# REACTIONS OF CYCLOPENTADIENYL TIN(II)-BASED COMPOUNDS

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**Abstract**

This paper describes a series of exploratory reactions employing bis-cyclopentadienyl Sn(II) derivatives as starting materials. Compounds such as $[Sn(\eta^5\text{-}C_5R_5)_2]$ { R = H and Me } were submitted to a series of reactions in order to reach new synthetic strategy to prepare novel heteroleptic half sandwich Sn(II) derivatives. The compound $[Sn(\eta^5\text{-}C_5H_5)_2]$ was reacted with $Li\{\mu\text{-}N(SiMe_3)\}_2C(Ph)$ and $Li(\eta^5\text{-}C_5Me_5)$ yielding $Sn(\eta^5\text{-}C_5H_5)\{\mu\text{-}N(SiMe_3)\}_2C(Ph)$ **(1)** and $[Sn(\eta^5\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ **(2)** correspondingly. Similar reactions were attempted with the analogous $[Sn(\eta^5\text{-}C_5Me_5)_2]$ with different results. Instead of the heteroleptic derivative, the reaction with $[Li(thf)_3][Si\{SiMe_3\}]$ and $LiBu^t$ yielded a mixture of products such as (i) $Sn(\eta^5\text{-}C_5Me_5)_2$/$[Sn\{Si(SiMe_3)_3\}_2]$ **(3)** and (ii) $Sn(\eta^5\text{-}C_5Me_5)_2$/$[\{Sn(Bu^t)_2\}_4]$ **(4)**, respectively. Finally, the last reaction consisted in mixing together $[Sn(\eta^5\text{-}C_5Me_5)_2]$ and $YbI_2$ from which $[Yb(\eta^5\text{-}C_5Me_5)_2I(thf)_2]$, **(5)** was isolated. All the compounds were characterised by Multinuclear Magnetic Resonance ($^1H$, $^{13}C$, $^{119}Sn$ or $^7Li$), elemental analysis and mass spectrometry.

**Introduction**

Due to their sterical and electronic properties, cyclopentadienyl ligands may be classified as some of the most important and interesting ligands in organometallic chemistry.[2] Their use in Sn chemistry led to the formation of the first monomeric and stable compound of this metal in the oxidation state 2+, $[Sn(\eta^5\text{-}C_5H_5)_2]$, which by analogy with ferrocene was called stanocene. A number of such compounds are documented in the literature by now.[3]

Stannocene-like species are potentially suitable as starting material for other type compounds, such as half sandwich tin(II) derivatives. However, few are the examples in the literature of this sort of species.[4] Until recently compounds such as $[Sn(\eta^5\text{-}C_5H_5)R]$ {$R = N(SiMe_3)_2$, $N{=}C(NMe_2)_2$ } remained as the solely examples of heteroleptic half sandwich Sn(II) derivatives. They were originated in the reaction of $[Sn(\eta^5\text{-}C_5H_5)_2]$ with $Li\{N(SiMe_3)_2\}$ or $Li\{N{=}C(NMe_2)_2\}$[5,6] where a $Li(\eta^5\text{-}C_5H_5)$ elimination was observed. The reaction of $[Sn(\eta^5\text{-}C_5H_5)_2]$ with $Li(\eta^5\text{-}C_5Me_5)$ or $Na(\eta^5\text{-}C_5Me_5)$ in thf in the presence of pmdeta {pentamethylethilenediamine) formed interesting derivatives, $[\{Li(pmdeta)\}\{Sn(\eta^5\text{-}C_5H_5)_3\}]$ and $[\{Na(pmdeta)\}\{Sn(\eta^5\text{-}C_5H_5)_3\}]$ respectively. In such compounds the Sn(II) centre is $\eta^5$ bonded to three $C_5H_5$ rings.

