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► **To cite this version:**

Christoph Janiak. Stannocene as cyclopentadienyl transfer agent in transmetallation reactions with lanthanide metals for the synthesis of tris(cyclopentadienyl)lanthanides. *Journal of Inorganic and General Chemistry / Zeitschrift für anorganische und allgemeine Chemie*, 2010, 636 (13-14), pp.2387. 10.1002/zaac.201000239 . hal-00569390

HAL Id: hal-00569390

<https://hal.science/hal-00569390>

Submitted on 25 Feb 2011

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Journal:	<i>Zeitschrift für Anorganische und Allgemeine Chemie</i>
Manuscript ID:	zaac.201000239
Wiley - Manuscript type:	Article
Date Submitted by the Author:	11-Jun-2010
Complete List of Authors:	Janiak, Christoph; der Universität, Inst. f. Anorganische und Analyt. Chemie
Keywords:	stannocene , tris(cyclopentadienyl)lanthanide, ligand transfer, samarium, ytterbium



ARTICLE

DOI: 10.1002/zaac.200((will be filled in by the editorial staff))

Stannocene as cyclopentadienyl transfer agent in transmetallation reactions with lanthanide metals for the synthesis of tris(cyclopentadienyl)lanthanides

Christoph Janiak

In Memoriam to Prof. Dr. Herbert Schumann and in recognition to his seminal contributions in organotin and organolanthanide chemistry

Keywords: stannocene; tris(cyclopentadienyl)lanthanide; ligand transfer; samarium; ytterbium.

Transmetalation of the lanthanide metals samarium and ytterbium with bis(cyclopentadienyl)tin(II), stannocene, $(\eta^5\text{-C}_5\text{H}_5)_2\text{Sn}$ as cyclopentadienyl transfer agent yields the tris(cyclopentadienyl)lanthanides $(\eta^5\text{-C}_5\text{H}_5)_3\text{Ln}$ (in toluene), $(\eta^5\text{-C}_5\text{H}_5)_3\text{Ln}\cdot\text{THF}$ (Ln = Sm, Yb) and bis(cyclopentadienyl)ytterbium, $(\eta^5\text{-C}_5\text{H}_5)_2\text{Yb}\cdot\text{THF}$ in a direct, facile, high-yield and halide-free route.

In toluene the base-free forms $(\eta^5\text{-C}_5\text{H}_5)_3\text{Ln}$ are isolated directly. In THF the adducts $(\eta^5\text{-C}_5\text{H}_5)_3\text{Ln}\cdot\text{THF}$ are obtained in crystalline form. At a 1:1 molar ratio of Yb:Sn the ytterbium metal reduces the initially formed $(\eta^5\text{-C}_5\text{H}_5)_3\text{Yb}\cdot\text{THF}$ to $(\eta^5\text{-C}_5\text{H}_5)_2\text{Yb}\cdot\text{THF}$.

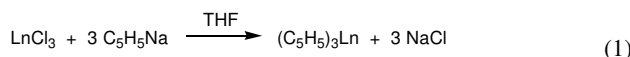
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Unlike for cyclopentadienylthallium,^[19] we are not aware of any use of stannocene as a cyclopentadienyl transfer agent. There is one report on the reaction of the stannocene derivative $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Sn}$ with YbI_2 to give $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{YbI}(\text{THF})_2]$.^[20]

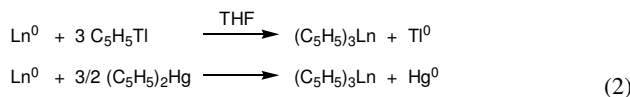
Introduction

The bent sandwich compound bis(cyclopentadienyl)tin(II) [stannocene, $(\eta^5\text{-C}_5\text{H}_5)_2\text{Sn}$]^[11] and the tris(cyclopentadienyl)lanthanides, $(\eta^5\text{-C}_5\text{H}_5)_3\text{Ln}$ ^[2,3] (also with one or two donor [solvent] molecules)^[4,5,6] were among the prototypical early cyclopentadienyl-metal compounds synthesized by Fischer and Wilkinson in the 1950s following the discovery of ferrocene.^[7]

Complexes $(\eta^5\text{-C}_5\text{H}_5)_3\text{Ln}$ 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 $(\eta^5\text{-C}_5\text{H}_5)_3\text{Ln}$ are typically synthesized from the metathesis of anhydrous lanthanide trichlorides with a large excess of sodium cyclopentadienide in tetrahydrofuran (THF) (eq. 1).^[2,3,4,5,15]



