

Synthesis, structural characterization and reactivity of new tin bridged *ansa*-bis(cyclopentadiene) compounds: X-ray crystal structures of $\text{Me}_2\text{Sn}(\text{C}_5\text{Me}_4\text{R}-1)_2$ ($\text{R} = \text{H}, \text{SiMe}_3$)

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This paper is dedicated to the memory of our friend Dr. Anthony G. Avent, University of Sussex.

Abstract

The organo-tin compounds, $\text{Me}_2\text{Sn}(\text{C}_5\text{H}_4\text{R}-1)_2$ ($\text{R} = \text{Me}$ (**1**), Pr^i (**2**), Bu^i (**3**), SiMe_3 (**4**)) and $\text{Me}_2\text{Sn}(\text{C}_5\text{Me}_4\text{R}-1)_2$ ($\text{R} = \text{H}$ (**5**), SiMe_3 (**6**)), were prepared by the reaction of Me_2SnCl_2 with the lithium or sodium derivative of the corresponding cyclopentadiene. Compounds **1–6** have been characterized by multinuclear NMR spectroscopy (^1H , ^{13}C , ^{119}Sn). In addition the molecular structures of **5** and **6** were determined by single crystal X-ray diffraction studies. The transmetalation reaction of **1–6** with ZrCl_4 or $[\text{NbCl}_4(\text{THF})_2]$ gave the corresponding metallocene complexes in high yields.

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Keywords: Stannylicyclopentadiene; *ansa*-Compounds; Tin; Zirconium; Niobium

1. Introduction

Since the discovery of ferrocene in 1951 by Pauson and Miller [1], transition metal compounds with cyclopentadienyl ligands has been one of the most important fields in organometallic chemistry [2], due to their application in organic synthesis [3], homogeneous [4] and heterogeneous catalysis [5] and even as anti-tumoral agents [6]. Tin cyclopentadiene compounds were initially synthesised in 1964 in order to study and develop ^{117}Sn and ^{119}Sn NMR spectroscopic techniques [7]. Twenty years later these compounds were prepared for the principal purpose of synthetic and structural studies [8]. An excellent appli-

cation of these tin complexes is that of transmetalation reactions which has proved to be an efficient synthetic route in the preparation of early transition metallocene complexes providing not only high yields but also a high degree of selectivity [9]. As a continuation of our work in group 4 and 5 metallocene chemistry [10], we report in this paper the synthesis of novel tin bridged *ansa*-cyclopentadiene compounds and their use in the synthesis of zirconocene and in the optimization of the preparation of niobocene complexes.

2. Results and discussion

The preparation of dimethyltin bridged *ansa*-bis(cyclopentadiene) compounds was achieved via the reaction of 2 equiv. of the lithium or sodium cyclopentadienyl derivative with SnMe_2Cl_2 .

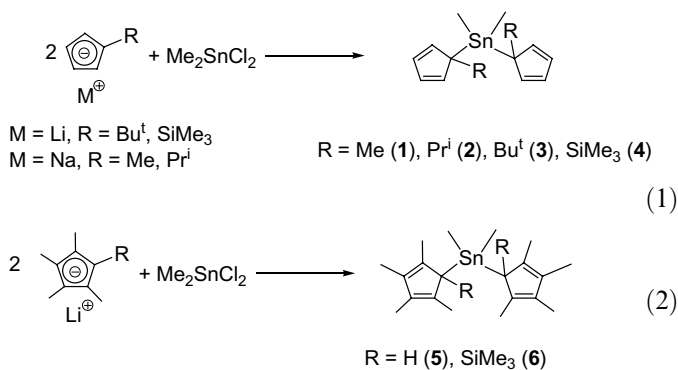
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Table 1
¹H NMR data for 1–6^a