This work is concerning attempts to reach alternative strategies for the preparation of new Sn(II) compounds. Herein we describe: (i) the preparation $Sn(\eta^5\text{-}C_5H_5)\{\mu\text{-}N(SiMe_3)\}_2C(Ph)$ **(1)** which was characterised by multinuclear NMR spectroscopy ($^1H$, $^{13}C$ and $^{119}Sn$ ) in solution and in the solid state; (ii) the preparation of $[Sn(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)]$ **(2)** also characterised by multinuclear NMR spectroscopy ($^1H$, $^{13}C$ and $^{119}Sn$ ) in solution and in the solid state; (iii) the reactions of $[Sn(\eta^5\text{-}C_5Me_5)_2]$ with $[Li(thf)_3][Si\{SiMe_3\}]$ **(3)** and $LiBu^t$ **(4)**. (iv) Finally, it is described the reaction $[Sn(\eta^5\text{-}C_5Me_5)_2]$ with $YbI_2$ yielding $[Yb(\eta^5\text{-}C_5Me_5)_2(I)(thf)]$, **(5)**. All the compounds showed satisfactory elemental analysis.

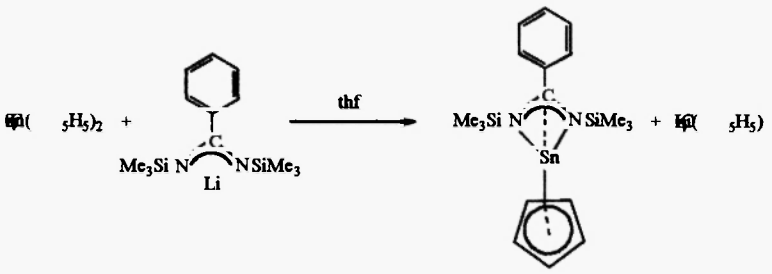
**Results and discussions**

*1) Reaction of $[Sn(\eta^5\text{-}C_5H_5)_2]$ with $Li\{\mu\text{-}N(SiMe_3)\}_2C(Ph)$:*

The ligand $Li\{\mu\text{-}N(SiMe_3)\}_2C(Ph)$ was prepared as described in the literature,[7] eq. 1.


Eq. 1

After satisfactory analysis the ligand, $Li\{\mu\text{-}N(SiMe_3)\}_2C(Ph)$, was reacted with $[Sn(\eta^5\text{-}C_5H_5)_2]$ in thf. No colour change or precipitate was observed. After removing the thf in vacuum, the derivative $Sn(\eta^5\text{-}C_5H_5)\{\mu\text{-}N(SiMe_3)\}_2C(Ph)$ **(1)**, was extracted with $Et_2O$ and isolated as an air- and moisture-sensitive white solid 82% yield, eq. 2.




Eq. 2

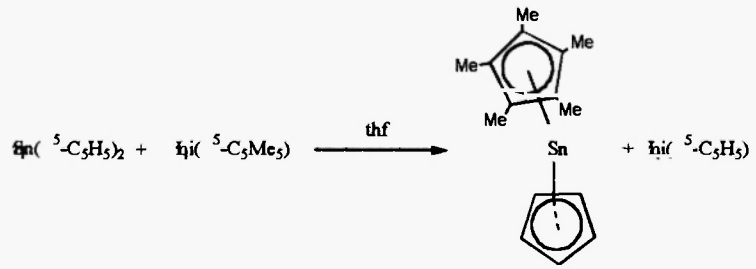
The solution-state NMR experiments were carried out using a $C_6D_6$ solution of **(1)** sealed in a 10mm NMR tube. The NMR spectrum of $^1H$ displayed signal related to $C_6H_5$, δ 6.9-7.1, $C_5H_5$, δ 6.6, and $SiMe_3$ at δ 0.1 with relative integral of 5:5:18, which indicates the presence of $C_5H_5$ and $N(SiMe_3)C(Ph)N(SiMe_3)$ groups in a ratio of 1:1. The NMR spectrum of $^{13}C\{^1H\}$ exhibited indeed resonances at δ 181 { $N(SiMe_3)C(Ph)N(SiMe_3)$}, 144, 129, 128 {$C_6H_5$}, 110 {$C_5H_5$} and 0.2 {$SiMe_3$}. In the $^{119}$Sn-NMR spectrum a single resonance at δ -560 was observed. This signal is farther from the $^{119}$Sn-chemical shift of the starting material $[Sn(\eta\text{-}C_5H_5)_2]$, δ -2199 and closer to the $^{119}$Sn signal displayed by $Sn[\{\mu\text{-}N(SiMe_3)\}_2C(Ph)]_2$, δ -247, prepared for comparison. This may be a consequence of a drastic change in the Sn-$C_5H_5$ bonding scheme. A similar variation was first observed when $[Sn(\eta^5\text{-}C_5H_5)Cl]$ reacted with $[Li\{\mu_3\text{-}OBu^t\}_3Ge]$ yielding $[Sn(\eta^5\text{-}C_5H_5)\{\mu_2\text{-}OBu^t\}_2Ge(OBu^t)]$. [8] This compound displayed a single signal at δ -286 in the $^{119}$Sn-NMR spectrum resulting from a change in the Sn-$C_5H_5$ interaction from $\eta^5$ in the starting material, $[Sn(\eta^5\text{-}C_5H_5)Cl]$, to an average $\eta^3$ - $\eta^1$ in $[Sn(\eta^5\text{-}C_5H_5)\{\mu_2\text{-}OBu^t\}_2Ge(OBu^t)]$, as confirmed by the X-ray experiment.

