# *Communications*

## A Half-Sandwich Perfluoroorganoytterbium(II) Complex from a Simple Redox Transmetalation/Ligand Exchange Synthesis

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*Summary: Reaction of ytterbium metal with HgPh($C_6F_5$) and $HC_5Me_5$ in THF (THF = tetrahydrofuran) affords seven-coordinate, monomeric [Yb($C_5Me_5$)($C_6F_5$)(THF)$_3$] (**1**), which is presumed to be formed by protolysis of a transitory "YbPh($C_6F_5$)" species with $HC_5Me_5$. In the absence of the latter, reaction of ytterbium metal and HgPh($C_6F_5$) gave a mixture of products, including the structurally characterized [Yb($C_6F_5$)$_2$(THF)$_4$] (**2**) and the ytterbium(III) complex [YbPh$_3$(THF)$_3$] (**3**).*

The organometallic chemistry of the lanthanoid elements in the less common II oxidation state is dominated by symmetrical LnR$_2$ species. In particular, those with $\pi$-bound carbocyclic $C_5R_5$ ligands have been extensively studied for their remarkable structures, redox chemistry, and Lewis acid behavior.[1] Much less is known of the half-sandwich complexes Ln($C_5R_5$)X (X = halide, organoamide, organooxide),[2] and there is only one example of a structurally characterized organometallic derivative, viz. [Eu($C_5Me_5$)($\mu$-CCPh)(THF)$_2$]$_2$.[3] By comparison with Ln($C_5Me_5$)$_2$ species, the presence of a Ln−C $\sigma$-bond in Ln($C_5Me_5$)R (R = alkyl, aryl) adds new dimensions to their potential reaction chemistry: e.g., small-molecule insertion and $\sigma$-bond metathesis. The latter has recently been exploited for analogous Ln-

(L)R (L = HB(3-Bu$^t$-5-Me-pz)$_3$), complexes,[4] stabilized by a very bulky tris(pyrazolyl)borate ligand. While metathetical precursors to Ln($C_5R_5$)R exist (e.g. [Ln($C_5$-Me$_5$)I(THF)$_2$]$_2$; Ln = Sm, Yb),[5,6] the synthesis of these potentially highly reactive species would benefit from a simple one-step route. We now report the successful synthesis and structure of the half-sandwich organoytterbium(II) complex [Yb($C_5Me_5$)($C_6F_5$)(THF)$_3$] by a new redox-transmetalation/ligand-exchange reaction.

Ytterbium powder reacted with a mixture of HgPh-($C_6F_5$) and $HC_5Me_5$ in THF at room temperature and gave red-orange [Yb($C_5Me_5$)($C_6F_5$)(THF)$_3$] (**1**) in moderate yield (eq 1).[7] Crystalline **1** was characterized by Yb

$$Yb + HgPh(C_6F_5) + HC_5Me_5 \xrightarrow{THF} \mathbf{1} + Hg + PhH \tag{1}$$
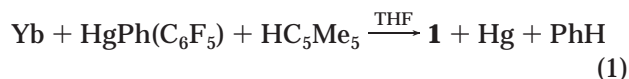
analysis, IR and NMR spectroscopy, and a single-crystal X-ray structure determination (see below). The presence of THF and the $C_6F_5$ groups was clearly evident in the IR spectrum of **1** ($\nu$(C−O) 1023, 875 cm$^{-1}$; $\nu$(C−F) 1072, 924 cm$^{-1}$), while the $^{19}$F NMR spectrum showed resonances apparently attributable to a single $C_6F_5$ environment but with a slight asymmetry of the $o$-F resonance

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(5) Evans, W. J.; Grate, J. W.; Choi, H. W.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 941.

