

Experimental

The compounds described herein are extremely air- and moisture-sensitive and they were prepared and handled using conventional glove box and Schlenk line techniques under an atmosphere of purified nitrogen or argon. IR spectra were recorded as Nujol mulls between NaCl plates using either a Perkin Elmer Spectrum RX 1 FTIR Spectrometer or an Agilent Technologies Cary 630 FTIR instrument over the range 4000–650 cm^{-1} . Multinuclear NMR spectra were recorded on a Bruker DPX 300 spectrometer or on a 500 MHz Bruker Avance III spectrometer equipped with a BBFO+ probe. Chemical shifts were referenced to the residual ^1H resonances of the deuterated solvents (^1H), external CCl_3F (^{19}F) or external $[\text{Yb}(\text{Cp}^*)_2(\text{thf})_2]$ (0.16 M, $\text{thf}/\text{C}_6\text{D}_6$, 9/1 (v/v), ^{171}Yb , $\delta = 0$).¹ Melting points were determined in sealed glass capillaries under nitrogen and are not calibrated. Microanalyses were determined by the elemental analysis service at the Université de Reims, Reims, France. High resolution ESI-MS spectra were recorded on a hybrid tandem quadrupole/time-of-flight (Q-TOF) instrument, equipped with a pneumatically assisted electrospray (Z-spray) ion source (Micromass, Manchester, UK) operated in positive mode. GC-MS experiments were performed on a Thermoquest Trace GC 2000 Series/Finnigan Trace MS machine. Hexane and thf were pre-dried over sodium metal and distilled over sodium benzophenone ketyl (solubilised with tetraglyme in the still used for hexane) before being stored under an atmosphere of nitrogen. Toluene and C_6D_6 were pre-dried over sodium and then distilled under nitrogen from sodium metal before being stored under an atmosphere of nitrogen. Ytterbium metal was stored under nitrogen in a glove box. HgPh_2 was used as received from Alfa Inorganic Chemicals. $\text{Hg}(\text{C}_6\text{F}_5)_2$ ² and $\text{C}_5\text{Ph}_4\text{H}_2$ ³ were synthesised by literature methods.

*Synthesis of $[\text{Yb}(\text{C}_5\text{Ph}_4\text{H})(\mu\text{-F})(\text{thf})_2]_2$ (**1**)*

Method 1

Thf (10 mL) was added to a Schlenk flask charged with ytterbium pieces (0.50 g, 2.9 mmol), $\text{Hg}(\text{C}_6\text{F}_5)_2$ (0.24 g, 0.45 mmol) and $\text{C}_5\text{Ph}_4\text{H}_2$ (0.33 g, 0.88 mmol) and the suspension was placed in an ultrasonic bath for three days giving a dark orange solution. The solution was filtered and then concentrated under vacuum. After overnight storage at $-30\text{ }^\circ\text{C}$, a few orange single crystals of **1** deposited. Complex **2** was also detected by ^{171}Yb NMR spectroscopy.