A single resonance was also observed in the $^{119}$Sn MAS-NMR spectrum at $\delta_{iso}$ -475. This little variation between $^{119}$Sn chemical shifts, δ -560 and $\delta_{iso}$ -475 indicates that the structures in solution- and solid-state do not differ very much. The difference is probably due to the packing forces in the solid state arrangements. The $^{119}$Sn MAS chemical shift observed for compound **(1)** is comparable to the value obtained for $Sn\{\eta^5\text{-}C_5H_5\}\{N(SiMe_3)_2\}$, $\delta_{iso}$ -580.[5]

Ligands such as $Li\{\mu\text{-}N(SiMe_3)\}_2C(Ph)$ are employed to stabilise low oxidation states of some metal ions. Also, due to its bulkiness it has the ability of preventing the formation of polymer-like structure. In this case the presence of hindered groups, $SiMe_3$, may avoid the dimerisation of **(1)**. So it is reasonable to suppose that compound **(1)** is monomeric in the solid state, eq. 2. This proposition is in accordance with the NMR results that showed little difference in the solution- and solid-state $^{119}$Sn chemical shifts.

*2) Reaction of $[Sn(\eta^5\text{-}C_5H_5)_2]$ with $[Li(\eta^5\text{-}C_5Me_5)]$*

The reaction of $[Li(\eta^5\text{-}C_5Me_5)]$ and $[Sn(\eta^5\text{-}C_5H_5)_2]$ in thf at a temperature of –78°C was performed, eq. 3.




Eq. 3

Soon after the slow addition of $[Li(\eta^5\text{-}C_5Me_5)]$ to $[Sn(\eta^5\text{-}C_5H_5)_2]$ the solution was left to warm up to ambient temperature. The colourless solution of $[Sn(\eta^5\text{-}C_5H_5)_2]$ became yellow. After a further 1 hour of stirring, the solvent was removed in vacuum and a yellow solid was obtained, $[Sn(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)]$, **(2)**. This solid was dissolved and extracted with $Et_2O$ leaving behind $[Li(\eta^5\text{-}C_5H_5)]$. After re-crystallisation in benzene compound **(2)** was employed in NMR experiments. The $^{119}$Sn-NMR spectrum showed a single signal at δ-2129 which is at the middle point of the frequencies registered for $[Sn(\eta^5\text{-}C_5H_5)_2]$ δ-2199 [9] and $[Sn(\eta^5\text{-}C_5Me_5)_2]$ δ-2140 [10]. The $^1$H-NMR displayed signals for $C_5Me_5$, δ 1,8 and $C_5H_5$, δ 6.0 with integrals 15:5. Finally the $^{13}C\{^1H\}$-NMR spectrum registered signals at δ 10.0 {$C_5Me_5$}, 117.2 {$C_5Me_5$} and 109.2 {$C_5H_5$}.