Compound	SnMe ₂	C ₅ H ₄ or C ₅ H ₃	C ₅ Me ₄	R
Me ₂ Sn(C ₅ H ₄ Me-1) ₂ (1)	−0.23 (s, 6H) ² J(¹ H– ¹¹⁹ Sn) 53.6 Hz ² J(¹ H– ¹¹⁷ Sn) 51.2 Hz	5.54 (m, 4H), ³ J(¹ H– ^{117,119} Sn) 33.6 Hz 5.88 (m, 4H)		2.10 (s, 6H) ³ J(¹ H– ^{117,119} Sn) 13.6 Hz
Me ₂ Sn(C ₅ H ₄ Pr ⁱ -1) ₂ (2)	−0.26 (s, 6H) ² J(¹ H– ¹¹⁹ Sn) 52.0 Hz ² J(¹ H– ¹¹⁷ Sn) 49.6 Hz	5.26 (m, 4H), ³ J(¹ H– ^{117,119} Sn) 41.6 Hz 6.18 (m, 4H)		1.19 (d, 12H), ³ J(¹ H– ¹ H) 7.0 Hz 2.75 (sept, 2H) ³ J(¹ H– ^{117,119} Sn) 41.4 Hz
Me ₂ Sn(C ₅ H ₄ Bu ^t -1) ₂ (3)	−0.21 (s, 6H) ² J(¹ H– ¹¹⁹ Sn) 52.8 Hz ² J(¹ H– ¹¹⁷ Sn) 51.2 Hz	5.15 (m, 4H), ³ J(¹ H– ^{117,119} Sn) 46.4 Hz 6.42 (m, 4H)		1.30 (s, 18H)
Me ₂ Sn(C ₅ H ₄ SiMe ₃ -1) ₂ (4)	−0.20 (s, 6H) ² J(¹ H– ¹¹⁹ Sn) 52.8 Hz ² J(¹ H– ¹¹⁷ Sn) 50.4 Hz	6.05 (m, 4H), ³ J(¹ H– ^{117,119} Sn) 29.2 Hz 6.54 (m, 4H)		0.11 (s, 18H)
Me ₂ Sn(C ₅ Me ₄ H-1) ₂ (5)	−0.20 (s, 6H) ² J(¹ H– ¹¹⁹ Sn) 49.6 Hz ² J(¹ H– ¹¹⁷ Sn) 47.6 Hz		1.86 (s, 12H), 1.91 (s, 12H)	3.51 (s, 2H) ² J(¹ H– ^{117,119} Sn) 91.6 Hz
Me ₂ Sn(C ₅ Me ₄ {SiMe ₃ }-1) ₂ (6)	0.53 (s, 6H) ² J(¹ H– ¹¹⁹ Sn) 47.2 Hz ² J(¹ H– ¹¹⁷ Sn) 44.8		1.79 (s, 12H), 1.84 (s, 12H)	−0.09 (s, 18H)

^a 400 MHz, C₆D₆, chemical shifts in δ.



Compounds 1–6 have been characterized by ¹H (Table 1), ¹³C{¹H} (Table 2) and ¹¹⁹Sn (Table 3) NMR spectroscopy and by mass spectrometry (see Section 4). NMR spectral data for 1–6 indicated that only one of the possible isomers was present and differs from the observation of multiple isomers in analogous silicon and germanium bridged *ansa*-bis-cyclopentadiene ligands [8c,11]. In the ¹H NMR spectra of 1–6, a singlet, at ca. −0.2 ppm, corresponding to the six protons of the SnMe₂ bridging unit, was observed. In addition, the satellite signals due to coupling with the ¹¹⁷Sn and ¹¹⁹Sn isotopes at a two bond distance could be easily distinguished and gave values of approximately, ¹H–¹¹⁷Sn 50 Hz and ¹H–¹¹⁹Sn 52 Hz.

In the ¹H NMR spectra of 1–4, two multiplets, at ca. 5.5 and 5.9 ppm, were assigned to the four C₅ ring protons. This indicates that the symmetry of the molecule is such that the alkyl substituent is located in the C¹ position of the cyclopentadienyl ring. For the equivalent cyclopentadienyl ring protons, C² and C⁵, at three bond distance to

the tin atom, tin satellite signals were observed with values of ³J ¹H–^{117,119}Sn of ca. 30 Hz.¹

In the ¹H NMR spectrum of 1, a singlet was observed for the protons of the methyl substituent of the cyclopentadienyl ring along with its tin satellite signals (³J ¹H–^{117,119}Sn 13.6 Hz). Compound 2 gave, in the ¹H NMR spectrum, a doublet signal, assigned to the methyl groups of the isopropyl unit, at 1.19 ppm and a septuplet, at 2.75 ppm, with its tin satellite signals (³J ¹H–^{117,119}Sn 41.6 Hz), corresponding to the remaining proton. For 3 and 4, a singlet signal was observed, in the ¹H NMR spectra, for the protons of the *tert*-butyl or trimethylsilyl groups, respectively.

The ¹H NMR spectra of 5 and 6 are similar in nature. Two singlets were observed for the methyl substituents of the cyclopentadienyl rings between 1.8 and 1.9 ppm. For 5 a signal, at 3.51 ppm, with tin satellites (²J ¹H–^{117,119}Sn 91.6 Hz) was recorded for the proton in the C¹ position. For 6 a singlet was observed at −0.09 ppm and assigned to the trimethylsilyl protons.

In the ¹³C{¹H} NMR spectra of 1–6, a signal, at ca. −10 ppm, was observed for the SnMe₂ carbon atoms. Tin–carbon coupling gave values of approximately ¹J ¹³C–¹¹⁷Sn 330 Hz and ¹³C–¹¹⁹Sn 350 Hz. Three signals were recorded for the cyclopentadienyl carbon atoms. The C¹ atom gave a signal at ca. 100 ppm for 1–4 and 60 ppm for 5 and 6. In all cases, the coupling constant, at one bond distance, between the ¹³C and ¹¹⁷Sn and ¹¹⁹Sn nuclei were of the order of 45 Hz.

¹ In some cases we were unable to resolve the independent satellite signals corresponding to the two tin nuclei and therefore the coupling constant given is an approximate value that can be applied to either nucleus.