Also, molten $(\text{C}_5\text{H}_5)_2\text{Be}$ or $(\text{C}_5\text{H}_5)_2\text{Mg}$ were used as cyclopentadienyl transfer reagents with LnX_3 ,^[16] and $\text{C}_5\text{H}_5\text{Ti}$ ^[17] or $(\text{C}_5\text{H}_5)_2\text{Hg}$ ^[18] in transmetalation reactions with rare earth metal powders (eq. 2) to yield $(\eta^5\text{-C}_5\text{H}_5)_3\text{Ln}$.^[4]

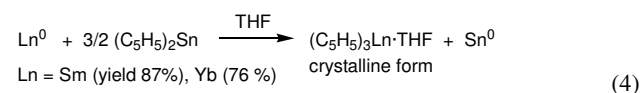
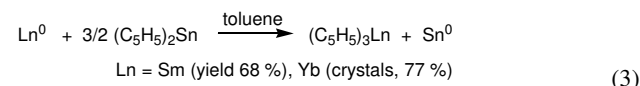


Here we report the use of stannocene as a cyclopentadienyl transfer agent in transmetalation reactions with lanthanide metals for the synthesis of tris(cyclopentadienyl)lanthanides.

Results and Discussion

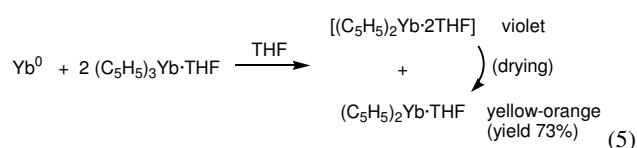
Stannocene, $(\eta^5\text{-C}_5\text{H}_5)_2\text{Sn}$ can be easily prepared in large quantities and good yield from cyclopentadienyl sodium and tin(II) dichloride. It can be very well purified by sublimation, is moderately air-sensitive and storable for prolonged times under inert gas at room temperature.

Stannocene reacts with samarium and ytterbium metal powder in toluene or tetrahydrofuran under formation of tris(cyclopentadienyl)samarium and -ytterbium in high yield. In toluene the base-free form $(\eta^5\text{-C}_5\text{H}_5)_3\text{Ln}$ is isolated directly (eq. 3). In THF the adducts $(\eta^5\text{-C}_5\text{H}_5)_3\text{Ln}\cdot\text{THF}$ are obtained in crystalline form (eq. 4), from which THF-free compounds would be available after vacuum sublimation above 200 °C.^[2,3]



In THF and a 1:1 molar ratio of Yb:Sn the (excess) ytterbium metal reduces the initially formed $(\eta^5\text{-C}_5\text{H}_5)_3\text{Yb}\cdot\text{THF}$ to $(\eta^5\text{-C}_5\text{H}_5)_2\text{Yb}\cdot\text{THF}$.

$C_5H_5)_3Yb \cdot THF$ (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 (eq. 5).



In toluene such a reduction with excess Yb metal is not observed. An excess of samarium metal does not exhibit such a reduction either, in line with the transmetallation with C_5H_5Tl which also gave solely $(\eta^5-C_5H_5)_3Sm$.^[21] Thus, even at a 1:1 molar ratio of Sm and $(\eta^5-C_5H_5)_2Sn$ tris(cyclopentadienyl)samarium is obtained in high yield. In analogy to the transmetallation 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 transmetallation reactions of samarium and ytterbium with stannocene, $(\eta^5-C_5H_5)_2Sn$ is provided in Table 1.

Table 1. Transmetallation reactions of lanthanide metals with stannocene.^[a]

Ln metal	molar ratio Ln:Sn	solvent	temperature /°C; time /d	product (yield /%)
Sm	1:1	toluene	60; 4	$(C_5H_5)_3Sm$ (68) ^[b]
Sm	2:3	THF	RT; 7	$(C_5H_5)_3Sm \cdot THF$ (74)
Sm	1:1	THF	RT; 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	RT; 2	$(C_5H_5)_3Yb \cdot THF$ (76)
Yb	1:1	THF	RT; 3	$(C_5H_5)_2Yb \cdot THF$ (73)

[a] RT = 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 transmetallation agree with the literature values of the compounds.^[4]