*3) Reaction of $[Sn(\eta^5\text{-}C_5H_5)_2]$ with $[Li(thf)_3][Si\{SiMe_3\}]$*

The starting material $[Li(thf)_3][Si\{SiMe_3\}]$ was prepared by reacting $Si\{Si(Me)_3\}_4$ with LiMe in thf.

Once isolated and satisfactorily analysed it was slowly added to a thf solution of $[Sn(\eta^5\text{-}C_5Me_5)_2]$ at a temperature of -78°C. There was no colour change at the beginning. However, when the dry-ice bath was removed, allowing a raise of temperature, the golden-yellow colour started to fade. The stirring was kept for a further hour when the solvent was removed in vacuum and the resultant material was washed with n-hexane and then transferred to another Schlenk flask by a filtrating cannula. The residue was characterised as $Li(\eta^5\text{-}C_5Me_5)$ that displayed signals at δ -10 and δ 1.78 in the $^7Li$ and $^1H$-NMR experiments, respectively.

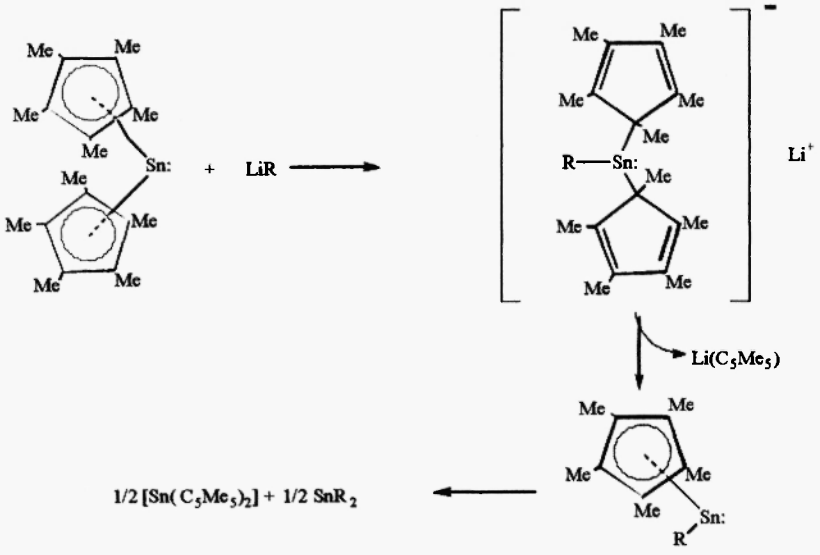
A $^{119}Sn$-NMR study of the material extracted with n-hexane revealed the presence of two resonances δ -2140 attributed to $[Sn(\eta^5\text{-}C_5Me_5)_2]$ and δ 540 which may be attempted associated to the formation of $[Sn\{Si(SiMe_3)_3\}_2]$.[11] The $^{29}Si$-NMR spectrum showed the signals at δ -7.5, $Si(SiMe_3)_3$, and δ-184 relative to $Si(SiMe_3)_3$. Our results suggest that the reaction occurred according to the eq. 4.

$$Sn(\eta^5\text{-}C_5Me_5)_2 + [Li(thf)_3][Si\{SiMe_3\}] \rightarrow Li(\eta^5\text{-}C_5Me_5) + \_\ Sn(\eta^5\text{-}C_5Me_5)_2 + \_\ [Sn\{Si(SiMe_3)_3\}_2] \qquad \text{Eq. 4}$$