Method 2

Thf (3 mL) was added to a Schlenk flask charged with ytterbium filings (0.025 g, 0.14 mmol), $\text{Hg}(\text{C}_6\text{F}_5)_2$ (0.072 g, 0.13 mmol) and $\text{C}_3\text{Ph}_4\text{H}_2$ (0.10 g, 0.26 mmol) and the suspension was stirred for two days at room temperature giving an orange/brown solution. Further ytterbium filings (0.045 g, 0.26 mmol) were added and stirring was continued for another four days leading to a dark red solution. The reaction mixture was centrifuged and the solution was concentrated under vacuum. After overnight storage at room temperature, orange crystals of **1** deposited (0.080 g, 0.11 mmol, 44 %). M.p. > 330°C (decomp.); IR (Nujol, cm^{-1}): 1595s, 1510sh, 1505sh, 1495s, 1260m, 1071s, 1028s, 911w, 873w, 792m, 754s, 733w, 720w, 697s, 668m, 659w; ^1H NMR (thf- d_8 , 500 MHz, 298 K): δ 7.34 (m, 8H, H_{ortho}), 7.16 (m, 8H, H_{ortho}), 7.05 (m, 8H, H_{meta}), 6.93 (m, 4H, H_{para}), 6.90 (m, 12H, $\text{H}_{\text{meta}}+\text{H}_{\text{para}}$), 6.51 (s, 2H, H_{Cp}); $^{13}\text{C}\{^1\text{H}\}$ NMR (thf- d_8 , 125 MHz, 298 K): δ 140.10 (C_{ring}), 139.39 (C_{ring}), 131.6 (C_{ortho}), 127.39 (C_{ortho}), 127.15 (C_{meta}), 126.69 (C_{meta}), 123.57 (C_{para}), 122.81 (C_{para}), 122.16 (C_{ipso}), 121.48 (C_{ipso}), 106.66 (C_{ring}); $^{19}\text{F}\{^1\text{H}\}$ NMR (C_6D_6 , 282.4 MHz, 303 K): δ -81.82 (s, 2F; ^{171}Yb satellites at -81.03 and -82.62 ppm, $^1J_{\text{Yb,F}} = 449$ Hz); ^{171}Yb NMR (thf/ C_6D_6 , 9/1 (v/v), 52.5 MHz, 298 K): δ 376 (t, $^1J_{\text{Yb,F}} = 449$ Hz, 2Yb); HRMS (ESI-MS) m/z calculated for $\text{C}_{58}\text{H}_{42}\text{F}_2^{174}\text{Yb}_2$ (loss of four thf molecules) $[\text{M}]^+$ 1124.2032; found 1124.2034; elemental analysis calculated (%) for $\text{C}_{74}\text{H}_{74}\text{F}_2\text{O}_4\text{Yb}_2$ (1411.51): C 62.97, H 5.28; found C 61.61, H 5.26.

Method 3

The sandwich complex **2** was synthesised as described below and then an excess of $\text{C}_6\text{F}_5\text{H}$ was added to the reaction mixture. After stirring for several days at room temperature a $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of the crude reaction mixture showed the presence of **1** and $\text{C}_6\text{F}_4\text{H}_2$ -*p*.

Method 4

Freshly filed ytterbium metal (2 mmol), $\text{C}_6\text{F}_5\text{H}$ (1 mmol) and a small amount of I_2 were stirred in a mixture of thf/ d_8 -thf. After four hours, $\text{C}_6\text{F}_4\text{H}_2$ -*p* and $\text{Yb}(\text{C}_6\text{F}_5)_2$ were detected in the $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum. After 24 hours, the amounts of both products had increased with a concomitant decrease in the amount of $\text{C}_6\text{F}_5\text{H}$ and the formation of a dark solid. The orange solution was decanted and the solid was washed once with thf. A solution of

[Yb(C₅Ph₄H)₂(thf)] (**2**) in thf was then added and the mixture was stirred for 24 hours. The formation of **1** was evident in the ¹H and ¹⁹F{¹H} NMR spectra.