Conclusions

The transmetallation 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 atmosphere of dried nitrogen or argon with Schlenk and vacuum techniques. The glass ware was flame dried prior to its usage. Solvent were dried over 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 on a Bruker WP 80 SI and are referenced against TMS. The line width for the paramagnetic Sm and Yb probes is given as the frequency width at half-height maximum (FWHM). IR spectra were measured on a Perkin-Elmer 580B infrared spectrometer in CsI (2-3 mg sample/300 mg CsI) with a CsI reference, Raman spectra on a Jobin-Yvon spectrometer (Kr Laser, room temperature, 100-2000 cm^{-1}). For both the IR and Raman spectra only peaks classified from weak (w), medium (m) to strong (s) and shoulders (sh) but no very weak peaks are listed. C,H analyses were done on a Perkin-Elmer 240C CHN elemental analyzer. Melting points were measured capillaries which were sealed under vacuum. Cyclopentadienyl sodium was prepared from freshly cracked cyclopentadiene, C_5H_6 (42.0 ml, 0.51 mol, density ~0.8 g/ml) which was slowly added dropwise to a suspension of finely cut sodium metal (14.0 g, 0.61 mol, excess) in 250 ml of tetrahydrofuran. After stirring for 18 h the slightly pink THF solution was decanted from unreacted excess sodium and the solvent removed under vacuum to yield C_5H_5Na as a white 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) are weighed into a 250 ml Schlenk flask. THF (150 ml) is added under ice cooling to start an immediate exothermic reaction. Stirring is continued for 1.5 h, then the solvent is removed under vacuum with gentle warming. The product is sublimed from the residue at 80 °C/10⁻¹ Torr and obtained as white 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) is added a very small drop of mercury and toluene (20 ml). The suspension is stirred at 60 °C for 4 d. Additional 50 ml of toluene are added to the off-white to yellow suspension and the product is separated from the metal residue through a glass frit equipped with a bypass to enable a continuous hot extraction. The toluene solution is decanted from the precipitated product in the filtrate and discarded. The orange-yellow product powder is 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, cm^{-1}): 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) (lit. [24]). **Raman** (cm^{-1}): 1126. **1H -NMR** (C_6D_6 , ppm): 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) is added a very small drop of mercury and THF (20 ml). After 12 h a yellow, finely crystalline product residue can already be observed. The suspension is stirred at room temperature for 7 d. Then additional 30 ml of THF are added and the clear yellow

1
2 solution is decanted from the metal and product precipitate.
3 Cooling ($-20\text{ }^{\circ}\text{C}$) of the THF solution yields yellow crystals
4 whose yield is increased through repeated residue extraction and
5 cooling of the bridge-connected residue and product flask.
6 Finally the volume of the mother liquor was decreased in
7 vacuum to further enhance the yield (1.24 g, 74%). M.p. 348-
8 $350\text{ }^{\circ}\text{C}$ with irreversible darkening from $200\text{ }^{\circ}\text{C}$ and softening at
9 $335\text{ }^{\circ}\text{C}$.

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

13 **IR** (CsI , cm^{-1}): 3090 (w), 3075 (sh), 2980 (w), 2890 (w), 2875
14 (sh), 1660 (w), 1441 (w), 1341 (m), 1244 (w), 1235 (sh), 1060
15 (sh), 1035 (sh), 1016 (s), 889 (sh), 861 (m), 839 (m), 795 (sh),
16 786 (vs), 775 (sh), 760 (sh), 755 (vs), 667 (w), 240 (sh), 211 (m)
17 (lit. [21]). **Raman** (cm^{-1}): 1356 (w), 1226 (s), 774 (w), 752 (w),
18 230 (s), 210 (m), 132 (m to s). **$^1\text{H-NMR}$** (C_6D_6 , ppm): 0.81 (m,
19 THF- CH_2), 2.26 (m, THF- CH_2), 12.7 (s, C_5H_5 , FWHM 18 Hz);
20 (THF- d_8 , ppm): 12.4 (s, FWHM 17 Hz). $\text{C}_{19}\text{H}_{23}\text{SmO}$ (417.79):
21 calcd. C 54.62, H 5.55; found C 54.22, H 5.57%.