*4) Reaction of $[Sn(\eta^5\text{-}C_5Me_5)_2]$ with $LiBu^t$*

A hexane solution of $LiBu^t$ was added to a Schlenk flask containing $[Sn(\eta^5\text{-}C_5Me_5)_2]$ dissolved in thf at a temperature of -78°C. Once finished the addition the dry ice/acetone bath was removed and stirring was continued for a further 1 hour. As the temperature was raised it was observed a colour change from golden yellow to pale yellow. At ambient temperature the original golden colour returned with the concomitant formation of an orange precipitate. After removing the thf, the product was washed with n-hexane (3x 50 mL), which removed unreacted $[Sn(\eta^5\text{-}C_5Me_5)_2]$. Hot xylene promoted the extraction of a compound later identified as $[Sn(Bu^t_2)_4]$. Experiments of $^{119}Sn$-NMR revealed for this compound a single signal at δ 89 with $^1J(^{119}Sn\text{-}^{117}Sn)$ 1658 Hz and $^2J(^{117}Sn\text{-}^{117}Sn)$ 1195 Hz. This derivative has been prepared previously and the results of melting point, mass spectrometry and $^{119}Sn$-NMR are in good agreement with this report.[12]

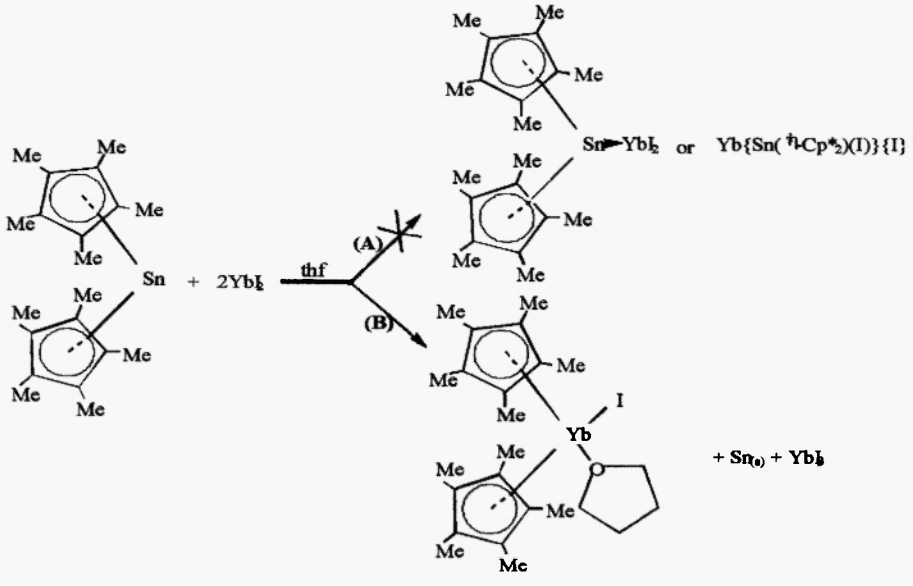
The pathways of reactions 3 and 4 were remarkably different from 1 and 2, which yielded the expected heteroleptic half sandwich Sn(II) derivatives. For 1 and 2 the Cp ring was replaced by R [$\{N(SiMe_3)\}_2C(Ph)$ and $C_5Me_5$] ligands in a nucleophilic substitution. Reactions 3 and 4 appear to occur in three steps, first an insertion of $[Sn(\eta^5\text{-}C_5Me_5)_2]$ into the Li-R bond producing an unstable intermediate, $Li\{Sn(\eta^5\text{-}C_5Me_5)_2R\}$. In a second step a $Li(\eta^5\text{-}C_5Me_5)$ elimination would produce the $Sn(\eta^5\text{-}C_5Me_5)R$ which undergoes a redistribution reaction producing _ mole of $[Sn(\eta^5\text{-}C_5Me_5)_2]$ and _ mole of $SnR_2$, R = $Si(SiMe_3)_3$ and $Bu^t$. Since the $Bu^t$ group is not hindered enough as $Si(SiMe_3)_3$, it does not stabilise $SnR_2$ keeping it in the monomeric form. Hence the monomers combine producing in this case $[Sn(Bu^t_2)_4]$, scheme 1.