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**Table 1. $^{171}$Yb NMR Data for Yb(II) Aryl and Iodide Complexes**

| compd | CN | $\delta(^{171}Yb)$ (ppm) | ref |
|---|---|---|---|
| $[Yb(C_5Me_5)_2(THF)_2]$ | 8 | 0 | 10 |
| $[Yb(C_5Me_5)(C_6F_5)(THF)_3]$ | 7 | 254 | this work |
| $[Yb(C_5Me_5)(I)(THF)_2]_2$ | 7 | 250 | 6 |
| $[Yb(C_6F_5)_2(THF)_4]$ | 6 | 463 | this work |
| $[Yb(I)_2(THF)_4]$ | 6 | 456 | 6 |
| $[Yb(Dpp)(I)(THF)_3]^a$ | 5 | 667 | 23 |
| $[Yb(Dpp)_2(THF)_2]$ | 4 | 927 | 23 |

$^a$ Dpp = 2,6-$Ph_2C_6H_3$.

at high resolution (see below). The chemical shift values are almost identical with those reported for $Yb(C_6F_5)_2$ in THF.[9] The $^{171}$Yb NMR data were particularly diagnostic, with the chemical shift of **1** in THF lying between those of $Yb(C_5Me_5)_2$[10] and $Yb(C_6F_5)_2$ (Table 1). Indeed, the value is very similar to that of the analogous organoytterbium(II) iodide species[6] (Table 1), consistent with the pseudo-halide nature of $C_6F_5^-$. THF solutions of **1** were stable for approximately 24 h at room temperature, and the isolated product could be stored for several weeks at $-20$ °C. However, in nonpolar solvents, rapid decomposition of **1** was observed, precluding workup and spectroscopic measurements in these media. Decomposition was accompanied by the formation of complex fluoroaromatic species (as detected by $^{19}$F NMR) and suggests fluoride abstraction by the ytterbium(II) center as the dominant pathway, similar to that proposed for $Yb(C_6F_5)_2$.[9,11]

The structure[12] of **1** is shown in Figure 1, and pertinent bond distances and angles are listed in Table 2. The complex is monomeric, with the ytterbium atom bound to a $\eta^5$-$C_5Me_5$ group, $C_6F_5$, and three coordinated THF ligands. This arrangement is in contrast with that in dimeric $[Ln(C_5Me_5)(\mu\text{-}I)(THF)_2]_2$ (Ln = Sm,[5] Yb[6]) and $[Eu(C_5Me_5)(\mu\text{-}CCPh)(THF)_2]_2$[3] and may reflect the poorer bridging capacity of the $C_6F_5$ anion, owing to delocalization of electron density from the ipso carbon by the inductively electron-withdrawing fluorine substituents.

(7) **1**: a mixture of Yb metal filings (1.4 g, 8.0 mmol), HgPh($C_6F_5$)[8] (2.2 g, 5.0 mmol), and $HC_5Me_5$ (0.68 g, 5.0 mmol) was stirred in THF (60 mL) at room temperature for 6 h. After filtration and reduction of the volume to 10 mL, the red-orange solution was treated with hexanes (30 mL) and cooled to $-20$ °C. Red-orange crystals of **1** deposited overnight (1.41 g, 41%). IR (Nujol): 1628 w, 1595 w, 1494 m (sh), 1416 s, 1297 w, 1222 w, 1173 w, 1072 m, 1039 vs, 1023 vs, 924 s, 875 m cm$^{-1}$. $^1$H NMR (THF-$d_8$): $\delta$ 1.96 (s, 15H, $C_5Me_5$). $^{19}$F NMR (THF-$d_8$): $-109.8$ (m, 2F, F2, 6), $-162.4$ (m, 2F, F3,5), $-162.9$ (m, 1F, F4). Anal. Calcd for $C_{28}H_{39}F_5O_3Yb$: Yb, 24.9. Found: Yb, 25.1. Solid **1** decomposed to an intractable black material after 1–2 days at room temperature but could be stored at $-20$ °C for several weeks without significant deterioration.

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(11) Deacon, G. B.; Koplick, A. J.; Raverty, W. D.; Vince, D. G. *J. Organomet. Chem.* **1979**, *182*, 121.

