

Stannocene as Cyclopentadienyl Transfer Agent in Transmetalation Reactions with Lanthanide Metals for the Synthesis of Tris(cyclopentadienyl)lanthanides

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In Memory of Professor Herbert Schumann

Keywords: Stannocenes; Ligand transfer; Samarium; Ytterbium; Metallocenes; Cyclopentadienyl ligands

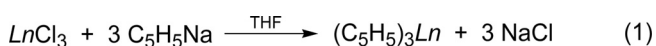
Abstract. Transmetalation of the lanthanide metals samarium and ytterbium with bis(cyclopentadienyl)tin(II), stannocene, ($\eta^5\text{-C}_5\text{H}_5$)₂Sn as cyclopentadienyl transfer agent yields the tris(cyclopentadienyl)lanthanides ($\eta^5\text{-C}_5\text{H}_5$)₃Ln (in toluene), ($\eta^5\text{-C}_5\text{H}_5$)₃Ln·THF (Ln = Sm, Yb) and bis(cyclopentadienyl)ytterbium, ($\eta^5\text{-C}_5\text{H}_5$)₂Yb·THF in a direct, facile,

high-yield and halide-free route. In toluene the base-free forms ($\eta^5\text{-C}_5\text{H}_5$)₃Ln are isolated directly. In THF the adducts ($\eta^5\text{-C}_5\text{H}_5$)₃Ln·THF are obtained in crystalline form. At a 1:1 molar ratio of Yb:Sn the ytterbium metal reduces the initially formed ($\eta^5\text{-C}_5\text{H}_5$)₃Yb·THF to ($\eta^5\text{-C}_5\text{H}_5$)₂Yb·THF.

Introduction

The bent sandwich compound bis(cyclopentadienyl)tin(II) [stannocene, ($\eta^5\text{-C}_5\text{H}_5$)₂Sn] [1] and the tris(cyclopentadienyl)lanthanides, ($\eta^5\text{-C}_5\text{H}_5$)₃Ln [2, 3] (also with one or two donor [solvent] molecules) [4–6] were among the prototypical early cyclopentadienyl-metal compounds synthesized by Fischer and Wilkinson in the 1950s following the discovery of ferrocene [7].

Complexes ($\eta^5\text{-C}_5\text{H}_5$)₃Ln are sublimable compounds with interest in their electronic structure [8], optical properties [9], uses as synthetic starting materials [10] and dopants [11] for semiconductive thin films [12], organic UV photocathodes [13], or mesoporous activated carbon [14]. Compounds ($\eta^5\text{-C}_5\text{H}_5$)₃Ln are typically synthesized from the metathesis of anhydrous lanthanide trichlorides with a large excess of sodium cyclopentadienide in tetrahydrofuran (THF) [Equation (1)] [2–5, 15].



Also, molten (C_5H_5)₂Be or (C_5H_5)₂Mg were used as cyclopentadienyl transfer reagents with LnX₃ [16], and C₅H₅Tl [17] or (C_5H_5)₂Hg [18] in transmetalation reactions with rare earth metal powders [Equation (2)] to yield ($\eta^5\text{-C}_5\text{H}_5$)₃Ln [4].



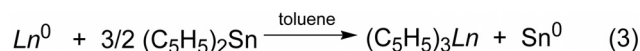
Unlike for cyclopentadienylthallium [19], we are not aware of any use of stannocene as a cyclopentadienyl transfer agent. There is one report on the reaction of the stannocene derivative ($\eta^5\text{-C}_5\text{Me}_5$)₂Sn with YbI₂ to give [($\eta^5\text{-C}_5\text{Me}_5$)₂YbI(THF)₂] [20].

Here we report the use of stannocene as a cyclopentadienyl transfer agent in transmetalation reactions with lanthanide metals for the synthesis of tris(cyclopentadienyl)lanthanides.