*Synthesis of [Yb(C₅Ph₄H)₂(thf)] (**2**)*

Thf (15 mL) was added to a Schlenk flask charged with ytterbium pieces (0.36 g, 2.1 mmol), HgPh₂ (0.16 g, 0.45 mmol) and C₅Ph₄H₂ (0.34 g, 0.92 mmol) and the suspension was stirred for three days giving a dark orange/brown solution. The solution was filtered into another Schlenk flask and the solvent was removed under vacuum. Hot toluene was added onto the residue and after concentration under vacuum, dark orange blocks of **2** crystallised. The filtrate was concentrated further yielding another crop of crystals (combined yield: 0.29 g, 65 %). M.p. 258–260 °C; IR (Nujol, cm⁻¹): 1594s, 1574sh, 1509m, 1495s, 1261w, 1197w, 1155vw, 1072m, 1014m, 927w, 909w, 863s, 841w, 803w, 789m, 758vs, 697vs, 661vw, 635w, 616vw; ¹H NMR (C₆D₆, 300 MHz, 303 K): δ 7.34–7.37 (overlapping signals, 8H, H_{ortho}), 6.88–7.24 (overlapping signals, 32H; H_{meta}+H_{para}), 6.69 (s, 2H, H_{Cp}), 3.13 (br s, 4H; α-H C₄H₈O), 1.11 (br m, 4H; β-H C₄H₈O); ¹³C{¹H} NMR (C₆D₆, 300 MHz, 303 K): δ 138.87 (C_{ring}), 138.66 (C_{ring}), 132.36 (C_{ortho}), 129.71 (C_{ortho}), 126.06 (C_{para}), 125.87 (C_{para}), 125.48 (C_{ipso}), 124.60 (C_{ipso}), 111.86 (C_{ring}), the C_{meta} carbon atoms are obscured by the C₆D₆ peaks; ¹⁷¹Yb NMR (thf/C₆D₆, 9/1 (v/v), 52.5 MHz, 298 K): δ 116 (s); elemental analysis calcd (%) for C₆₂H₅₀OYb (984.11): C 75.67, H 5.12; found: C 74.92, H 5.12.

*Synthesis of [Yb(C₅Ph₄H)(C₆F₅)(thf)₂] (**3**)*

Thf (10 mL) was added to a Schlenk flask charged with freshly filed ytterbium metal (0.19 g, 1.1 mmol), Hg(C₆F₅)₂ (0.16 g, 0.30 mmol), C₅Ph₄H₂ (0.11 g, 0.30 mmol) and one drop of mercury for activation. The suspension was stirred for about four hours giving a dark orange solution. The solution was filtered into another Schlenk flask and was then concentrated under vacuum until it was an oily liquid. Hexane (10 mL) was added precipitating a dark orange solid. The hexane was decanted and the solid was dried under vacuum to yield dark orange **3** (0.22 g, 87 %). CD₃CN (0.7 mL) was added to a small amount of the dried sample and then a few drops of trifluoroacetic acid were added. The ratio of thf:C₅Ph₄H₂ in the ¹H NMR spectrum was determined to be approximately 2:1. IR (Nujol, cm⁻¹): 1596s, 1532sh, 1509sh, 1497s, 1420s, 1298w, 1198w, 1180w, 1072m, 1023s, 922s, 870m, 790m, 759s, 731w, 698s, 669w; ¹H NMR (thf-d₈, 600 MHz, 298 K): δ 7.31–7.40 (m, 4H, H_{ortho}), 7.05–7.11 (m, 8H, H_{ortho}+H_{meta}), 6.94 (br m, 8H, H_{meta}+H_{para}), 6.66 (s, 1H, H_{Cp}); ¹³C{¹H} NMR (thf-d₈, 62.5 MHz, 298 K): δ 140.18 (C_{ring}), 139.82 (C_{ring}), 132.73 (C_{ortho}), 128.52 (C_{ortho}), 128.20

(C_{meta}), 127.71 (C_{meta}), 125.32 (C_{para}), 124.29 (C_{para}), 123.67 (2 C_{ipso}), 107.73 (C_{ring}), no signals were detected for the C₆F₅ group; ¹⁹F{¹H} NMR (thf/hexane/C₆D₆, 4.5/4.5/1 (v/v), 282.4 MHz, 303 K): δ -160.4 (m, 2F; F3,5), -159.3 (t, ³J_{F,F} = 21 Hz, 1F; F4), -111.1 (m, 2F; F2,6); ¹⁹F{¹H} NMR (thf/hexane/C₆D₆, 4.5/4.5/1 (v/v), 282.4 MHz, 213 K): δ -160.4 (br s, 2F; F3,5), -155.2 (br s, 1F; F4), -108.3 (br s, 2F; F2,6); ¹⁷¹Yb NMR (thf/hexane/C₆D₆, 4.5/4.5/1 (v/v), 52.5 MHz, 303 K): δ 359 (s); ¹⁷¹Yb NMR (thf/hexane/C₆D₆, 4.5/4.5/1 (v/v), 52.5 MHz, 213 K): δ 220 (s). No correct elemental analyses could be obtained due to rapid decomposition of the isolated compound in the solid state. When C₆D₆ was added to a d₈-thf solution of **3**, gradual decomposition into small amounts of unidentified fluoroarenes, as indicated by both the ¹H and ¹⁹F{¹H} NMR spectra, was observed.