Table 2
 $^{13}\text{C}\{^1\text{H}\}$ NMR data for **1–6**^a

Compound	SnMe_2	C_5	C_5Me_4	R
$\text{Me}_2\text{Sn}(\text{C}_5\text{H}_4\text{Me}-1)_2$ (1)	−9.6 $^1J(^{13}\text{C}-^{119}\text{Sn})$ 346.2 Hz $^1J(^{13}\text{C}-^{117}\text{Sn})$ 331.6 Hz	103.4, $^1J(^{13}\text{C}-^{117,119}\text{Sn})$ 40.1 Hz 115.7, 138.9		15.4
$\text{Me}_2\text{Sn}(\text{C}_5\text{H}_4\text{Pr}^i-1)_2$ (2)	−9.3 $^1J(^{13}\text{C}-^{119}\text{Sn})$ 346.0 Hz $^1J(^{13}\text{C}-^{117}\text{Sn})$ 329.2 Hz	96.0, $^1J(^{13}\text{C}-^{117,119}\text{Sn})$ 37.3 Hz 120.5, 150.0		24.0, 29.4
$\text{Me}_2\text{Sn}(\text{C}_5\text{H}_4\text{Bu}^t-1)_2$ (3)	−9.2 $^1J(^{13}\text{C}-^{119}\text{Sn})$ 344.4 Hz $^1J(^{13}\text{C}-^{117}\text{Sn})$ 329.2 Hz	92.0, $^1J(^{13}\text{C}-^{117,119}\text{Sn})$ 43.6 Hz 123.8, 152.9		31.5, 32.5
$\text{Me}_2\text{Sn}(\text{C}_5\text{H}_4\text{SiMe}_3-1)_2$ (4)	−7.2 $^1J(^{13}\text{C}-^{119}\text{Sn})$ 356.6 Hz $^1J(^{13}\text{C}-^{117}\text{Sn})$ 341.4 Hz	100.1, $^1J(^{13}\text{C}-^{117,119}\text{Sn})$ 44.0 Hz 112.5, 133.2		−0.4
$\text{Me}_2\text{Sn}(\text{C}_5\text{Me}_4\text{H}-1)_2$ (5)	−10.4 $^1J(^{13}\text{C}-^{119}\text{Sn})$ 348.3 Hz $^1J(^{13}\text{C}-^{117}\text{Sn})$ 330.7 Hz	57.3, $^1J(^{13}\text{C}-^{117,119}\text{Sn})$ 45.6 Hz 130.4, 133.2	11.3, 13.9	
$\text{Me}_2\text{Sn}(\text{C}_5\text{Me}_4\{\text{SiMe}_3\}-1)_2$ (6)	−2.1 $^1J(^{13}\text{C}-^{119}\text{Sn})$ 354.4 Hz $^1J(^{13}\text{C}-^{117}\text{Sn})$ 340.4 Hz	59.5, $^1J(^{13}\text{C}-^{117,119}\text{Sn})$ 44.2 Hz 133.0, 135.1	11.9, 15.7	−0.1

^a 100 MHz, C_6D_6 , chemical shifts in δ .Table 3
 ^{119}Sn NMR data for **1–6**^a

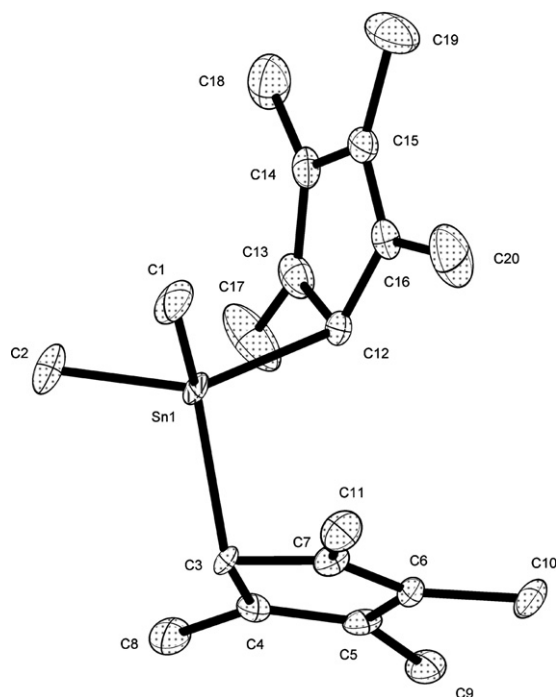
Compound	SnMe_2
$\text{Me}_2\text{Sn}(\text{C}_5\text{H}_4\text{Me}-1)_2$ (1)	18.0
$\text{Me}_2\text{Sn}(\text{C}_5\text{H}_4\text{Pr}^i-1)_2$ (2)	22.9
$\text{Me}_2\text{Sn}(\text{C}_5\text{H}_4\text{Bu}^t-1)_2$ (3)	24.0
$\text{Me}_2\text{Sn}(\text{C}_5\text{H}_4\text{SiMe}_3-1)_2$ (4)	11.7
$\text{Me}_2\text{Sn}(\text{C}_5\text{Me}_4\text{H}-1)_2$ (5)	34.1
$\text{Me}_2\text{Sn}(\text{C}_5\text{Me}_4\{\text{SiMe}_3\}-1)_2$ (6)	−16.6

^a 149 MHz, C_6D_6 , chemical shifts in δ .