(12) Data were collected on an Enraf-Nonius CCD diffractometer ($\lambda = 0.710\,73$ Å) at 123 K. Crystal data for $C_{28}H_{39}F_5O_3Yb$ (**1**): $M_r = 691.63$, monoclinic, space group $P2_1/n$, with cell dimensions $a = 9.1980(2)$ Å, $b = 25.2911(5)$ Å, $c = 12.3206(3)$ Å, $\beta = 95.052(1)°$ and $V = 2855(1)$ Å$^3$ with $D_{calcd} = 1.609$ g/cm$^3$ ($Z = 4$). $R = 4.29\%$ and $R_w = 8.47\%$ (4419 data with $I > 2\sigma(I)$); $R = 9.26\%$ and $R_w = 9.58\%$ for all data). The structure was solved by conventional heavy-atom methods and refined by full-matrix least squares on $F^2$ (29 095 total and 6998 unique data, $R_{int} = 9.3\%$) with anisotropic thermal parameters for the non-hydrogen atoms. Hydrogen atoms were placed in calculated positions using a riding model.
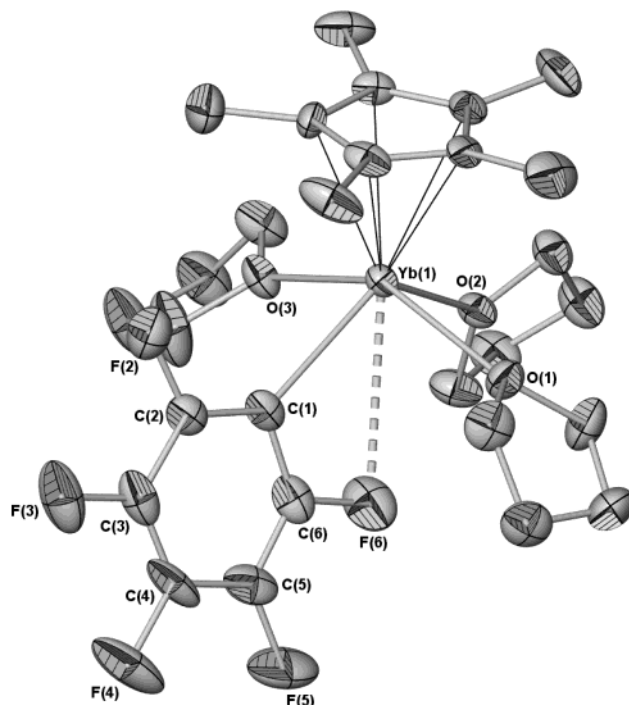


**Figure 1.** Molecular structure of $[Yb(C_5Me_5)(C_6F_5)(THF)_3]$ (**1**) with 50% thermal ellipsoids and hydrogen atoms omitted for clarity.

**Table 2. Selected Bond Distances (Å) and Angles (deg) for $[Yb(C_5Me_5)(C_6F_5)(THF)_3]$**

| | | | |
|---|---|---|---|
| Yb(1)−C(7) | 2.694(5) | Yb(1)−C(1) | 2.597(5) |
| Yb(1)−C(8) | 2.664(5) | Yb(1)−O(1) | 2.456(4) |
| Yb(1)−C(9) | 2.699(5) | Yb(1)−O(2) | 2.445(3) |
| Yb(1)−C(10) | 2.744(5) | Yb(1)−O(3) | 2.489(4) |
| Yb(1)−C(11) | 2.744(5) | Yb(1)−Cp | 2.430 |
| | | Yb(1)···F(6) | 3.162(4) |
| | | | |
| O(1)−Yb(1)−Cp$^a$ | 104.6 | O(1)−Yb(1)−O(2) | 82.7(1) |
| O(2)−Yb(1)−Cp | 117.6 | O(1)−Yb(1)−O(3) | 143.9(1) |
| O(3)−Yb(1)−Cp | 111.3 | O(2)−Yb(1)−O(3) | 77.2(1) |
| C(1)−Yb(1)−Cp | 122.3 | Cp−Yb(1)···F(6) | 161.8 |
| C(1)−Yb(1)−O(1) | 84.3(1) | Yb(1)−C(1)−C(2) | 137.5(4) |
| C(1)−Yb(1)−O(2) | 120.1(2) | Yb(1)−C(1)−C(6) | 109.9(4) |
| C(1)−Yb(1)−O(3) | 80.4(1) | | |

$^a$ Cp = calculated centroid of C(7)−C(11).

