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NOVEL HYDROCARBYL AND HYDRIDE COMPOUNDS OF BIS-PENTAMETHYLCYCLOPENTADIENYLCELIUM (III).

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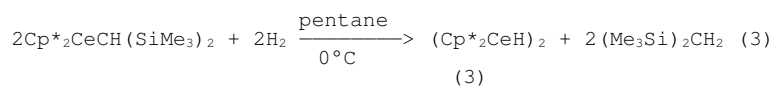
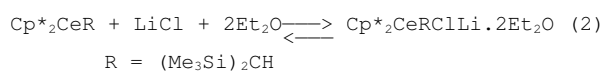
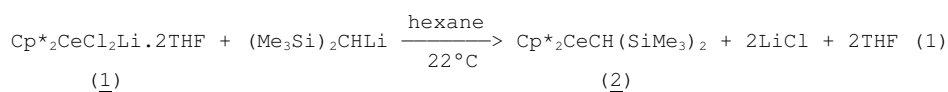
Abstract. The synthesis of novel hydrocarbyl and hydride cerium complexes $\text{Cp}^*_2\text{CeCH}(\text{SiMe}_3)_2$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) and $(\text{Cp}^*_2\text{CeH})_2$ is reported. The hydrocarbyl shows Lewis acid properties and complexes salts like LiCl . The hydride is exceptionally reactive and activates P-C bonds in PMe_3 .

In the rapidly growing field of permethylmetallo-cene derivatives of the 4f-elements Cp^*_2MX_n , cerium (III) and (IV) analogs were unknown until recently [1]. Some time ago we started investigations aimed at the synthesis of complexes of the type Cp^*_2CeR (R = alkyl, aryl) and Cp^*_2CeH , starting from chloride precursors $(\text{Cp}^*_2\text{CeCl})_n$ or related complexes. The recent publications of the synthesis and structure of $\text{Cp}^*_2\text{CeCl}_2\text{Li}(\text{OEt}_2)_2$ by Rausch et al. [2] prompt us to report here preliminary results and reactivity of a cerium hydrocarbyl $\text{Cp}^*_2\text{CeCH}(\text{SiMe}_3)_2$ (2). The compound can be obtained from a THF analog of the published $\text{Cp}^*_2\text{CeCl-LiCl}$ -diethylether complex, $\text{Cp}^*_2\text{CeCl}_2\text{Li} \cdot 2 \text{THF}$ (1) by treatment with $(\text{Me}_3\text{Si})_2\text{CHLi}$ (reaction 1). Compound 1 is accessible from Cp^*Li and $\text{CeCl}_3 \cdot n\text{THF}$ in THF and can be used either *in situ* or as a pure complex after crystallization from pentane. The pure cerium hydrocarbyl (2) crystallizes nicely from pentane as a bright red compound and was characterized fully by elemental analysis, IR and $^1\text{H-NMR}$ [4]. The coordinative unsaturation, which is so manifest in monomeric Group 3 and 4f-element complexes of the type Cp^*_2MX that they

either form di- or oligomers, adducts with Lewis bases e.g. THF or ether, coordinate salt molecules e.g. LiCl or form agostic interactions with C-H bonds [1,5], is very emphatically present in Cp^*_2CeX complexes, even when X is a bulky ligand like $(\text{Me}_3\text{Si})_2\text{CH}$. As an example we mention the behaviour of 2 towards LiCl in the presence of diethylether. The red compound then forms a bright yellow adduct [6] (reaction 2).

This complexation is the first observed for this type of compounds with this bulky alkyl ligand attached to the metal. In virtually all other cases known the bulk of the bistrimethylsilylmethyl ligand is sufficient to block complexation despite the coordinative unsaturation.

The complexed salt is rather loosely bound and work-up of the complex in non-coordinative hydrocarbon solvents suffices to shift eq. (2) to the left. This salt complexation for 2 indicates that this compound (probably together with its La analog) stands at an extreme side of the reactivity of Group 3 and 4f-element compound of this type. The atoms of Ce and La are the largest in this series and e.g. the pre-complexation step in vari-



ous reactions can be achieved here even with large substrate molecules while for steric reasons this may be impossible for the other metals [7].