One signal was observed in the ^{119}Sn NMR spectra of **1–6**. This signal was displaced upfield for the trimethylsilyl containing compounds (**4** and **6**). For **1–3** and **5**, increasing alkyl substitution results in downfield displacement of the tin signal.

The molecular structures of **5** and **6** were established by single-crystal X-ray diffraction studies. The molecular structures and atomic numbering schemes are shown in Figs. 1 and 2. Selected bond lengths and angles for **5** and **6** are given in Tables 4 and 5, respectively. For **5**, two distinct molecules were located in the asymmetric unit.

The molecular structures of **5** and **6** are of a similar nature. The geometry around the tin atom is clearly tetrahedral. The cyclopentadienyl units are essentially planar with the C^1 atom located only 0.100 Å, 0.100 Å, 0.094 Å and 0.087 Å for **5** and **6** out of the plane defined by the other four carbon atoms. Three long and two short bond distances are observed between the carbon atoms of the C_5 ring. The hybridization of C^1 atom of the cyclopentadienyl moiety is sp^3 and the σ -bond lengths with the tin atom are slightly longer than those recorded for the tin-methyl carbon distances. The tin-ring plane angles of (111.41°, 115.85°, 116.22° and 111.86° for **5**; 125.35° and 120.39° for **6**) rule out a $\pi\text{-}\eta^1$ type of interaction of the

Fig. 1. Molecular structure and atom-labeling scheme for $\text{Me}_2\text{Sn}(\text{C}_5\text{Me}_4\text{H}-1)_2$ (**5**), with thermal ellipsoids at 30% probability.

metal with the aromatic ring of the sort which has recently been reported for beryllium and zinc metallocene complexes [12]. Selected structural data of **5** and **6** can be compared with similar tin bridged *ansa*-bis(cyclopentadiene) compounds using Table 6.

The transmetalation reaction of **1–6** with ZrCl_4 or $[\text{NbCl}_4(\text{THF})_2]$ gave the corresponding metallocene complexes, **7–12**, in high yields (Eqs. (3) and (4)). The reaction was carried out in toluene in reflux and for 24 h. After

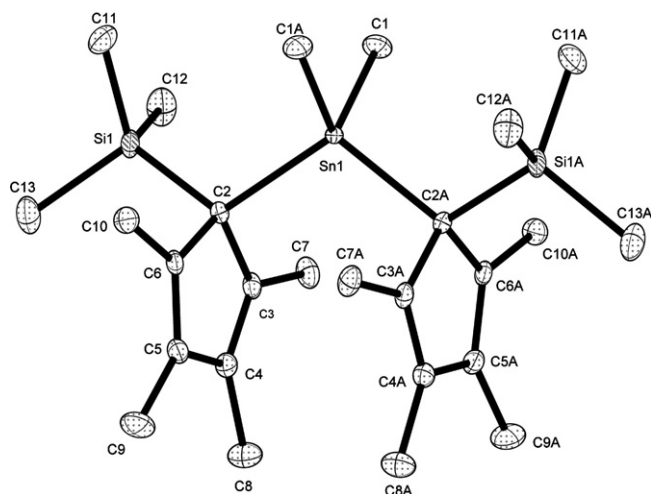


Fig. 2. Molecular structure and atom-labeling scheme for $\text{Me}_2\text{Sn}(\text{C}_5\text{Me}_4[\text{SiMe}_3]-1)_2$ (**6**), with thermal ellipsoids at 30% probability.

Table 4
Selected bond lengths (Å) and angles (°) for **5**

	5a	5b
<i>Bond lengths (Å)</i>		
Sn(1)–C(1)	2.145(4)	2.149(4)
Sn(1)–C(2)	2.144(4)	2.158(4)
Sn(1)–C(3)	2.195(4)	2.206(4)
Sn(1)–C(12)	2.205(4)	2.202(4)
C(3)–C(4)	1.480(5)	1.483(5)
C(4)–C(5)	1.356(5)	1.357(6)
C(5)–C(6)	1.459(5)	1.460(6)
C(6)–C(7)	1.359(5)	1.358(6)
C(3)–C(7)	1.497(5)	1.485(6)
C(12)–C(13)	1.475(6)	1.494(6)
C(13)–C(14)	1.353(6)	1.363(6)
C(14)–C(15)	1.457(6)	1.460(5)
C(15)–C(16)	1.353(6)	1.353(6)
C(12)–C(16)	1.480(6)	1.472(6)
<i>Bond angles (°)</i>		
C(1)–Sn(1)–C(2)	106.4(2)	107.0(2)
C(1)–Sn(1)–C(3)	110.7(2)	111.4(2)
C(1)–Sn(1)–C(12)	111.2(2)	112.1(2)
C(2)–Sn(1)–C(3)	110.1(2)	112.0(2)
C(2)–Sn(1)–C(12)	112.2(2)	108.9(2)
C(3)–Sn(1)–C(12)	106.3(1)	105.5(1)
Sn(1)–C(3)–C(4)	105.5(3)	107.5(2)
Sn(1)–C(3)–C(7)	103.5(2)	106.7(3)
Sn(1)–C(12)–C(13)	106.2(2)	104.1(2)
Sn(1)–C(12)–C(16)	107.6(3)	105.0(2)
C(3)–C(4)–C(5)	109.2(3)	108.7(4)
C(4)–C(5)–C(6)	108.9(3)	108.9(3)
C(5)–C(6)–C(7)	109.2(3)	109.3(4)
C(6)–C(7)–C(3)	108.3(3)	108.3(4)
C(4)–C(3)–C(7)	104.0(3)	104.5(3)
C(12)–C(13)–C(14)	108.5(4)	108.0(3)
C(13)–C(14)–C(15)	108.8(4)	109.2(3)
C(14)–C(15)–C(16)	109.4(4)	108.7(3)
C(12)–C(16)–C(15)	108.0(4)	109.4(3)
C(13)–C(12)–C(16)	104.9(3)	104.4(3)

