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Preliminary Communication

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FACILE SYNTHESIS OF PERMETHYL YTROCENE HYDRIDE

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Abstract. A convenient three step synthesis of $(\text{Cp}^*_2\text{YH})_n$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$) is described starting with $\text{YCl}_3 \cdot 3\text{thf}$, in which $\text{Cp}^*_2\text{YCl} \cdot \text{thf}$ and $\text{Cp}^*_2\text{YCH}(\text{SiMe}_3)_2$ are intermediates, which could be isolated and characterized. The hydride is active in the activation of sp^2 and sp^3 C-H bonds as was demonstrated by the H-D exchange between C_6D_6 and the methyl groups of $\text{CH}_2(\text{SiMe}_3)_2$ at room temperature.

The spectacular chemistry of organo-f-element compounds of the type Cp^*_2MR ($\text{M} = \text{4f-element}$, $\text{R} = \text{alkyl, allyl, H}$)^{1,2} has increased interest in the properties of the corresponding Group III B ($\text{M} = \text{Sc, Y, La}$) and early transition metal compounds. Recently investigations of Cp^*_2ScR have been published³.

An outstanding aspect of the chemistry of the f-element and Sc compounds is the surprisingly facile activation of both sp^2 and sp^3 C-H bonds by $(\text{Cp}^*_2\text{MH})_n$. Essential in the preparation of $(\text{Cp}^*_2\text{MH})_n$ 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 $\text{Cp}^*_2\text{LuH}^{2,4}$. To circumvent these synthetic problems we decided to work out a simple and short route to $(\text{Cp}^*_2\text{YH})_n$ through hydrogenolysis of monomeric coordinatively unsaturated Cp^*_2YR . Such compounds can easily be obtained by using steric bulky ligands like $\text{R} = \text{Me}_3\text{Si}_2\text{CH}$. The synthesis scheme for the hydride is as follows⁵

sp^3 C-H bonds in a smooth reaction at room temperature.

When 2 is treated with H_2 in C_6D_6 (0.1M, sealed NMR tube), $(\text{Me}_3\text{Si})_2\text{CH}_2$ is formed quantitatively within 10 minutes (25°C). After that a gradual exchange of hydrogen atoms of the methyl groups of $(\text{Me}_3\text{Si})_2\text{CH}_2$ with deuterium from solvent C_6D_6 is observed, (reaction 4).

The halflife of the reaction at room temperature is ca. 27 h. The methylene protons of $(\text{Me}_3\text{Si})_2\text{CH}_2$ are not exchanged. At elevated temperature

1, 2 and 3 were obtained as analytical pure compounds^{6,7}. The colourless 2 is monomeric in solution as was found by cryoscopic molecular weight determination⁸ and is thermally stable up to 125°C .

The hydrogenolysis of 2 (reaction 3) is a quantitative reaction as was shown by gas uptake (Töpler pump: 0.93 eq. H_2) and the quantitative formation of $\text{CH}_2(\text{SiMe}_3)_2$ (GC). The hydride 3 is probably dimeric with two Y-H bridges as the IR spectrum shows one single $\nu(\text{Y-H})$ at 1272 cm^{-1} , which shifts to 920 cm^{-1} on deuteration. The ratio $\nu(\text{Y-H})/\nu(\text{Y-D})$ of 1.38 is in accordance with the theoretical ratio of 1.41.

The hydride 3 is very reactive as it reacts with benzene under the formation of H_2 and the phenyl compound. This behaviour is quite analogous to that of the corresponding Sc and Lu compounds^{3,4}.

Further we found that 3 activates both sp^2 and

at room temperature (100°C) also all the hydrogen atoms of the pentamethylcyclopentadienyl ligand are exchanged for deuterium within five hours, but the methylene protons of $(\text{Me}_3\text{Si})_2\text{CH}_2$ are not. It is clear that $(\text{Cp}^*_2\text{YH})_n$ can be prepared very easily in a 3-step reaction from $\text{YCl}_3 \cdot 3\text{thf}$ 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, Marathea, Italy, September 1984.
1. H. Schumann, *Angew. Chem.*, **96**, 475 (1984).
 2. P.L. Watson, *J. Chem. Soc. Chem. Commun.*, 276 (1983).
 3. M.E. Thomson and J.E. Bercaw, *Pure Appl. Chem.*, **58**, 1 (1984).
 4. P.L. Watson, *J. Am. Chem. Soc.*, **104**, 337 (1983).
 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 en 2 were purified by recrystallization 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^{7,9}. The spectra are in complete accordance with the proposed formulas.
 7. 1 C₂₄H₃₈YClO (466.93): calc C 61.74; H 8.20; Y 19.04; Cl 7.59; found C 61.49; H 8.20; Y 18.90; Cl 7.64.
 - 2 C₂₇H₄₉YSi₂ (518.77): calc C 62.51; H 9.52; Y 17.14; found C 62.53; H 9.54; Y 17.06.
 - 3 C₂₀H₃₁Y (360.38): calc C 66.66; H 8.67; found C 66.59; H 8.72.
 8. M.W. 2 (cryosc., C₆H₆): calc 519; found 502 ±7.
 9. NMR data all spectra at 25°C in C₆D₆, δTMS = 0.0 in ¹H as well as ¹³C.
 - 1 ¹H NMR: 1.19 (m, 4H, βH-THF), 1.96 (s, 30H, Cp*), 3.42 (m, 4H, αH-THF); ¹³C NMR: 11.63 (C₅Me₅, ¹J_{C-H} = 125.2 Hz) 25.30 (βC-THF, ¹J_{C-H} = 133.9 Hz), 71.90 (αC-THF, ¹J_{C-H} = 149.6 Hz), 118.03 (C₅Me₅).
 - 2 ¹H NMR: -0.10 (d, 1H, ²J_{Y-H} = 2.3 Hz, Y-CHR₂), 0.17 (s, 18H, SiMe₃), 1.87 (s, 15H, C₅Me₅), 1.93 (s, 15H, C₅Me₅); ¹³C NMR: 5.02 (SiMe₃, ¹J_{C-H} = 116.6 Hz), 25.19 (d, Y-CHR₂, ¹J_{C-H} = 84.2 Hz, ¹J_{Y-C} = 36.6 Hz), 11.78 (C₅Me₅, ¹J_{C-H} = 125.5 Hz), 12.10 (C₅Me₅, ¹J_{C-H} = 125.6 Hz), 119.14 (C₅Me₅), 119.79 (C₅Me₅).
 - 3 ¹H NMR: 2.12 (s, 30 H, C₅Me₅). Y-H not observed possibly due to the reactivity of the hydride; ¹³C NMR not measured.