Both the iodide and phenylethynyl complexes have the same coordination number as **1**, whereas analogous half-sandwich complexes $[Yb(C_5Me_5)(L)(THF)_2]$ (L = $Si(SiMe_3)_3$, $N(SiMe_3)_2$) with very bulky trimethysilyl-substituted ligands are monomeric but six-coordinate.[13,14] The geometry around the Yb atom in **1** can be described as a pseudo-square-based pyramid with the centroid of the $C_5Me_5$ ring occupying the axial position. The range of $\pi$-Yb−C($C_5Me_5$) distances is comparable with that of $[Yb(C_5Me_5)(\mu\text{-}I)(THF)_2]_2$ (2.664(5)−2.744(5) Å).[6] However, the $\sigma$-Yb−C($C_6F_5$) bond (Table 2) is significantly shorter (0.225 Å) than that (2.822(3) Å) of the only earlier crystallographically characterized Ln−$C_6F_5$ complex, $[Eu(C_6F_5)_2(THF)_5]$,[15] and the difference is almost twice that between the respective ionic radii (ca. 0.12 Å).[16] This suggests a degree of steric

(13) Corradi, M. M.; Frankland, A. D.; Hitchcock, P. B.; Lappert, M. F.; Lawless, G. A. *Chem. Commun.* **1996**, 2323.
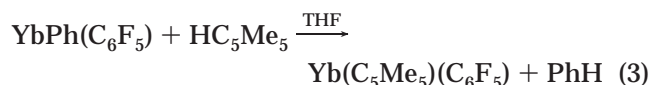
(14) Evans, W. J.; Johnston, M. A.; Clark, R. D.; Anwander, R.; Ziller, J. W. *Polyhedron* **2001**, *20*, 2483.

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(16) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *32*, 751.

unsaturation in **1**. The plane of the $C_6F_5$ group is approximately perpendicular to that of the $C_5Me_5$ ring carbon atoms (interplanar angle 72.6(2)°), and this arrangement places one of the *o*-F substituents, F(6), in a hole in the coordination sphere below the basal plane (Cp−Yb(1)···F(6) = 161.8°). While the Yb(1)···F(6) separation (3.162(4) Å) is long compared with reported dative $Ln^{III}$···F interactions of ∼2.55−2.90 Å[17] (cf. $Eu^{II}$···F = 3.006(6) Å in $[Eu(\mu\text{-}SC_6F_5)_2(THF)_2]_n$[17b]), the fact that the Yb(1)−C(1)−C(6) angle is considerably more acute than Yb(1)−C(1)−C(2) (Table 2) suggests at least a weak contact. However, the positioning of the $C_6F_5$ group is presumably also influenced by competitive ligand−ligand repulsions (i.e. $C_6F_5$−THF vs $C_6F_5$−$C_5$-$Me_5$). In any case, the location of F(6) would block the coordination of a further THF ligand to the ytterbium center. There is evidence that some Yb···*o*-F bonding persists in solution. Variable-temperature (+30 to −60 °C) $^{19}F$ NMR spectroscopy resolves two *o*-F resonances (108.9 and 109.6 ppm; integration 3F:1F) at 15 °C, representing resolution of the asymmetry in the room-temperature spectrum. We suggest that there are approximately equimolar amounts of two species, one with the solid-state structure and one with uncoordinated (freely rotating) $C_6F_5$ (possibly as a result of further THF coordination). There is no splitting or asymmetry of the other $^{19}F$ resonances on cooling, and similarly, the $^1H$ methyl ($C_5Me_5$) and $^{171}Yb$ resonances are narrow and symmetrical; hence, the two species present must be very similar in structure, consistent with the very small separation of the two *o*-F resonances.

The formation of **1** from eq 1 is consistent with previous observations that $HC_5Me_5$ does *not* exchange with $Yb(C_6F_5)_2$ but successfully displaces Ph, giving [Yb-$(C_5Me_5)_2(THF)_2$] in reactions with $Yb/HgPh_2$ (presumably initially yielding $YbPh_2$).[18] The $pK_a$ value (calculated for THF[19a] from refs 19b,c) of $HC_5Me_5$ (26.2) is similar to that of $C_6F_5H$ (25.6) but much lower than for PhH (42.5), favoring exchange with Yb−Ph but not Yb−$C_6F_5$ moieties. This supports the proposal that the initial product from eq 1 is the unsymmetrical $Yb^{II}$ diaryl species $YbPh(C_6F_5)$ (eq 2), which then undergoes preferential protolytic ligand exchange (eq 3). In an attempt

$$Yb + HgPh(C_6F_5) \xrightarrow{THF} \text{``}YbPh(C_6F_5)\text{''} + Hg \quad (2)$$

$$YbPh(C_6F_5) + HC_5Me_5 \xrightarrow{THF}$$
$$Yb(C_5Me_5)(C_6F_5) + PhH \quad (3)$$

