



Communication

Reactivity of di-*n*-butyl-dicyclopentadienylzirconium towards amido stabilized stannylenes

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ABSTRACT

Reaction of $\text{Sn}[(\text{N}(\text{C}_6\text{H}_3\text{iPr}_2-2,6)(\text{SiMe}_3))_2]$ and $[\{\text{Sn}(\text{N}(\text{C}_6\text{H}_3\text{iPr}_2-2,6)(\text{SiMe}_3)(\mu\text{-Cl})_2)]$ with di-*n*-butyl-dicyclopentadienylzirconium yielded the trimetallic a carbene-like complex $\{[(\text{N}(\text{C}_6\text{H}_3\text{iPr}_2-2,6)(\text{SiMe}_3))(n\text{-Bu})\text{Sn}]_2\text{Cp}_2\text{Zr}$. The oxidation of $\{[(\text{N}(\text{C}_6\text{H}_3\text{iPr}_2-2,6)(\text{SiMe}_3))(n\text{-Bu})\text{Sn}]_2\text{Cp}_2\text{Zr}$ by oxygen gives the five-membered dioxadistannazirconacyclic complex $\{[(\text{N}(\text{C}_6\text{H}_3\text{iPr}_2-2,6)(\text{SiMe}_3))(n\text{-Bu})\text{Sn}]_2\text{O}_2\text{Cp}_2\text{Zr}$.

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1. Introduction

Organometallic complexes of early transition metals and their p-block analogues were extensively studied in recent times, especially for their applications in organic synthesis. For example, Piers and coworkers have studied the reactivity of Lappert's stannylene towards zirconocene derivatives [1]. We have recently reported analogous reactivity and products of C,N-chelated stannylene (**1**) [2] and plumbylene (**2**) [3,4] toward the zirconocene derivative known as Negishi reagent [5] (Scheme 1), where the product is the trinuclear carbene-like complex **4** in the case of **1** and a zirconium complex formed by a C–H activation with C–C coupling containing two five-membered cycles in the case of plumbylene **2** [6]. Different products of transmetalation (**6**) with ligand transfer from plumbylene to zirconocene can be isolated when only one instead of two equivalents of *n*-butyllithium is used for *in situ* generated zirconocene [7]. This paper presents an analogous reaction using the bulky amido ligand (L^{N}) stabilized stannylenes ($\text{SnL}_2^{\text{N}} = (\text{Sn}[(\text{N}(\text{C}_6\text{H}_3\text{iPr}_2-2,6)(\text{SiMe}_3))_2])$ (**7**), $[\text{SnL}^{\text{N}}(\mu\text{-Cl})_2] = \{\text{Sn}[(\text{N}(\text{C}_6\text{H}_3\text{iPr}_2-2,6)(\text{SiMe}_3))(\mu\text{-Cl})_2]$ (**8**)) instead of a C,N-chelated one (**1**).

2. Results and discussion

The reaction of di-*n*-butyl-di-cyclopentadienylzirconium generated *in situ*, prepared by reaction of zirconocene dichloride with two equivalents of *n*-butyllithium, with stannylene (**7**) stabilized

by bulky amido ligand L^{N} (Scheme 2) at -78°C , leads to the formation of a red solution. Allowing the latter to raise to room temperature causes the colour to change from deep to light red and elemental tin to precipitate. Because of its thermal instability, even at 20°C , compound **9** could not be isolated and identified. The reaction course differs from the one reported by Piers et al. who used the bulky $\text{CH}(\text{SiMe}_3)_2$ ligand [**1**] as well as the C,N chelating ligand for ensuring the stabilization of stannylene **1** [6]. In the case of the stannylene stabilized by the amido ligand **7**, we observed migration of the *n*-butyl group from zirconium to tin, followed by elimination of one of the amido ligands and complexation with one half equivalent of dicyclopentadienylzirconium, providing compound **9**. This proposal is based on the isolation of the oxidation product **10** of compound **9**, as a light pink crystalline substance characterized by X-ray diffraction (Fig. 1). Elemental tin, $\text{HN}(\text{C}_6\text{H}_3\text{iPr}_2-2,6)(\text{SiMe}_3)$ and $\text{H}_2\text{N}(\text{C}_6\text{H}_3\text{iPr}_2-2,6)$ were identified by GC/MS and XRF (X-ray Fluorescence) techniques as products in the reaction mixture where substituted hydrazines were expected instead. The same compounds were also found in the reaction of **3** with **8**. The first crystals of **10** as an oxidation product of **9** were isolated by chance because the stop cock of the Schlenk tube was not sufficiently greased. Thus, subsequent air oxidation of **9** to **10** on purpose provided the desired product essentially quantitatively.