Results and Discussion

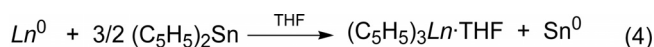
Stannocene, ($\eta^5\text{-C}_5\text{H}_5$)₂Sn can be easily prepared in large quantities and good yield from cyclopentadienylsodium and tin(II) dichloride. It can be very well purified by sublimation, is moderately air-sensitive and storable for prolonged times under inert gas at room temperature.

Stannocene reacts with samarium and ytterbium metal powder in toluene or tetrahydrofuran with formation of tris(cyclopentadienyl)samarium and -ytterbium in high yield. In toluene the base-free form ($\eta^5\text{-C}_5\text{H}_5$)₃Ln is isolated directly [Equation (3)]. In THF, the adducts ($\eta^5\text{-C}_5\text{H}_5$)₃Ln·THF are obtained in crystalline form [Equation (4)], from which THF-free compounds would be available after vacuum sublimation above 200 °C [2, 3].



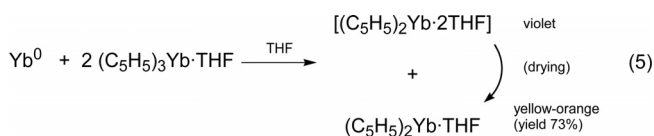
Ln = Sm (yield 68 %), Yb (crystals, 77 %)

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$Ln = Sm$ (yield 87%), Yb (76 %) crystalline form

In THF and a 1:1 molar ratio of Yb:Sn the (excess) ytterbium metal reduces the initially formed $(\eta^5-C_5H_5)_3Yb \cdot THF$ (verified by its green color) to bis(cyclopentadienyl)ytterbium which is isolated as the yellow-orange mono-tetrahydrofuran complex, $(\eta^5-C_5H_5)_2Yb \cdot THF$ complex [Equation (5)].



In toluene such a reduction with excess ytterbium metal is not observed. An excess of samarium metal does not exhibit such a reduction either, in line with the transmetalation with C_5H_5Tl , which also gave solely $(\eta^5-C_5H_5)_3Sm$ [21]. Thus, even at a 1:1 molar ratio of samarium and $(\eta^5-C_5H_5)_2Sn$ tris(cyclopentadienyl)samarium is obtained in high yield. In analogy to the transmetalation reactions of lanthanide metals with C_5H_5Tl a tiny amount of mercury was added to the reactions of samarium and ytterbium metal with stannocene [21]. The role of mercury is to facilitate the start of the reaction by cleaning the lanthanide metal surface through amalgamation. A summary of the transmetalation reactions of samarium and ytterbium with stannocene, $(\eta^5-C_5H_5)_2Sn$ is provided in Table 1.

Table 1. Transmetalation reactions of lanthanide metals with stannocene.^{a)}

| <i>Ln</i> metal | Molar ratio <i>Ln</i> :Sn | Solvent | Temperature /°C; time /d | Product(yield /%) |
|-----------------|---------------------------|---------|--------------------------|---|
| Sm | 1:1 | toluene | 60; 4 | $(C_5H_5)_3Sm$ (68) ^{b)} |
| Sm | 2:3 | THF | r.t.; 7 | $(C_5H_5)_3Sm \cdot THF$ (74) |
| Sm | 1:1 | THF | r.t.; 7 | $(C_5H_5)_3Sm \cdot THF$ (87) ^{b)} |
| Yb | 1:1 | toluene | 50; 7 | $(C_5H_5)_3Yb$ (77) ^{b)} |
| Yb | 2:3 | THF | r.t.; 2 | $(C_5H_5)_3Yb \cdot THF$ (76) |
| Yb | 1:1 | THF | r.t.; 3 | $(C_5H_5)_2Yb \cdot THF$ (73) |

a) R.t. = room temperature. b) Yield based on the minor stannocene component.

