}$_2$·7(thf) (**1**): C$_{216}$H$_{252}$O$_{19}$Yb$_2$ (3498.26), triclinic $P\bar{1}$, $a = 14.1148(2)$ Å, $b = 14.1430(2)$ Å, $c = 24.0136(6)$ Å, $\alpha = 79.845(1)°$, $\beta = 75.352(1)°$, $\gamma = 88.167(1)°$, $V = 4564.87(15)$ Å^3, D_{calcd} ($Z = 1$) 1.273 g cm^{-3}, $\mu_{Mo} = 1.08$ mm^{-1}, $T_{min,max}$ 0.70, 0.74, $N_{total} = 65\ 571$, $N = 50\ 345$ ($R_{int} = 0.097$), $R = 0.052$, $wR_2 = 0.100$ ($I > 2\sigma(I)$) ($R = 0.088$, $wR_2 = 0.113$ all data). GooF 1.014. Residual electron density max/min 1.03, 0.87 e Å^3.

{[Ca(thf)$_6$][C$_5$Ph$_5$]$_2$}$_2$·2(thf)·(toluene) (**2**): C$_{203}$H$_{220}$O$_{14}$Ca$_2$ (2968.10), triclinic $P\bar{1}$, $a = 14.1340(8)$ Å, $b = 14.5437(8)$ Å, $c = 21.2696(12)$ Å, $\alpha = 74.746(2)°$, $\beta = 82.574(2)°$, $\gamma = 86.212(2)°$, $V = 4180.43(15)$ Å^3.

[Yb(C$_5$Ph$_5$)$_2$] (**3**): C$_{70}$H$_{50}$Yb (1064.14), monoclinic $P2_1/n$, $a = 10.3460(2)$ Å, $b = 13.4649(3)$ Å, $c = 18.1324(4)$ Å, $\beta = 95.586(1)°$, $V = 2513.99(9)$ Å^3, D_{calcd} ($Z = 4$) 1.406 g cm^{-3}, $\mu_{Mo} = 1.904$ mm^{-1}, $T_{min,max}$ 0.60, 0.80, $N_{total} = 32\ 280$, $N = 5769$ ($R_{int} = 0.044$), $R = 0.030$, $wR_2 = 0.065$ ($I > 2\sigma(I)$) ($R = 0.062$, $wR_2 = 0.741$ all data). GooF 1.040. Residual electron density max/min 0.345, −0.789 e Å^3.

[Ba(C$_5$Ph$_5$)$_2$] (**6**): C$_{70}$H$_{50}$Ba (1028.44), monoclinic $P2_1/c$, $a = 13.0103(4)$ Å, $b = 13.7274(4)$ Å, $c = 17.9606(4)$ Å, $\beta = 128.559(2)°$, $V = 2508.37(21)$ Å^3, D_{calcd} ($Z = 2$) 1.362 g cm^{-3}, $\mu_{Mo} = 0.836$ mm^{-1}, $T_{min,max}$ 0.85, 0.95, $N_{total} = 32867$, $N = 5765$ ($R_{int} = 0.0661$), $R = 0.0365$, $wR_2 = 0.0740$ ($I > 2\sigma(I)$) ($R = 0.0662$, $wR_2 = 0.0836$ all data). GooF 1.011. Residual electron density max/min 0.39, −0.51 e Å^3.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-689373−689375. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int. code + 44(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk].

Supporting Information Available: CIF files giving crystallographic data for **1**, **3**, and **6** and a stick-and-ball drawing of **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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