Recently, we have described oxidation products of **4** [6]. A six-membered oxa-zircona cyclic complex was obtained from the zirconocene moiety, while the eight-membered oxa-stanna cyclic complex raised from the stannylene moiety bearing its ligands. The course of the oxidation of **9** is completely different, its resulting

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–78 °C in the presence of two equivalents of **7** or **8**. During warming, a slow darkening of the reaction mixture was observed. Above –20 °C a metal precipitation and colour disappearance were observed. The light red coloured solution was filtered off and kept at –20 °C for several days. Due to an erroneous manipulation of the stopcock of the Schlenk flask, crystals of **10**, as oxidation product of the actually desired $\text{Cp}_2\text{Zr}(\text{SnL}_2)_2$ compound, were isolated. Repeating the reaction several times with **7** and **8** gave the same results when the stopcock was not greased. Elemental Anal. Calc.: C, 52.7; H, 6.63; N, 2.56. Found: C, 52.7; H, 6.60; N, 2.5%. NMR characterization of **10**: ^1H NMR (500.13 MHz, THF- d_8 , 295 K, ppm): –0.24 (s, $\text{Si}(\text{CH}_3)_3$, 18H), 0.69 (t, $\text{CH}_3(\delta)$, 6H), 0.76 (m, $\text{CH}_2(\gamma)$, 4H), 0.90 (m, $\text{CH}_2(\beta)$, 4H), 1.31 (broad, $\text{CH}_2(\alpha)$, 4H), 0.65 (d, $\text{CH}(\text{CH}_3)_2$, $J = 8.6$ Hz, 12H), 0.80 (d, $\text{CH}(\text{CH}_3)_2$, $J = 8.6$ Hz, 12H), 3.24 (h, $\text{CH}(\text{CH}_3)_2$, $J = 8.6$ Hz, 4H), 5.78 (s, Cp, 10H), 6.49 (broad, H(meta), 4H), 6.57 (broad, H(para), 2H). ^{119}Sn NMR (186.5 MHz, THF- d_8 , 295 K, ppm): 62.7, $^2J(^{119}\text{Sn}, ^{117}\text{Sn}) = 5910$ Hz. Crystallographic data for **10**: $\text{C}_{48}\text{H}_{80}\text{N}_2\text{O}_2\text{Si}_2\text{Sn}_2\text{Zr}$, $M = 1101.92$, Monoclinic, $C 2/c$, $a = 17.0173(11)$, $b = 11.9137(9)$, $c = 25.8271(9)$ Å, $\beta = 101.887(12)^\circ$, $Z = 4$, $V = 5123.9(6)$ Å 3 , $D_c = 1.428$ g cm $^{-3}$, $\mu = 1.250$ mm $^{-1}$, $T_{\text{min}} = 0.659$, $T_{\text{max}} = 0.867$; 18461 reflections measured ($\theta_{\text{max}} = 27.50^\circ$), 5627 independent ($R_{\text{int}} = 0.0431$), 4931 with $I > 2\sigma(I)$, 258 parameters, $S = 1.162$, $R_1(\text{obs. data}) = 0.0452$, $wR_2(\text{all data}) = 0.0968$; max., min. residual electron density = 1.096, –1.016 e Å $^{-3}$.

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Appendix A. Supplementary material

CCDC 711068 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2009.01.041](https://doi.org/10.1016/j.jorganchem.2009.01.041).

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