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

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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 transmetallation (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 (SnL_2^N) $(Sn[(N(C_6H_3iPr_2-2, 6)(SiMe_3)]_2)$ (7), $[SnL^N(\mu-Cl)]_2 = \{Sn[(N(C_6H_3))]_2 \}$ $iPr_2-2,6)(SiMe_3)](\mu-Cl)]_2$ (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

ABSTRACT

Reaction of Sn[(N(C₆H₃iPr₂-2,6)(SiMe₃)]₂ and [{Sn(N(C₆H₃iPr₂-2,6)(SiMe₃)(μ -Cl)₂] with di-*n*-butyl-dicyclopentadienylzirconium yielded the trimetallic a carbene-like complex {[(N(C₆H₃iPr₂-2,6)(SiMe₃)](*n*-Bu)Sn}₂Cp₂Zr. The oxidation of {[(N(C₆H₃iPr₂-2,6)(SiMe₃)](*n*-Bu)Sn}₂Cp₂Zr by oxygen gives the fivemembered dioxadistannazirconacyclic complex {[(N(C₆H₃iPr₂-2,6)(SiMe₃)](*n*-Bu)Sn}₂O₂Cp₂Zr. © 2009 Elsevier B.V. All rights reserved.

> 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 CH[(SiMe₃)]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, $HN(C_6H_3iPr_2-2,6)(SiMe_3)$ and $H_2N(C_6H_3iPr_2-2,6)$ 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 sixmembered 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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Scheme 1. Reactivity of zirconocene 3 towards 1 and 2.



Scheme 2. Reactivity of zirconocene 3 towards amido stannylenes (7, 8) and further oxidation.

compound **10** being obtained by insertion of an oxygen atom from an O₂ molecule into each of the Zr–Sn bonds, with exclusive formation of a five-membered ring containing of one zirconium, two oxygen and two tin atoms (Fig. 1). The tin–tin bond length (2.804(4) Å) compares well to standard Sn–Sn bond distances of 2.78 Å in Me₆Sn₂, as found in the vapour phase by GED (gas electron diffrac-



Fig. 1. Molecular structure of **10**, ORTEP diagram, 50% probability level, hydrogen atoms are omitted for clarity. Selected interatomic distances and angles $[Å^\circ]$: Sn(1)–O(1) 1.986(4), Sn(1)–N(1) 2.043(3), Sn(1)–C(16) 2.148(5), Sn(1)–Sn(1a) 2.804(4), Sn(1a)–O(1a) 1.986(4), Zr(1)–O(1a) 1.956(3), Zr(1)–O(1) 1.956(4), Zr(1)–C(21) 2.561(4), Zr(1)–C(21) 2.561(4), Zr(1)–C(22) 2.565(4), Zr(1)–C(24) 2.577(5), Zr(1)–C(24) 2.577(5), Zr(1)–C(23) 2.583(5), Zr(1)–C(23) 2.583(5), Zr(1)–C(22) 2.587(5), Zr(1)–C(22) 2.587(4), Si(1)–N(1) 1.734(4), Si(1a)–N(1a) 1.733(4), O(1)–Zr(1)–O(1a) 95.09(17), C(1)–N(1)–Si(1) 124.6(3), C(1)–N(1)–Sn(1) 114.5(3), Si(1)–N(1)–Sn(1) 120.58(17), Zr(1)–O(1)–Sn(1) 128.23(15), Zr(1)–O(1a) 89.23(8), O(1a)–Sn(1a)–Sn(1a) 89.23(8), N(1)–Sn–C(16) 106.12(15).

tion), and of 2.763(2) Å in Ph₆Sn₂ [8]. On the other hand, the Sn–Sn bond distance of 4.2364 Å in the complex of Piers [1] and of 3.5567 Å in **4** [6] indicates very weak contacts in both complexes, if any. The coordination sphere of the zirconium and tin atoms is essentially tetrahedral, with the two Cp rings and the two oxygen atoms for the zirconium atom, and an oxygen atom, the nitrogen atom from the amidic ligand, the *n*-butyl carbon atom and the second tin atom for each of the tin atoms. The bond angles are almost ideally tetrahedral angle, except the O–Sn–Sn angles which are close to 90° (89.23°) because of the ring strength resulting from the Sn–Sn bond formation. The plane defined by zirconium and two oxygen atoms does not contain the tin atoms, located 0.414 Å above and below that plane. Most bond distances and angles in the tin moiety hardly differ from the corresponding ones in the parent stannylene **7** (see Fig. 1 caption) [9].