*Scheme 1 – Path way for the reactions of $[Sn(\eta^5\text{-}C_5Me_5)_2]$ with LiR {R = $Si(SiMe_3)_3$ and $Bu^t$}*

*5) Reaction of $[Sn(\eta^5\text{-}C_5Me_5)_2]$ with $YbI_2$*

The compound $[Sn(\eta^5\text{-}C_5Me_5)_2]$ was reacted with $YbI_2$ in an attempt to prepare $(\eta^1\text{-}C_5Me_5)_2SnYbI_2$ (Scheme 2). There was an immediate reaction as soon as the addition of $[Sn(\eta^5\text{-}C_5Me_5)_2]$ to a $YbI_2$ thf suspension at room temperature started. A colour-change from yellow-green [suspension of $YbI_2$] to brown [solution] with the concomitant formation of a grey precipitate was observed. The grey precipitate, assumed to be Sn metal, was separated by filtration. After removing the solvent, the resultant red-brown solid was washed with hexane to remove the unreacted $[Sn(\eta^5\text{-}C_5Me_5)_2]$, and the remaining solid was extracted with hot toluene from which purple needles were isolated. [13]




*Scheme 2 - Reaction of $[Sn(\eta^5\text{-}C_5Me_5)_2]$ with $YbI_2$*

No signal was observed in experiments of $^{119}$Sn-NMR nor $^{171}$Yb-NMR for **(5)** and only a resonance at δ -26 for the Me groups of the $C_5\mathbf{Me}_5$ ring was displayed in the $^{13}$C-NMR spectrum. The paramagnetic nature of **(5)** shifts the signal from the expected position observed for Yb(II) analogues, δ 10. No signal was displayed for the quaternary carbons $\mathbf{C}_5Me_5$.

The presence of a pattern at m/z at 571 ($M^+$) in the mass spectrum indicated the formation of $[Yb(\eta\text{-}C_5Me_5)_2(I)]$ **(5)** (Scheme 2).

**Conclusions**

Our results show that $[Sn(\eta^5\text{-}C_5H_5)_2]$ reacts with LiR, R= $^-C_5Me_5$ and $^-N(SiMe_3)\}_2C(Ph)$, producing $Sn(\eta^5\text{-}C_5H_5)\{\mu\text{-}N(SiMe_3)\}_2C(Ph)$ **(1)** and $[Sn(\eta^5\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ **(2)**, through a nucleophillic substitution. On the other $[Sn(\eta^5\text{-}C_5Me_5)_2]$ reacts with LiR, R= $^-Si(SiMe_3)_3$ and $Bu^-$ generating an instable intermediate, $Li\{Sn(\eta^5\text{-}C_5Me_5)_2R\}$[14] which eliminates $Li(\eta^5\text{-}C_5H_5)$ and by redistribution reaction originates $[Sn(\eta^5\text{-}C_5Me_5)_2]$ and $SnR_2$.

The reaction of $YbI_2$ with $[Sn(\eta^5\text{-}C_5Me_5)_2]$ promoted the reduction of Sn(II) in $[Sn(\eta^5\text{-}C_5Me_5)_2]$ to Sn(metal) whilst Yb(II) being oxidized to Yb(III), eq.5.

$$Sn(\eta^5\text{-}C_5Me_5)_2 + 2\ YbI_2 \rightarrow Yb(\eta^5\text{-}C_5Me_5)_2(I)(thf) + YbI_3 + Sn_{(metal)} \qquad \text{Eq.5}$$

The $C_5Me_5$ groups, previously bonded to the Sn atom in $[Sn(\eta^5\text{-}C_5Me_5)_2]$, were transferred to the Yb centre yielding $[Yb(\eta^5\text{-}C_5Me_5)_2(I)(thf)]$. Only half the amount of $[Sn(\eta^5\text{-}C_5Me_5)_2]$ took part in this reaction, since the other half was recovered by washing with hexane. The pale-yellow residue from the toluene extract was assumed to be $YbI_3$ since no resonance was displayed in $^{171}$Yb-NMR study and no organic group was observed in the mass spectrum.