The color, melting points, IR-, Raman- and ¹H NMR spectra of the $(\eta^5-C_5H_5)_3Ln$, $(\eta^5-C_5H_5)_3Ln \cdot THF$ ($Ln = Sm, Yb$) and $(\eta^5-C_5H_5)_2Yb \cdot THF$ products obtained here through transmetalation agree with the literature values of the compounds [4].

Conclusions

The transmetalation of the lanthanide metals samarium and ytterbium is a facile, high-yield and halide-free route to the tris(cyclopentadienyl)lanthanides $(\eta^5-C_5H_5)_3Ln$, $(\eta^5-C_5H_5)_3Ln \cdot THF$ ($Ln = Sm, Yb$) and to bis(cyclopentadienyl)ytterbium, $(\eta^5-C_5H_5)_2Yb \cdot THF$. The synthetic route should be extendable to $(\eta^5-C_5H_5-nR_n)_3Ln$ compounds with ring-substituted cyclopentadienyl ligands [4, 22] for which a wide range of stannocene derivatives is also available [23].

Experimental Section

Syntheses were routinely carried out under an inert gas of dried nitrogen or argon with Schlenk and vacuum techniques. The glass ware was flame-dried prior to its usage. Solvents were dried with and distilled from (blue) sodium/benzophenone (ketyl) or liquid Na/K alloy (25 wt.-% Na/75 wt.-% K) and stored under inert gas. Samarium and ytterbium powders were obtained from Auer-Remy/Hamburg. NMR spectra were obtained with samples in sealed NMR tubes with a Bruker WP 80 SI and are referenced against TMS. The line width for the paramagnetic samarium and ytterbium probes is given as the frequency width at half-height maximum (FWHM). IR spectra were measured with a Perkin-Elmer 580B infrared spectrometer in CsI (2–3 mg sample/300 mg CsI) with a CsI reference, Raman spectra with a Jobin-Yvon spectrometer (Kr Laser, room temperature, 100–2000 cm⁻¹). For both the IR and Raman spectra only signals classified from weak (w), medium (m) to strong (s) and shoulders (sh) but no very weak signals are listed. C,H analyses were done with a Perkin-Elmer 240C CHN elemental analyzer. Melting points were measured in capillaries, which were sealed under vacuum. Cyclopentadienylsodium was prepared from freshly cracked cyclopentadiene, C_5H_6 (42.0 mL, 0.51 mol, density ca. 0.8 g·mL⁻¹), which was slowly added dropwise to a suspension of finely cut sodium metal (14.0 g, 0.61 mol, excess) in tetrahydrofuran (250 mL). After stirring for 18 h the slightly pink THF solution was decanted from unreacted excess sodium and the solvent was removed under vacuum to yield C_5H_5Na as a colorless powder (43.0 g, 96 %).

Bis(cyclopentadienyl)tin(II), Stannocene, $(C_5H_5)_2Sn$: Solid C_5H_5Na (43.0 g, 0.49 mol) and tin(II) dichloride (46.4 g, 0.245 mol) were weighed into a 250-mL Schlenk flask. THF (150 mL) was added under ice cooling to start an immediate exothermic reaction. Stirring was continued for 1.5 h, afterwards the solvent was removed under vacuum with gentle warming. The product was sublimed from the residue at 80 °C/10⁻¹ Torr and obtained as colorless to slightly yellow crystals (yield 33.4 g, 55 %).