In solution, with different solvents, THF as a tin coordinating one and toluene as a non-coordinating one, the ¹H and ¹¹⁹Sn NMR spectra reveal the same patterns and chemical shift values, evidencing that the metal atoms display the same coordination in both solvents. The ¹H NMR spectrum reveals broad signals, suggesting some dynamic exchange. The ¹¹⁹Sn chemical shift at 62.7 ppm is about 400 ppm upfield to the parent stannylene **7** (439.9 ppm), as a result of the tin oxidation state increase from II to IV. The covalent bond formation between the tin atoms, evidenced above by the short Sn–Sn bond distances, is reflected by a huge value of the ²J(¹¹⁹Sn, ¹¹⁷Sn) coupling constant, being 5910 Hz.

3. Experimental

3.1. X-ray diffraction

Single crystals of compound **10** suitable for X-ray diffraction studies were obtained at -20 °C from various solvents among which mainly diethylether. Crystallographic data were obtained on a Nonius KappaCDD diffractometer with area detector, source of Mo K α and a graphite monochromator. A single crystal was mounted on a glass fibre in inert oil and measured at wave length 0.71073 Å.

The structure was solved by direct methods (sIR92 [10]). All reflections were used in the structure refinement based on F^2 by a full-matrix least-squares technique (sHELXL97 [11]). Heavy atoms were refined anisotropically. Hydrogen atoms were mostly localized on a difference Fourier map, but in order to ensure the uniformity of treatment of the crystal, all hydrogen atoms were recalculated into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2 U_{eq}$ (pivot atom) or of 1.5 U_{eq} for the methyl moiety. Absorption correction was carried on, using GAUSSIAN integration from crystal shape [12].

A full list of crystallographic data and parameters including fractional coordinates is deposited at the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, UK [Fax: int. code +44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

3.2. NMR spectroscopy

The ¹H and ¹¹⁹Sn NMR spectra were recorded in deuterated solvents (THF- d_8) at 295 K on Bruker Avance 500 spectrometer in pulsed mode with Fourier transform, and tuned at, respectively, 500.14 MHz for ¹H, and 186.5 MHz for ¹¹⁹Sn, using a five mm wide-zone tuneable sampler. The ¹H chemical shifts were calibrated to residual THF (δ (¹H) = 1.73 ppm) resonance.

3.3. Attempts to prepare compound 10

In situ generated zirconocene [5] was trapped while warming up a THF solution of $Cp_2Zr(n-Bu)_2$ to room temperature from

-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 $Cp_2Zr(SnL_2^N)_2$ 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, Si(CH₃)₃, 18H), 0.69 (t, CH₃(δ), 6H), 0.76 (m, CH₂(γ), 4H), 0.90 (m, CH₂(β), 4H), 1.31 (broad, CH₂(α), 4H), 0.65 (d, CH(CH₃)₂, J = 8.6 Hz, 12H), 0.80 (d, CH(CH₃)₂, J = 8.6 Hz, 12H), 3.24 (h, *CH*(CH₃)₂, *J* = 8.6 Hz, 4H), 5.78 (s, Cp, 10H), 6.49 (broad, H(meta), 4H), 6.57 (broad, H(para), 2H). ¹¹⁹Sn NMR (186.5 MHz, THF-*d*₈, 295 K, ppm): 62.7, ²*I*(¹¹⁹Sn,¹¹⁷Sn) = 5910 Hz. Crystallographic data for **10**: $C_{48}H_{80}N_2O_2Si_2Sn_2Zr$, M = 1101.92, Monoclinic, $C_{2/c}$, $a = 17.0173(11), b = 11.9137(9), c = 25.8271(9) \text{Å}, \beta = 101.887$ $(12)^{\circ}$, Z = 4, V = 5123.9(6) Å³, D_c = 1.428 g cm⁻³, μ = 1.250 mm⁻¹, $T_{\rm min}$ = 0.659, $T_{\rm max}$ = 0.867; 18461 reflections measured ($\theta_{\rm max}$ = 27.50°), 5627 independent ($R_{int} = 0.0431$), 4931 with $I > 2\sigma I$), 258 parameters, S = 1.162, $R_1(obs. data) = 0.0452$, $wR_2(all data) =$ 0.0968; max., min. residual electron density = 1.096, $-1.016 \text{ e} \text{ \AA}^{-3}$.

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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.

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