Facile Synthesis of Permethyl Yttrocene Hydride
Haan, Klaas H. den; Teuben, Jan H.

Published in:
Recueil des Travaux Chimiques des Pays-Bas-Journal of the Royal Netherlands Chemical Society

DOI:
10.1002/recl.19841031107

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
1984

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

Copyright
Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

Take-down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): http://www.rug.nl/research/portal. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.
The spectacular chemistry of organo-f-element compounds of the type Cp*MR (M = 4f-element, R = alkyl, allyl, H) has increased interest in the properties of the corresponding Group III B (M = Sc, Y, La) and early transition metal compounds. Recently investigations of Cp*ScR have been published.

An outstanding aspect of the chemistry of the f-element and Sc compounds is the surprisingly facile activation of both sp³ and sp³ C-H bonds by (Cp*MR)₃. Essential in the preparation of (Cp*MR)₃ is that these hydrides must be free from donor ligands like ether molecules or even alkali halides. Such a synthesis is difficult and elaborate as Watson clearly demonstrated in the eight step synthesis of (Cp*LuH)₃. To circumvent these synthetic problems we decided to work out a simple and short route to (Cp*YH)₃ through hydrogenolysis of monomeric coordinatively unsaturated Cp*YR. Such compounds can easily be obtained by using steric bulky ligands like R = Me₂SiCH₃.

The synthesis scheme for the hydride is as follows:

\[
\begin{align*}
\text{YCl}_3, \text{thf} + 2 \text{Cp*Na} & \xrightarrow{\text{65°C}} \text{Cp*YCl, thf} + 2 \text{NaCl} & (1) \\
\text{Cp*YCl, thf} + \text{LiCH(SiMe}_3)_2 & \xrightarrow{\text{Et}_2\text{O}, \text{25°C}} \text{Cp*YCH(SiMe}_3)_2 + \text{LiCl} + \text{thf} & (2) \\
\text{Cp*YCH(SiMe}_3)_2 + \text{H}_2 & \xrightarrow{\text{(1 atm), 25°C}} \text{Cp*YH} + \text{CH(SiMe}_3)_2 & (3) \\
\end{align*}
\]

1/ₙ (Cp*YH)ₙ + PhH ———> Cp*YPh + H₂

Further we found that (1) activates both sp³ and sp³ C-H bonds in a smooth reaction at room temperature.

When (2) is treated with H₂ in C₆D₆ (0.1M, sealed NMR tube), (Me₂Si)CH₂ is formed quantitatively within 10 minutes (25°C). After that a gradual exchange of hydrogen atoms of the methyl groups of (Me₂Si)CH₂ with deuterium from solvent C₆D₆ is observed, (reaction 4).

\[
\text{C}_6\text{D}_6 + \text{Cp*YH} \xrightarrow{\text{25°C}} \text{C}_6\text{D}_6 + \text{YH} + \text{CH(SiMe}_3)_2
\]

The half-life of the reaction at room temperature is ca. 27 h. The methylene protons of (Me₂Si)CH₂ are not exchanged. At elevated temperatures (100°C) also all the hydrogen atoms of the pentamethylcyclopentadienyl ligand are exchanged for deuterium within five hours, but the methylene protons of (Me₂Si)CH₂ are not.

It is clear that (Cp*YH)₃ can be prepared very easily in a 3-step reaction from YCl₃, thf and that it has very interesting chemical properties. It also reacts with a variety of substrates (eq. pyridine, CO, acetone etc.) and the reactivity is under investigation at the moment.
References and Notes

† This work has been presented (in part) during the NATO-ASI on Organo-f-Element Chemistry, Maratea, Italy, September 1984.

5. T.J. Marks and coworkers used a similar approach to synthesize corresponding La, Nd, Lu compounds; results presented at the NATO-ASI, Maratea, Italy, September 1984.
6. The reactions were performed under N₂ on 1-5 g scale. Compounds 1 and 2 were purified by re-crystallization from toluene (2, pentane) and 3 was obtained pure after decanting the solution and drying the product in vacuum. The compounds were characterized by ¹H, ¹³C NMR, IR spectra and satisfactory elemental analyses

The spectra are in complete accordance with the proposed formulas.

7. ¹H NMR: 1.19 (m, 4H, b H-THF), 1.96 (s, 30H, C₅Me₅, ¹J₁C-H = 125.2 Hz), 3.42 (m, 4H, a H-THF); ¹³C NMR: 11.63 (C₅Me₅, ¹J₁C-H = 125.2 Hz), 25.30 (b C-THF, ¹J₁C-H = 125.3 Hz), 71.90 (a C-THF, ¹J₁C-H = 133.9 Hz), 118.03 (C₅Me₅).


9. NMR data all spectra at 25°C in C₆D₆, dTMS = 0.0 in ¹H as well as ¹³C.

1 ¹H NMR: 1.19 (m, 4H, b H-THF), 1.96 (s, 30H, C₅Me₅, ¹J₁C-H = 125.2 Hz), 3.42 (m, 4H, a H-THF); ¹³C NMR: 11.63 (C₅Me₅, ¹J₁C-H = 125.2 Hz), 25.30 (b C-THF, ¹J₁C-H = 125.3 Hz), 71.90 (a C-THF, ¹J₁C-H = 133.9 Hz), 118.03 (C₅Me₅).

2 ¹H NMR: -0.10 (d, 1H, ¹J₂Y-H = 2.3 Hz, Y-CHR), 0.17 (s, 18H, SiMe₃), 1.87 (s, 15H, C₅Me₅); ¹³C NMR: 5.02 (SiMe₃, ¹J₂C-H = 116.6 Hz), 25.19 (d, Y-CHR, ¹J₂C-H = 84.2 Hz, ¹J₁C-H = 36.6 Hz), 11.78 (C₅Me₅, ¹J₂C-H = 125.5 Hz), 12.10 (C₅Me₅, ¹J₂C-H = 125.6 Hz), 119.14 (C₅Me₅), 119.79 (C₅Me₅).

3 ¹H NMR: 2.12 (s, 30H, C₅Me₅).

Y-H not observed possibly due to the reactivity of the hydride; ¹³C NMR not measured.