evaporation of toluene and extraction with hexane, SnMe_2Cl_2 was easily removed by filtration and the metallocene dichloride obtained by crystallization of the hexane

Table 5
Selected bond lengths (Å) and angles (°) for **6**

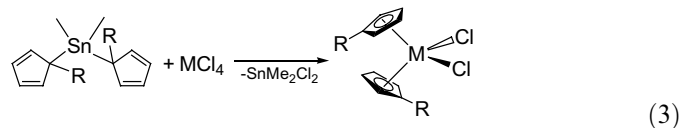
6	
<i>Bond lengths (Å)</i>	
Sn(1)–C(1)	2.151(2)
Sn(1)–C(2)	2.190(2)
Si(1)–C(2)	1.905(2)
Si(1)–C(11)	1.876(3)
Si(1)–C(12)	1.871(3)
Si(1)–C(13)	1.863(3)
C(2)–C(3)	1.502(3)
C(3)–C(4)	1.350(3)
C(4)–C(5)	1.456(3)
C(5)–C(6)	1.358(3)
C(2)–C(6)	1.505(3)
<i>Bond angles (°)</i>	
C(1)–Sn(1)–C(1A)	103.8(2)
C(1)–Sn(1)–C(2)	109.00(9)
C(1)–Sn(1)–C(2A)	111.98(9)
C(2)–Sn(1)–C(2A)	110.9(1)
Sn(1)–C(2)–Si(1)	114.3(1)
Sn(1)–C(2)–C(3)	109.5(1)
Sn(1)–C(2)–C(6)	111.8(1)
Si(1)–C(2)–C(3)	110.2(1)
Si(1)–C(2)–C(6)	107.6(1)
C(2)–C(3)–C(4)	109.4(2)
C(3)–C(4)–C(5)	109.4(2)
C(4)–C(5)–C(6)	109.2(2)
C(2)–C(6)–C(5)	109.1(2)
C(3)–C(2)–C(6)	102.8(2)

filtrate in the case of the zirconocene complexes and **12b**. For the remaining niobocene complexes, SnMe_2Cl_2 was eliminated by filtration of the toluene suspension and the final product obtained by crystallization of the filtrate. The zirconocene complexes were characterized satisfacto-

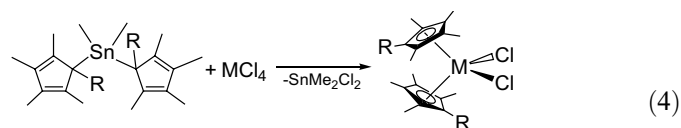
Table 6
Selected structural data of tin bridged *ansa*-bis(cyclopentadiene) compounds

Compound	Sn–C _(Cp) ¹ (Å)	C _(Cp) ¹ –Sn– C _(Cp) ¹ (°)	Ref.
$\text{Me}_2\text{Sn}(\text{C}_5\text{Me}_4\text{H})_2$ (5)	2.195(4)		This work
	2.205(4)	106.3(1)	
	2.206(4) 2.202(4)	105.5(1)	
$\text{Me}_2\text{Sn}(\text{C}_5\text{Me}_4\text{SiMe}_3)_2$ (6)	2.190(2)	110.9(1)	This work
<i>meso</i> - $\text{Me}_2\text{Sn}(\text{C}_5\text{H}_3\text{Bu}^f)_2\text{SiMe}_2$	2.214(4)	102.6(2)	[9h]
<i>meso</i> - $\text{Me}_2\text{Sn}(\text{C}_5\text{Me}_2\text{H}_2)_2\text{SiMe}_2$	2.206(4)	103.7(2)	[9h]
<i>meso</i> - $\text{Me}_2\text{Sn}(\text{C}_5\text{MeH}_2\text{Bu}^f)_2\text{SiMe}_2$	2.197(2)	109.0(1)	[9h]
<i>rac</i> - $\text{Me}_2\text{Sn}(\text{C}_5\text{MeH}_2\text{Bu}^f)_2\text{SiMe}_2$	2.215(7)	109.3(3)	[9e]
	2.205(8)		
<i>rac</i> - $\text{Sn}\{(\text{C}_5\text{H}_3\text{Bu}^f)_2(\text{SiMe}_2)_2(\text{C}_5\text{H}_3\text{Bu}^f)_2\}$	2.204(2)	108.8(1)	[9e]
	2.196(2)	110.6(1)	
	2.197(2)	108.8(1)	
	2.203(2)	110.0(1)	
		108.4(1) 110.1(1)	
<i>meso</i> - $\text{Me}_2\text{Sn}(\text{C}_5\text{H}_3\text{Bu}^f)_2\text{Si}(\text{Me})\text{CH}_2\text{Ph}$	2.206(2)		[9f]
	2.199(2)	100.6(1)	