Tris(cyclopentadienyl)samarium, $(C_5H_5)_3Sm$: To a mixture of stannocene (2.26 g, 9.08 mmol) and samarium metal powder (1.37 g, 9.08 mmol) was added a very small drop of mercury and toluene (20 mL). The suspension was stirred at 60 °C for 4 d. Additional toluene (50 mL) was added to the off-white to yellow suspension and the product was separated from the metal residue through a glass frit equipped with a bypass to enable a continuous hot extraction. The toluene solution was decanted from the precipitated product in the filtrate and discarded. The orange-yellow product powder was dried under vacuum (yield 1.42 g, 68 %, based on stannocene). M. p. 346–348 °C (lit. 365 °C [3], ca. 330 °C) [24]. **IR** (CsI): $\tilde{\nu} = 3100$ (m), 3085 (m), 3070 (m), 1607 (m), 1442 (m), 1438 (m), 1363 (w), 1263 (w), 1238 (w), 1072 (w), 1008 (s), 914 (sh), 890 (m), 840 (m), 792 (sh), 770 (vs, br), 664 (m), 621 (w), 550 (w, br) cm⁻¹ (lit. [24]). **Raman**: 1126 cm⁻¹. **¹H NMR** (C_6D_6): $\delta = 12.8$ (s, FWHM 22 Hz). $C_{15}H_{15}Sm$ (345.68): calcd. C 52.12, H 4.37; found C 51.37, H 4.36.

Tris(cyclopentadienyl)samarium·Tetrahydrofuran,

$(C_5H_5)_3Sm \cdot THF$: To a mixture of stannocene (1.49 g, 5.99 mmol) and samarium metal powder (0.60 g, 3.99 mmol) was added a very small drop of mercury and THF (20 mL). After 12 h a yellow, finely crystalline product residue has already been observed. The suspension was stirred at room temperature for 7 d. Afterwards, additional THF (30 mL) was added and the clear yellow solution was decanted from the metal and product precipitate. Cooling (–20 °C) of the THF solution yielded yellow crystals whose yield was increased through repeated residue extraction and cooling of the bridge-connected residue

and product flask. Finally the volume of the mother liquor was decreased in vacuo to further enhance the yield (1.24 g, 74 %). M.p. 348–350 °C with irreversible darkening from 200 °C and softening at 335 °C.

A 1:1 molar ratio of stannocene (1.85 g, 7.43 mmol) and samarium metal powder (1.12 g, 7.43 mmol) yielded the same product (yield 1.81 g, 87 %, based on stannocene).

IR (CsI): $\tilde{\nu}$ = 3090 (w), 3075 (sh), 2980 (w), 2890 (w), 2875 (sh), 1660 (w), 1441 (w), 1341 (m), 1244 (w), 1235 (sh), 1060 (sh), 1035 (sh), 1016 (s), 889 (sh), 861 (m), 839 (m), 795 (sh), 786 (vs), 775 (sh), 760 (sh), 755 (vs), 667 (w), 240 (sh), 211 (m) cm^{-1} (lit. [21]). **Raman**: 1356 (w), 1226 (s), 774 (w), 752 (w), 230 (s), 210 (m), 132 (m to s) cm^{-1} . **$^1\text{H NMR}$** (C_6D_6): δ = 0.81 (m, THF- CH_2), 2.26 (m, THF- CH_2), 12.7 (s, C_5H_5 , FWHM 18 Hz); ($[\text{D}_8]\text{THF}$): δ = 12.4 (s, FWHM 17 Hz). $\text{C}_{19}\text{H}_{23}\text{OSm}$ (417.79): calcd. C 54.62, H 5.55; found C 54.22, H 5.57.

Tris(cyclopentadienyl)ytterbium, (C_5H_5)₃Yb: To a mixture of stannocene (2.88 g, 11.57 mmol) and ytterbium metal powder (2.00 g, 11.56 mmol) was added a very small drop of mercury and toluene (30 mL). After 5 min the solution assumed a light green color. The suspension was stirred at 50 °C for 7 d. Afterwards, additional toluene (30 mL) was added and the deep-green solution was decanted hot (80 °C) from the grey metal residue. Upon cooling to room temperature dark-green crystals were obtained and the yield was increased by cooling to –20 °C for 3 d. The crystalline product was collected by decanting the mother liquor (yield 2.20 g, 77 %, based on stannocene). M.p. 267–270 °C (lit. 273 °C) [3]. **IR** (CsI): $\tilde{\nu}$ = 3090 (w), 3075 (w), 1439 (w), 1012 (s), 810 (sh), 780 (vs), 740 (sh), 668 (w), 500 (w), 435 (w), 255 (w), 212 (w) cm^{-1} (lit. [15b]). **$^1\text{H NMR}$** (C_6D_6): δ = –59.5 (s, FWHM 409 Hz) (lit. in C_6D_{12} , –59, FWHM 300 Hz; in C_6D_6 –56 ppm, FWHM 290 Hz) [25]. $\text{C}_{15}\text{H}_{15}\text{Yb}$ (368.32): calcd. C 48.91, H 4.10; found C 49.87, H 4.13.