**Experimental Section:**

*Material and procedures*

Experimental work was carried out under an atmosphere of dry nitrogen. All manipulations were conducted using Schlenk techniques, employing a vacuum/nitrogen line or using a glove box under an atmosphere of nitrogen. Solvents were distilled from K or Na suspension and kept in Schlenks with K or Na mirror. The compound $Sn(\eta^5\text{-}C_5Me_5)_2$ were prepared according to normal procedure described in the literature. NMR spectra were recorded at 100.62 MHz $^{13}C\{^1H\}$) and 148.97 MHz ($^{119}Sn$ $\{^1H\}$) using a Bruker DMX-400 spectrometer equipped with an 89mm wide-bore magnet. Samples (100-150 mg) were ground in a glove box and packed into Zirconia rotors with a Kel-F end cap. Samples were spin at the magic angle with $N_2$. No sample decomposition was observed. Spin rates between 2.5 and 15 kHz were utilized. High power $^1H$ decoupling was applied during acquisition. $^{13}C$ shifts are reported relative to $SiMe_4$ and $^{119}Sn$ shifts relative to $SnMe_4$.

*Synthesis of $Sn(\eta^5\text{-}C_5H_5)\{\mu\text{-}N(SiMe_3)\}_2C(Ph)$*

To a Schlenk flask charged with $[Sn(\eta^5\text{-}C_5H_5)_2]$ (1.5 g, 6.02 mmol) in thf (70 ml) at -78°C, was added $Li\{\mu\text{-}N(SiMe_3)\}_2C(Ph)$ (1.6 g, 6.02 mmol) in thf. Neither precipitation nor colour change was observed on warming the solution to ambient temperature. Within 12 h of stirring, the solvent was removed under vacuum and $Et_2O$ was added. After filtration, the solvent was removed and the compound $Sn(\eta^5\text{-}C_5H_5)\{\mu\text{-}N(SiMe_3)\}_2C(Ph)$ was isolated as an air and moisture sensitive pale yellow solid in 88 % yield (2.43 g, 5.43 mmol). Mp 120-121 °C. $^1H$-NMR ($C_6D_6$, 400.13 MHz), δ 7.1 - 6.9, 6.6 and 0.1; $^{13}C\{^1H\}$-NMR ($C_6D_6$, 100.61 MHz), δ 181, 144, 129, 128, 110 and 0.2; $^{29}Si\{^1H\}$-NMR ($C_6D_6$, 79.49 MHz), δ -0.2; $^{119}Sn\{^1H\}$-NMR ($C_6D_6$, 149.21 MHz) δ -560; $^{119}Sn$-MAS NMR (149.21 MHz) δ -475. Elemental analysis for $C_{18}H_{28}Si_2N_2Sn$: C 47.40(48.33), H 6.24(6.31) and N 6.18(6.26).

*Reaction of $[Sn(\eta^5\text{-}C_5H_5)_2]$ with $[Li(\eta^5\text{-}C_5Me_5)]$*

To a Schlenk flask charged with $[Sn(\eta^5\text{-}C_5H_5)_2]$ (2.49g, 10 mmol) dissolved in thf (50 mL) was added *via* cannula a solution of $[Li(\eta^5\text{-}C_5Me_5)]$ (1.42g, 10 mmol) also in thf (20mL), cooled to a temperature of –78°C. After accomplishing the addition the dry-ice acetone bath was removed and the mixture was allowed to warm up to ambient temperature and remained a further hour stirring. The solution initially colourless turned pale-yellow on warming. Then, the solvent was removed under vacuum and the product, $[Sn(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)]$, was extracted with $Et_2O$, purified by re-crystallization in benzene. Yield 82%. The residue was identified as $[Li(\eta^5\text{-}C_5H_5)]$. $^1H$-NMR ($C_6D_6$, 400.13 MHz), δ 6.0, 1.8; $^{13}C\{^1H\}$-NMR ($C_6D_6$, 100.61 MHz), δ 117.2, 109.2, 10.0; $^{119}Sn\{^1H\}$-NMR ($C_6D_6$, 149.21 MHz) δ-2129; Elemental analysis for $C_{15}H_{20}Sn$: C 56.48(57.12%), H 6.33(6.34).