*Attempted conversion of [Yb(C₅Ph₄H)(C₆F₅)(thf)₂] (**3**) into [Yb(C₅Ph₄H)(μ-F)(thf)₂]₂ (**1**)*

Complex **3** was generated in situ following the procedure above. An aliquot of the reaction mixture was placed in an NMR tube fitted with a J. Young valve. The solution, which also showed the presence of C₆F₅H and a small amount of **1**, was heated at 50 °C. After 40 min., monitoring by ¹⁹F{¹H} NMR spectroscopy showed that the peak corresponding to **1** had diminished and after 140 min. it had disappeared completely. The ratio of **3**:C₆F₅H only diminished slightly during that time. After prolonged heating of solutions containing **3**, the signals corresponding to it completely disappeared without the concomitant formation of **1**.

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 (**1**) equipped with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å), or at -173 °C (100 K) on the MX1: Macromolecular Crystallography beamline at the Australian Synchrotron, Victoria, Australia (**2**). Data collected on the Bruker X8 APEX II CCD were empirically corrected for absorption (SADABS)⁴ then merged. Data collection and integration on the MX1: Macromolecular Crystallography beamline were initially processed using the Blu-Ice⁵ and the XDS⁶ software programs. The structures were solved using SHELXS⁷ and refined by full-matrix least-squares on all *F*² data using SHELX-97,⁷ in conjunction with the X-Seed graphical user interface.⁸ All hydrogen atoms were placed in calculated positions using the riding model. CCDC numbers: 1007139 (**1**) and 1007140 (**2**).

Crystal data for **1**: C₇₄H₇₄F₂O₄Yb₂, *M* = 1411.51, dark orange rectangular prism, 0.50 × 0.25 × 0.25 mm³, monoclinic, space group *P*2₁/*n* (No. 14), *a* = 12.9940(4), *b* = 12.4469(4), *c* = 18.4353(6) Å, β = 95.132(2)°, *V* = 2969.68(16) Å³, *Z* = 2, *D*_c = 1.578 g/cm³, *F*₀₀₀ = 1416, Bruker X8 Apex II CCD, MoK_α radiation, λ = 0.71073 Å, *T* = 123(1) K, 2θ_{max} = 55.0°, 41015 reflections collected, 6808 unique (*R*_{int} = 0.0576). Final *Goof* = 1.022, *RI* = 0.0264, *wR2* = 0.0594, *R* indices based on 5699 reflections with *I* > 2σ(*I*) (refinement on *F*²), 370 parameters, 0 restraints. Lp and absorption corrections applied, μ = 3.188 mm⁻¹.

Crystal data for **2**: C₆₂H₅₀OYb, *M* = 984.06, dark orange block, monoclinic, space group *P*2₁/*n* (No. 14), *a* = 10.272(2), *b* = 40.410(8), *c* = 11.140(2) Å, β = 105.41(3)°, *V* = 4457.9(16) Å³, *Z* = 4, *D*_c = 1.466 g/cm³, *F*₀₀₀ = 2000, ADSC Quantum 210r, Synchrotron radiation, λ = 0.71073 Å, *T* = 100 K, 2θ_{max} = 50.0°, 7739 reflections collected, 7739 unique (*R*_{int} = 0.0000). Final *Goof* = 1.310, *RI* = 0.0458, *wR2* = 0.1083, *R* indices based on 7632 reflections with *I* > 2σ(*I*) (refinement on *F*²), 578 parameters, 0 restraints. Lp and absorption corrections applied, μ = 2.142 mm⁻¹.

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