Tris(cyclopentadienyl)ytterbium-Tetrahydrofuran,

(C_5H_5)₃Yb·THF: To a mixture of stannocene (2.94 g, 11.81 mmol) and ytterbium metal powder (1.36 g, 7.88 mmol) was added a very small drop of mercury and THF (30 mL). After about 5 min the solution started to turn green and warmed up slightly. The suspension was stirred at room temperature for 2 d. Afterwards, additional THF (30 mL) was added and the clear green solution was decanted from the metal residue and product precipitate. Cooling (–20 °C) of the THF solution yielded dark-green crystals whose yield was increased through repeated residue extraction and cooling of the bridge-connected residue and product flask. Finally, the volume of the mother liquor was decreased in vacuo to further enhance the yield (2.65 g, 76 %). M.p. 220–222 °C (lit. 223–226 °C) [15b]. **IR** (CsI): $\tilde{\nu}$ = 3555 (m), 3095 (w), 3070 (sh), 2980 (w), 2890 (w), 1440 (w), 1331 (w), 1245 (w), 1059 (w), 1040 (sh), 1012 (s), 890 (w), 862 (w), 838 (w), 795 (vs), 770 (s), 735 (sh), 666 (w), 440 (m), 420 (sh), 390 (w), 250 (m) (lit. [15b]) cm^{-1} . **$^1\text{H NMR}$** (C_6D_6): δ = –48.5 (s, C_5H_5 , FWHM 345 Hz), 38.7 (s, THF- CH_2 , FWHM 73 Hz), 80.3 (s, THF- CH_2 , FWHM 327 Hz) (lit. in $[\text{D}_8]\text{THF}$, –54 ppm, FWHM 280 Hz) [25]. $\text{C}_{19}\text{H}_{23}\text{OYb}$ (440.43): calcd. C 51.82, H 5.26; found C 51.45, H 5.18 %.

Bis(cyclopentadienyl)ytterbium-Tetrahydrofuran,

(C_5H_5)₂Yb·THF: To a mixture of stannocene (1.83 g, 7.35 mmol) and ytterbium metal powder (1.27 g, 7.36 mmol) was added a very small drop of mercury and THF (20 mL). The solution immediately turned green, warmed up slightly and soon became dark-green. The suspension was stirred at room temperature for 3 d when apparently all ytterbium metal powder was consumed. The now violet solution was decanted from the grey tin metal residue. Reduction of the THF volume

in vacuo and overlaying with hexane yielded yellow-orange crystals of the mono-THF complex and violet, feather-like crystals of the bis-THF complex. The latter turned to a yellow powder upon drying in vacuo by giving off one solvent molecule (yield 2.00 g, 73 %). M.p. dec. at about 170 °C (no melting up to 350 °C). **$^1\text{H NMR}$** ($[\text{D}_8]\text{THF}$): δ = 5.67 (s, C_5H_5 , no line broadening) (lit. in $[\text{D}_8]\text{THF}$ 5.64 ppm) [15b]. $\text{C}_{14}\text{H}_{18}\text{OYb}$ (375.34): calcd. C 44.80, H 4.83; found C 44.96, H 5.03.

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