rily by elemental analysis and gave NMR spectra identical to those previously reported for these compounds [13]. The successful synthesis of the niobocene complexes [14] was also confirmed by elemental analysis and mass spectrometry. The yields of the metallocene complexes, **7–12**, prepared via the tin transmetalation reactions were comparable or superior to those reported using the traditional metathesis reactions with group one cyclopentadienyl compounds [13,14].



R = Me (**7**), Pr^{*i*} (**8**), Bu^{*t*} (**9**), SiMe₃ (**10**)
M = Zr (**a**); Nb (**b**)



R = H (**11**), SiMe₃ (**12**)
M = Zr (**a**); Nb (**b**)

3. Conclusions

In this paper we have reported the synthesis and characterization of new tin bridged *ansa*-bis(cyclopentadiene) compounds. The molecular structures of two of the compounds have been described. The transmetalation reaction with zirconium or niobium tetrachloride proved to be successful and yielded the metallocene dichloride complexes.

4. Experimental

4.1. Materials and procedures

All reactions were performed using standard Schlenk tube techniques in an atmosphere of dry nitrogen. Solvents were distilled from the appropriate drying agents and degassed before use. SnMe₂Cl₂, Na(C₅H₄Pr^{*i*}), Li(C₅H₄Bu^{*t*}) and ZrCl₄, were purchased from Aldrich and used without further purification. Na(C₅H₅) [15], Li(C₅H₄SiMe₃) [16], Li(C₅Me₄H) [10a] and Li(C₅Me₄SiMe₃) [13f] were prepared as previously reported. ¹H, ¹³C{¹H} and ¹¹⁹Sn NMR spectra were recorded on a Varian Mercury FT-400 spectrometer and referenced to the residual deuterated solvent. Microanalyses were carried out with a Perkin–Elmer 2400 microanalyzer. Mass spectroscopic analyses were performed on a Hewlett-Packard 5988A (*m/z* 50–1000) instrument.

4.2. Synthesis of Me₂Sn(C₅H₄Me-1)₂ (**1**)

Li(C₅H₄Me) (2.00 g, 23.24 mmol) was added to a solution of SnMe₂Cl₂ (2.55 g, 11.62 mmol) in THF (50 ml) at –78 °C. The reaction mixture was allowed to reach room temperature and stirred for 16 h. Solvent was removed by applying

reduced pressure and hexane (40 ml) added. The suspension was filtered and the filtrate concentrated (5 ml). Cooling to –30 °C yielded the title compound as a yellow crystalline solid (2.57 g, 72%). MS electron impact (*m/e* (relative intensity)): 308 (15) [M⁺], 293 (25) [M⁺–Me], 229 (55) [M⁺–C₅H₄Me], 79 (100) [M⁺–Me₂SnC₅H₄Me]. Anal. Calc. for C₁₄H₂₀Sn: C, 54.77; H, 6.57. Found: C, 54.51; H, 6.55%.

4.3. Synthesis of Me₂Sn(C₅H₄Pr^{*i*}-1)₂ (**2**)

The preparation of **2** was carried out in an identical manner to **1**. Li(C₅H₄Pr^{*i*}) (2.00 g, 15.36 mmol) and SnMe₂Cl₂ (1.69 g, 7.68 mmol). Yield: 1.95 g, 70%. MS electron impact (*m/e* (relative intensity)): 363 (1) [M⁺], 348 (9) [M⁺–Me], 256 (47) [M⁺–C₅H₄Pr^{*i*}], 226 (39) [M⁺–C₅H₄Pr^{*i*}, –2 × Me], 106 (100) [M⁺–Me₂SnC₅H₄Pr^{*i*}]. Anal. Calc. for C₁₈H₂₈Sn: C, 59.54; H, 7.77. Found: C, 59.51; H, 7.76%.

4.4. Synthesis of Me₂Sn(C₅H₄Bu^{*t*}-1)₂ (**3**)

The preparation of **3** was carried out in an identical manner to **1**. Li(C₅H₄Bu^{*t*}) (2.00 g, 15.60 mmol) and SnMe₂Cl₂ (1.71 g, 7.80 mmol). Yield: 2.29 g, 76%. MS electron impact (*m/e* (relative intensity)): 392 (1) [M⁺], 377 (9) [M⁺–Me], 270 (100) [M⁺–C₅H₄Bu^{*t*}], 241 (94) [M⁺–C₅H₄Bu^{*t*}, –2 × Me]. Anal. Calc. for C₂₀H₃₂Sn: C, 61.41; H, 8.25. Found: C, 61.01; H, 8.20%.