We are now exploring the reactivity of 2 and as an example we report here the hydrogenolysis of 2, [8], to give an exceptionally reactive hydride $(\text{Cp}^*_2\text{CeH})_2$ (3), (reaction 3).

The hydride, 3, reacts with MeI with formation of methane (Töpler pump experiment) and $(\text{Cp}^*_2\text{CeI})_n$.

Studies of 3 in aromatic solvents (benzene and toluene) show that under ambient conditions (25°C, 24 h) the solvent does not react in the way well-known for the heavier 4f-element analogs [9].

Formation of aryl or benzyl compounds could not be established nor was H_2 liberated. Attempts to break up the dimeric structure by complexation with bases e.g. PMe_3 led to an unique observation of presumably P-C bond activation.

When 3 is exposed in benzene or toluene to PMe_3 , methane (0,5 mol/Ce) is liberated. The cerium containing product could not yet be identified. This reaction and others are under investigation at the moment.

References and Notes

1. *H. Schumann*, *Angew. Chem.*, **96**, 475 (1984).
2. *M.D. Rausch, K.M. Morlaty, J.L. Atwood, J.A. Weeks, W.E. Hunter, and H.G. Brittain*, *Organometallics*, **5**, 1281 (1986).
3. To a solution of 2,57 g $\text{Cp}^*_2\text{CeCl}_2\text{Li} \cdot 2\text{THF}$ in 100 ml of n-hexane was added an equivalent amount of $(\text{Me}_3\text{Si})_2\text{CHLi}$ (0.9 M solution in Et_2O) at room temperature, which gave an instantaneous reaction. After solvent removal and washing with toluene, the bright red product was extracted with pentane and crystallized: yield 1,6 g (75%).
4. $^1\text{H-NMR}$ (d_8 -toluene, 20°C, $\delta_{\text{TMS}}=0,0$, lw = line-width): 39.4 (s, 1H, lw = 70 Hz $(\text{Me}_3\text{Si})_2\text{CH}$); 3,64 (s, 15 H, lw 9 Hz, Cp^*); 3.29 (s, 15 H, lw 9 Hz, Cp^*); -10,5 (s, 18 H, lw 9 Hz, Me_3Si). IR (nujol, cm^{-1}): 2710 (w), 1255 (s), 1240 (s), 1040 (s), 1030 (m), 860 (vs), 820 (s), 655 (m), 580 (m), 370 (m).
5. *K.H. den Haan and J.H. Teuben* *Recl. Trav. Chim. Pays-Bas*, **103**, 333 (1984).
6. The adduct was not obtained analytically pure. A related TMEDA adduct $\text{Cp}^*_2\text{CeCH}(\text{SiMe}_3)_2 \cdot \text{LiCl} \cdot 2\text{TMEDA}$, was obtained in a pure state from 2, LiCl and TMEDA in pentane.
7. *G. Jeske, H. Lauke, H. Mauermann, P.N. Swebston, H. Schumann, and T.J. Marks*, *J. Am. Chem. Soc.*, **107**, 8091 (1985).
8. A solution of 2 (0.149 g, 0.261 mmol) in 10 ml of pentane was stirred under hydrogen (1 atm) at 0°C. The hydrogen uptake was monitored by Töpler pump technique (consumed: 0.276 mmol H_2). The green product was isolated and characterized.
 $^1\text{H-NMR}$ (C_6D_6 , 20°C, $\delta_{\text{TMS}} = 0.0$): -1.0 lw = 35 Hz, Cp^* ; the hydride resonance could not be located due to the paramagnetism of the compound. IR (Nujol, cm^{-1}): 2705 (w), 1120 (s, br), 1015 (m), 760 (w); reaction with D_2 gave $(\text{Cp}^*_2\text{CeD})_2$ $\nu_{\text{CeD}} = 795 \text{ cm}^{-1}$; $\nu_{\text{CeH}}/\nu_{\text{CeD}} = 1,41$. Anal. Found (Calcd) dimer: MW 770 (825) (cryoscopic in benzene).
9. *P.L. Watson*, *J. Chem. Soc. Chem. Comm.*, 267 (1983).