to isolate (as a THF complex) or characterize $YbPh$-$(C_6F_5)$, the reaction of Yb powder with $HgPh(C_6F_5)$ in THF at room temperature in the absence of $HC_5Me_5$ was studied.[20] This gave a brown-orange solution, and the $^{19}F$ NMR spectrum showed a single $C_6F_5$ environment, very similar to the spectra of both **1** and $[Yb(C_6F_5)_2$-
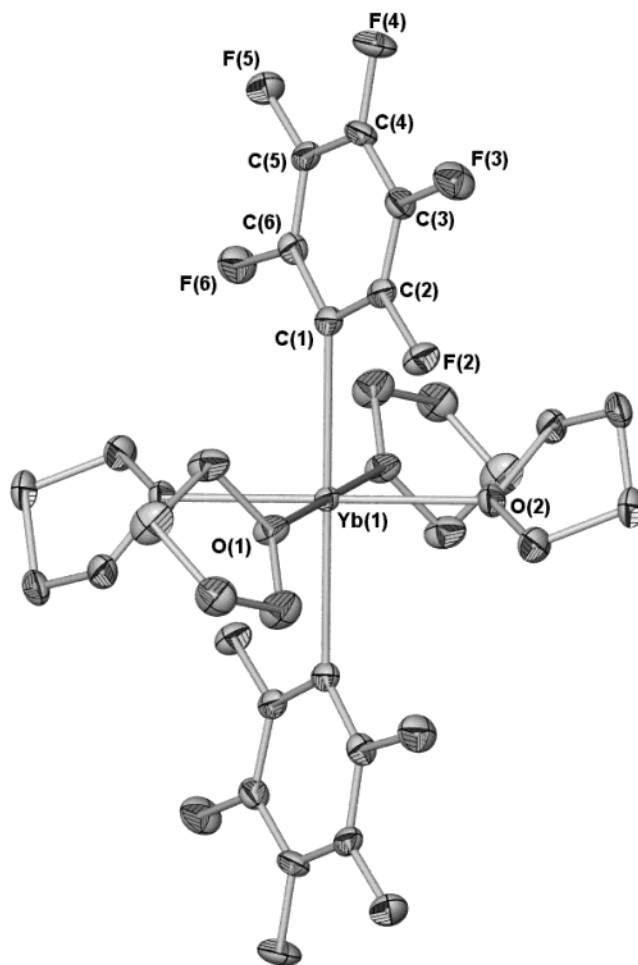


**Figure 2.** Molecular structure of $[Yb(C_6F_5)_2(THF)_4]$ (**2**) with 50% thermal ellipsoids and hydrogen atoms omitted for clarity.

$(THF)_4$].[9] More significantly, only one $^{171}Yb$ NMR resonance ($\delta$ 459 ppm) was observed between −100 and +1300 ppm and the chemical shift value was close to that of $[Yb(C_6F_5)_2(THF)_4]$ (Table 1). An attempted crystallization of the putative "$YbPh(C_6F_5)$" complex by cooling a concentrated THF/hexanes solution to −20 °C gave an unidentified dark brown powder mixed with orange crystals, which were shown to be $[Yb(C_6F_5)_2$-$(THF)_4]$ (**2**) (Figure 2) by X-ray crystallography (see below). However, crystallization from THF only deposited a small amount of yellow crystals of the $Yb^{III}$ complex *fac*-$[YbPh_3(THF)_3]$ (**3**).[20] The X-ray structure[21] of **3** shows that it has the same structure as the previously reported Tm and Er analogues.[22] While the presence of **3** would be undetected by the NMR experiments above owing to paramagnetism, its isolation and

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(20) A mixture of Yb metal (1.4 g, 8.0 mmol) and $HgPh(C_6F_5)$ (2.22 g, 5.0 mmol) was stirred in THF (60 mL) at room temperature for 6 h. After filtration, a portion (∼2−3 mL) of the brown-orange solution was removed and examined by $^{19}F$ and $^{171}Yb$ NMR spectroscopy. The remaining solution was concentrated and hexanes added. Cooling to −20 °C overnight deposited orange crystals of **2**, some of which were hand-picked for crystallographic examination, mixed with a tacky brown powder. From a separate preparation, the initial filtrate was concentrated and cooled to −20 °C. Bright yellow crystals of **3** deposited after several days (0.13 g, 13%). IR (Nujol): 3031 w, 1560 w, 1410 m, 1226 m, 1188 w, 1051 m, 1020 s, 987 w, 914 w, 867 s br, 718 m, 706 s, 673 w, 630 m cm$^{-1}$. The sample partly decomposed during weighing for microanalysis. Anal. Calcd for $C_{30}H_{39}O_3Yb$: C, 58.1; H, 6.3. Found: C, 55.5; H, 6.1.