4.5. Synthesis of Me₂Sn(C₅H₄{SiMe₃}-1)₂ (**4**)

The preparation of **4** was carried out in an identical manner to **1**. Li(C₅H₄SiMe₃) (2.00 g, 13.87 mmol) and SnMe₂Cl₂ (1.52 g, 6.93 mmol). Yield: 2.38 g, 81%. MS electron impact (*m/e* (relative intensity)): 424 (2) [M⁺], 409 (39) [M⁺–Me], 286 (100) [M⁺–C₅H₄SiMe₃], 256 (77) [M⁺–C₅H₄SiMe₃, –2 × Me]. Anal. Calc. for C₁₈H₃₂Si₂Sn: C, 51.07; H, 7.62. Found: C, 51.09; H, 7.58%.

4.6. Synthesis of Me₂Sn(C₅Me₄H-1)₂ (**5**)

The preparation of **5** was carried out in an identical manner to **1**. Li(C₅Me₄H) (2.00 g, 15.60 mmol) and SnMe₂Cl₂ (1.71 g, 7.80 mmol). Yield: 2.22 g, 73%. MS electron impact (*m/e* (relative intensity)): 392 (7) [M⁺], 271 (100) [M⁺–C₅Me₄H], 241 (77) [M⁺–C₅Me₄H, –2 × Me]. Anal. Calc. for C₂₀H₃₂Sn: C, 61.41; H, 8.25. Found: C, 61.30; H, 8.21%.

4.7. Synthesis of Me₂Sn(C₅Me₄{SiMe₃}-1)₂ (**6**)

The preparation of **6** was carried out in an identical manner to **1**. Li(C₅Me₄SiMe₃) (2.00 g, 9.98 mmol) and SnMe₂Cl₂ (1.10 g, 4.99 mmol). Yield: 1.82 g, 68%. MS electron impact (*m/e* (relative intensity)): 536 (1) [M⁺], 343 (100) [M⁺–C₅Me₄SiMe₃], 313 (59) [M⁺–C₅Me₄SiMe₃, –2 × Me], 73 (94) [M⁺–Me₂Sn(C₅Me₄SiMe₃)(C₅Me₄)]. Anal. Calc. for C₂₆H₄₈Si₂Sn: C, 58.31; H, 9.03. Found: C, 57.79; H, 8.92%.

4.8. Synthesis of $[\text{Zr}(\text{C}_5\text{H}_4\text{Me})_2\text{Cl}_2]$ (**7a**)

$\text{Me}_2\text{Sn}(\text{C}_5\text{H}_4\text{Me}-1)_2$ (**1**) (1.00 g, 3.26 mmol) was added to ZrCl_4 (0.76 g, 3.26 mmol) in toluene (50 ml). The reaction mixture was then stirred, under reflux, for 24 h. The resulting suspension was evaporated and hexane (100 ml) added. The mixture was filtered and the filtrate concentrated (10 ml). The title compound was obtained, as a crystalline solid, on cooling this solution (0.70 g, 67%). Anal. Calc. for $\text{C}_{12}\text{H}_{14}\text{Cl}_2\text{Zr}$: C, 44.99; H, 4.40. Found: C, 44.81; H, 4.36%.

4.9. Synthesis of $[\text{Zr}(\text{C}_5\text{H}_4\text{Pr}^i)_2\text{Cl}_2]$ (**8a**)

The preparation of **8a** was carried out in an identical manner to **7a**. $\text{Me}_2\text{Sn}(\text{C}_5\text{H}_4\text{Pr}^i-1)_2$ (**2**) (1.00 g, 2.75 mmol) and ZrCl_4 (0.64 g, 2.75 mmol). Yield: 0.60 g, 58%. Anal. Calc. for $\text{C}_{16}\text{H}_{22}\text{Cl}_2\text{Zr}$: C, 51.04; H, 5.89. Found: C, 50.89; H, 5.83%.

4.10. Synthesis of $[\text{Zr}(\text{C}_5\text{H}_4\text{Bu}^t)_2\text{Cl}_2]$ (**9a**)

The preparation of **9a** was carried out in an identical manner to **7a**. $\text{Me}_2\text{Sn}(\text{C}_5\text{H}_4\text{Bu}^t-1)_2$ (**3**) (1.00 g, 2.56 mmol) and ZrCl_4 (0.60 g, 2.56 mmol). Yield: 0.65 g, 63%. Anal. Calc. for $\text{C}_{18}\text{H}_{26}\text{Cl}_2\text{Zr}$: C, 53.44; H, 6.48. Found: C, 53.15; H, 6.46%.