22
23 **Tris(cyclopentadienyl)ytterbium, (C_5H_5) $_3\text{Yb}$.** To a mixture of
24 stannocene (2.88 g, 11.57 mmol) and ytterbium metal powder
25 (2.00 g, 11.56 mmol) is added a very small drop of mercury and
26 toluene (30 ml). After 5 min the solution assumes a light green
27 color. The suspension is stirred at $50\text{ }^{\circ}\text{C}$ for 7 d. Then additional
28 30 ml of toluene are added and the deep-green solution is
29 decanted hot ($80\text{ }^{\circ}\text{C}$) from the grey metal residue. Upon cooling
30 to room temperature dark-green crystals are obtained and the
31 yield is increased by cooling to $-20\text{ }^{\circ}\text{C}$ for 3 d. The crystalline
32 product is collected by decanting the mother liquor (yield 2.20 g,
33 77 %, based on stannocene) M.p. $267\text{-}270\text{ }^{\circ}\text{C}$ (lit. $273\text{ }^{\circ}\text{C}$).^[3] **IR**
34 (CsI , cm^{-1}): 3090 (w), 3075 (w), 1439 (w), 1012 (s), 810 (sh),
35 780 (vs), 740 (sh), 668 (w), 500 (w), 435 (w), 255 (w), 212 (w)
36 (lit. [15b]). **$^1\text{H-NMR}$** (C_6D_6 , ppm): -59.5 (s, FWHM 409 Hz)
37 (lit. in C_6D_{12} , -59 ppm, FWHM 300 Hz; in C_6D_6 -56 ppm,
38 FWHM 290 Hz).^[25] $\text{C}_{15}\text{H}_{15}\text{Yb}$ (368.32): calcd. C 48.91, H 4.10;
39 found C 49.87, H 4.13%.

40
41 **Tris(cyclopentadienyl)ytterbium tetrahydrofuran,**
42 **(C_5H_5) $_3\text{Yb}\cdot\text{THF}$.** To a mixture of stannocene (2.94 g, 11.81
43 mmol) and ytterbium metal powder (1.36 g, 7.88 mmol) is
44 added a very small drop of mercury and THF (30 ml). After
45 about 5 min the solution starts to turn green and warms up
46 slightly. The suspension is stirred at room temperature for 2 d.
47 Then additional 30 ml of THF are added and the clear green
48 solution is decanted from the metal residue and product
49 precipitate. Cooling ($-20\text{ }^{\circ}\text{C}$) of the THF solution yields dark-
50 green crystals whose yield is increased through repeated residue
51 extraction and cooling of the bridge-connected residue and
52 product flask. Finally the volume of the mother liquor was
53 decreased in vacuum to further enhance the yield (2.65 g, 76%).
54 M.p. $220\text{-}222\text{ }^{\circ}\text{C}$ (lit. $223\text{-}226\text{ }^{\circ}\text{C}$).^[15b] **IR** (CsI , cm^{-1}): 3555
55 (w), 3095 (w), 3070 (sh), 2980 (w), 2890 (w), 1440 (w), 1331
56 (w), 1245 (w), 1059 (w), 1040 (sh), 1012 (s), 890 (w), 862 (w),
57 838 (w), 795 (vs), 770 (s), 735 (sh), 666 (w), 440 (m), 420 (sh),
58 390 (w), 250 (m) (lit. [15b]). **$^1\text{H-NMR}$** (C_6D_6 , ppm): -48.5 (s,
59 C_5H_5 , FWHM 345 Hz), 38.7 (s, THF- CH_2 , FWHM 73 Hz), 80.3
60 (s, THF- CH_2 , FWHM 327 Hz) (lit. in THF- d_8 , -54 ppm,
FWHM 280 Hz).^[25] $\text{C}_{19}\text{H}_{23}\text{YbO}$ (440.43): calcd. C 51.82, H
5.26; found C 51.45, H 5.18%.

Bis(cyclopentadienyl)ytterbium tetrahydrofuran,
(C_5H_5) $_2\text{Yb}\cdot\text{THF}$. To a mixture of stannocene (1.83 g, 7.35
mmol) and ytterbium metal powder (1.27 g, 7.36 mmol) is
added a very small drop of mercury and THF (20 ml). The
solution immediately turns green, warms up slightly and is soon
dark-green. The suspension is stirred at room temperature for 3
d when apparently all Yb metal powder has been consumed.
The now violet solution is decanted from the grey tin metal
residue. Reduction of the THF volume in vacuum and
overlayering with hexane yields yellow-orange crystals of the
mono-THF complex and violet, feather-like crystals of the bis-
THF complex. The latter turn to a yellow powder upon drying in
vacuum by giving off one solvent molecule (yield 2.00 g, 73%).
M.p. dec. at about $170\text{ }^{\circ}\text{C}$ (no melting up to $350\text{ }^{\circ}\text{C}$). **$^1\text{H-NMR}$**
(THF- d_8 , ppm): 5.67 (s, C_5H_5 no line broadening) (lit. in THF- d_8
5.64 ppm).^[15b] $\text{C}_{14}\text{H}_{18}\text{YbO}$ (375.34): calcd. C 44.80, H 4.83;
found 44.96, H 5.03%.

Received: ((will be filled in by the editorial staff))
Published online: ((will be filled in by the editorial staff))

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