*Reaction of $[Sn(\eta^5\text{-}C_5Me_5)_2]$ with $[Li(thf)_3][Si\{SiMe_3\}]$*

It was added *via* cannula to a Schlenk vessel containing $[Sn(\eta^5\text{-}C_5Me_5)_2]$ (1.75 g, 4.50 mmol) in thf (70 ml), $[Li(thf)_3][Si\{SiMe_3\}_3]$ (2.12 g, 4.50 mmol) dissolved in thf, in a temperature of -78°C. The mixture was kept in this temperature until the end of the addition. Then the reaction was allowed to warm up to ambient temperature. When the temperature reached 0°C the golden-yellow colour had fade completely to pale-yellow. However, at the ambient temperature the initial colour returned. After removing the solvent, the product was washed with n-hexane (3x 50 mL) which extracted the both unreacted $[Sn(\eta^5\text{-}C_5Me_5)_2]$ and $[Sn\{Si(SiMe_3)\}_2]$. The insoluble material was identified as $Li(\eta^5\text{-}C_5Me_5)$.
$^{13}C\{^1H\}$-NMR ($C_6D_6$, 100.61 MHz), δ 181, 144, 129, 128, 110 and 0.2; $^{29}Si\{^1H\}$-NMR ($C_6D_6$, 79.49 MHz), δ -184 -*Si*$\{SiMe_3\}$ and -7.5 -Si$\{$*Si*$Me_3\}$; $^{119}Sn\{^1H\}$-NMR ($C_6D_6$, 149.21 MHz) δ -131.

*Reaction of $[Sn(\eta^5\text{-}C_5Me_5)_2]$ with $LiBu^t$*

To a Schlenk flask containing $[Sn(\eta^5\text{-}C_5Me_5)_2]$ (1.75 g, 4.50 mmol) in thf (70 ml) at a temperature of -78°C, was added *via* cannula $LiBu^t$ (2.85 mL, 4.50 mmol) in n-hexane. The mixture was kept in this temperature until the end of the addition when the dry ice bath was removed and the temperature left to raise. It was observed a fading of the original golden-yellow colour. About the ambient temperature occurred the formation of a precipitate. After removing the solvent, unreacted $[Sn(\eta^5\text{-}C_5Me_5)_2]$ was removed with n-hexane (3x50 mL). The remaining material was washed with thf (2x50mL) which removed $Li(\eta^5\text{-}C_5Me_5)$. The final product, an orange solid, was characterised as $[Sn(Bu^t_2)_4]$. Pf. 205°C(d). $^{119}Sn\{^1H\}$-NMR ($C_7D_8$, 148,91 MHz) δ 89 $^1J_{(119_{Sn}\text{-}117_{Sn})}$ 1658 Hz, $^2J_{(119_{Sn}\text{-}117_{Sn})}$ 1195 Hz. Elemental analysis for $C_{32}H_{72}Sn_4$: Calc(exp): C 41.24(42.15%), H 7.80(7.91%)

*Synthesis of $[Yb(\eta^5\text{-}C_5Me_5)_2(I)(thf)]$*

To a Schlenk tube charged with $YbI_2$ (1 g, 2.3 mmol) in thf (50 ml) at room temperature, was added with stirring $Sn(\eta^5\text{-}C_5Me_5)_2$ ( 0.9 g, 2.3 mmol ) dissolved in thf. There was an immediate change in the reaction

mixture, the initial yellow-green suspension originated a brown solution and a grey precipitate. After 4 h stirring the brown solution was filtered and the solvent was removed under vacuum resulting in a red brown residue. This solid was washed with hexane which removed unreacted $Sn(\eta^5\text{-}C_5Me_5)_2$.Following extraction with hot xylene a purple solution was filtrated and an insoluble yellow residue was left behind. Within 24 h at -30°C, purple needles of $[Yb(\eta^5\text{-}C_5Me_5)_2(I)(thf)]$(0.35g, **1**.17 mmol) were isolated from the solution in 46 %. Mp 174 °C(d). $^{13}C\{^1H\}$-NMR ($C_6D_6$, 100.61 MHz), δ -26. EI-MS: $M^+$-thf *m/z* 571, $M^+$ -thf-$C_5Me_5$ *m/z* 435. Elemental analysis for $C_{24}H_{38}YbOI$: C 43.16(44.87), H 5.64(5.96).

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