**Table 3. Selected Bond Distances (Å) and Angles (deg) for [Yb(C$_6$F$_5$)$_2$(THF)$_4$]$^a$**

| | | | |
|---|---|---|---|
| Yb(1)−C(1) | 2.649(3) | Yb(1)−O(1) | 2.428(2) |
| Yb(1)−O(2) | 2.440(2) | | |
| | | | |
| C(1)−Yb(1)−C(1$^i$) | 180.0 | O(1)−Yb(1)−O(2) | 98.44(8) |
| C(1)−Yb(1)−O(1) | 88.6(1) | O(1)−Yb(1)−O(1$^i$) | 180.0 |
| C(1)−Yb(1)−O(1$^i$) | 91.4(1) | O(1)−Yb(1)−O(2$^i$) | 81.56(8) |
| C(1)−Yb(1)−O(2) | 87.54(9) | O(2)−Yb(1)−O(2$^i$) | 180.0 |
| C(1)−Yb(1)−O(2$^i$) | 92.46(9) | | |

$^a$ Symmetry transformation: (i) $-x + 1$, $-y + 1$, $-z + 1$.

that of **2** confirm the occurrence of a ligand redistribution process (eq 4) similar to that observed for the bulky

$$\text{YbPh(C}_6\text{F}_5) \xrightarrow{\text{THF}} \text{YbPh}_2 + \text{Yb(C}_6\text{F}_5)_2 \qquad (4)$$
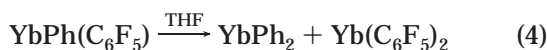
Yb$^{II}$ aryl halides [Yb(Dpp)I(THF)$_3$] (Dpp = 2,6-Ph$_2$C$_6$H$_3$).[23] However, in the presence of HC$_5$Me$_5$, rapid ligand exchange with the transitory YbPh(C$_6$F$_5$) species (eq 3) enables the isolation of **1**. The failure to observe YbPh$_2$ by $^{171}$Yb NMR and the subsequent isolation of trivalent **3** suggests rapid oxidation of the YbPh$_2$ complex, and it is noteworthy that a well-defined YbPh$_2$ complex has not yet been isolated (cf. mixed-valent [Yb$^{III}$Ph$_2$(THF)($\mu$-Ph)$_3$Yb$^{II}$(THF)$_3$][24]).

Despite being been known for more than 20 years,[9] **2** is one of a very limited class of divalent organolanthanoids devoid of cyclopentadienyl ligands and we have now determined its molecular structure (Figure 2) for the first time,[21] only the third structure of a Ln$^{II}$ diaryl.[15,23] Many previous attempts to collect X-ray data for **2** were thwarted by very poor diffraction (due to extensive twinning) of visually excellent crystals, compounded by the extreme air and thermal instability of the sample. Selected bond distances and angles for **2** are listed in Table 3. Monomeric **2** has a six-coordinate Yb surrounded by two *trans*-C$_6$F$_5$ ligands with four equatorial THF ligands completing an octahedral coordination geometry, analogous to that of [YbI$_2$(THF)$_4$][25] as predicted earlier.[15] Intriguingly, the two C$_6$F$_5$ groups are coplanar, whereas in [Eu(C$_6$F$_5$)$_2$(THF)$_5$] the trans

C$_6$F$_5$ groups are rotated ~65° to each other,[15] and presumably C$_6$F$_5$−THF repulsions are the dominant influence. The Ln−$\sigma$-C distances of **2** (Table 3) and the larger Eu analogue [Eu(C$_6$F$_5$)$_2$(THF)$_5$] (2.822(3) Å)[15] are comparable, after accounting for the difference in the appropriate ionic radii (0.18 Å),[16] but the value for **2** is greater (ca. 0.1 Å) than that of **1** above. In contrast, estimations of steric crowding in **1**, **2**, and [Eu(C$_6$F$_5$)$_2$-(THF)$_5$] from comparison of ligand steric coordination number[26] summations (7.4 for **1**, 7.4 for **2**, and 8.6 for [Eu(C$_6$F$_5$)$_2$(THF)$_5$], assuming C$_6$F$_5$ ≈ Ph in bulkiness) suggest that the Ln−C bond lengths of **1** and **2** should be similar, with that of [Eu(C$_6$F$_5$)$_2$(THF)$_5$] much longer. Thus, the Ln−C bonding in **2** and [Eu(C$_6$F$_5$)$_2$(THF)$_5$] appear influenced largely by the trans disposition of the C$_6$F$_5$ anions, which may exhibit a repulsive trans influence (see ref 27 for trans influences in lanthanoid complexes).

In this contribution we have demonstrated that the unique, half-sandwich perfluoroaryl−ytterbium(II) complex [Yb(C$_5$Me$_5$)(C$_6$F$_5$)(THF)$_3$] (**1**) can be successfully synthesized in one step from Yb metal, HgPh(C$_6$F$_5$), and HC$_5$Me$_5$. Analogous metal-based syntheses provide competitive, halide- and alkali-metal-free, preparative routes to a wide variety of Ln(L)$_n$ ($n$ = 2, 3) compounds,[18,28] but this is the first application leading to a complex with disparate ligands. The simplicity of the reaction and ready availability of unsymmetrical HgPhR compounds[29] potentially make this a highly versatile and attractive synthetic method. Extrapolation to a wide range of novel organolanthanoid(II) complexes is envisaged. The reactivity of **1** toward both oxidative and protolytic substrates is currently under investigation. Two new structures of lanthanoid−fluorocarbon complexes add to the understanding of the nature of polyfluorophenyl−lanthanoid bonding, as there is only one such previous structure,[15] and **1** has the first organometallic lanthanoid agostic F interaction.

**Supporting Information Available:** X-ray crystallographic data for [Yb(C$_5$Me$_5$)(C$_6$F$_5$)(THF)$_3$], [Yb(C$_6$F$_5$)$_2$(THF)$_4$], and [YbPh$_3$(THF)$_3$]. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data have also been deposited with the Cambridge Crystallographic Data Centre. Copies of this information may be obtained free of charge from the CCDC, 12 Union Rd, Cambridge CB2 1EZ, U.K. (fax +44 1223 336033; e-mail, deposit@cam.ac.uk or http://www.ccdc.cam.ac.uk).

(21) Data were collected on an Enraf-Nonius CCD diffractometer ($\lambda$ = 0.710 73 Å) at 123 K. Crystal data for C$_{28}$H$_{32}$F$_{10}$O$_4$Yb (**2**): $M_r$ = 795.58, monoclinic, space group $P2_1/c$, with cell dimensions $a$ = 9.3175-(2) Å, $b$ = 18.9505(3) Å, $c$ = 8.3634(1) Å, $\beta$ = 98.151(1)°, and $V$ = 1461.8-(5) Å$^3$ with $D_{calcd}$ = 1.807 g/cm$^3$ ($Z$ = 2). $R$ = 2.48% and $R_w$ = 5.65% (2543 data with $I > 2\sigma(I)$; $R$ = 5.19% and $R_w$ = 6.28% for all data). Crystal data for C$_{30}$H$_{39}$O$_3$Yb (**3**): $M_r$ = 620.65, monoclinic, space group $C2/c$, with cell dimensions $a$ = 36.0443(8) Å, $b$ = 11.1995(2) Å, $c$ = 13.9736(3) Å, $\beta$ = −103.369(2)°, and $V$ = 5510(1) Å$^3$ with $D_{calcd}$ = 1.496 g/cm$^3$ ($Z$ = 8). $R$ = 4.40% and $R_w$ = 7.51% (4469 data with $I > 2\sigma(I)$; $R$ = 9.21% and $R_w$ = 8.63% for all data). The structures were solved by conventional heavy-atom methods and refined by full-matrix least squares on $F^2$ (**2**, 18 486 total and 3534 unique data, $R_{int}$ = 5.0%; **3**, 32 605 total and 6714 unique data, $R_{int}$ = 12.6%) with anisotropic thermal parameters for the non-hydrogen atoms. Hydrogen atoms were placed in calculated positions using a riding model.
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