4.11. Synthesis of $[\text{Zr}(\text{C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}_2]$ (**10a**)

The preparation of **10a** was carried out in an identical manner to **7a**. $\text{Me}_2\text{Sn}(\text{C}_5\text{H}_4\text{SiMe}_3-1)_2$ (**4**) (1.00 g, 2.36 mmol) and ZrCl_4 (0.55 g, 2.36 mmol). Yield: 0.68 g, 66%. Anal. Calc. for $\text{C}_{16}\text{H}_{26}\text{Cl}_2\text{Si}_2\text{Zr}$: C, 44.01; H, 6.00. Found: C, 43.92; H, 6.00%.

4.12. Synthesis of $[\text{Zr}(\text{C}_5\text{Me}_4\text{H})_2\text{Cl}_2]$ (**11a**)

The preparation of **11a** was carried out in an identical manner to **7a**. $\text{Me}_2\text{Sn}(\text{C}_5\text{Me}_4\text{H}-1)_2$ (**5**) (1.00 g, 2.56 mmol) and ZrCl_4 (0.60 g, 2.56 mmol). Yield: 0.60 g, 58%. Anal. Calc. for $\text{C}_{18}\text{H}_{26}\text{Cl}_2\text{Zr}$: C, 53.44; H, 6.48. Found: C, 53.27; H, 6.43%.

4.13. Synthesis of $[\text{Zr}(\text{C}_5\text{Me}_4\text{SiMe}_3)_2\text{Cl}_2]$ (**12a**)

The preparation of **12a** was carried out in an identical manner to **7a**. $\text{Me}_2\text{Sn}(\text{C}_5\text{Me}_4\{\text{SiMe}_3\}-1)_2$ (**6**) (1.36 g, 2.55 mmol) and ZrCl_4 (0.59 g, 2.55 mmol). Yield: 0.95 g, 68%. Anal. Calc. for $\text{C}_{24}\text{H}_{42}\text{Cl}_2\text{Si}_2\text{Zr}$: C, 52.52; H, 7.71. Found: C, 52.23; H, 7.62%.

4.14. Synthesis of $[\text{Nb}(\text{C}_5\text{H}_4\text{Me})_2\text{Cl}_2]$ (**7b**)

$\text{Me}_2\text{Sn}(\text{C}_5\text{H}_4\text{Me}-1)_2$ (**1**) (1.00 g, 3.26 mmol) was added to $[\text{NbCl}_4(\text{THF})_2]$ (1.23 g, 3.26 mmol) in toluene (50 ml). The reaction mixture was stirred, under reflux, for 24 h.

The resulting suspension was filtered and the filtrate concentrated (10 ml) to yield the title compound as a crystalline solid (0.78 g, 74%). Anal. Calc. for $\text{C}_{12}\text{H}_{14}\text{Cl}_2\text{Nb}$: C, 44.75; H, 4.38. Found: C, 44.67; H, 4.35%.

4.15. Synthesis of $[\text{Nb}(\text{C}_5\text{H}_4\text{Pr}^i)_2\text{Cl}_2]$ (**8b**)

The preparation of **8b** was carried out in an identical manner to **7b**. $\text{Me}_2\text{Sn}(\text{C}_5\text{H}_4\text{Pr}^i-1)_2$ (**2**) (1.00 g, 2.75 mmol) and $[\text{NbCl}_4(\text{THF})_2]$ (1.02 g, 2.75 mmol). Yield: 0.84 g, 81%. Anal. Calc. for $\text{C}_{16}\text{H}_{22}\text{Cl}_2\text{Nb}$: C, 50.82; H, 5.86. Found: C, 50.55; H, 5.79%.

4.16. Synthesis of $[\text{Nb}(\text{C}_5\text{H}_4\text{Bu}^t)_2\text{Cl}_2]$ (**9b**)

The preparation of **9b** was carried out in an identical manner to **7b**. $\text{Me}_2\text{Sn}(\text{C}_5\text{H}_4\text{Bu}^t-1)_2$ (**3**) (1.00 g, 2.56 mmol) and $[\text{NbCl}_4(\text{THF})_2]$ (0.94 g, 2.56 mmol). Yield: 0.86 g, 83%. Anal. Calc. for $\text{C}_{18}\text{H}_{26}\text{Cl}_2\text{Nb}$: C, 53.22; H, 6.45. Found: C, 53.01; H, 6.42%.

4.17. Synthesis of $[\text{Nb}(\text{C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}_2]$ (**10b**)

The preparation of **10b** was carried out in an identical manner to **7b**. $\text{Me}_2\text{Sn}(\text{C}_5\text{H}_4\text{SiMe}_3-1)_2$ (**4**) (1.00 g, 2.36 mmol) and $[\text{NbCl}_4(\text{THF})_2]$ (0.88 g, 2.36 mmol). Yield: 0.79 g, 77%. Anal. Calc. for $\text{C}_{16}\text{H}_{26}\text{Cl}_2\text{NbSi}_2$: C, 43.84; H, 5.98. Found: C, 43.81; H, 5.96%.

4.18. Synthesis of $[\text{Nb}(\text{C}_5\text{Me}_4\text{H})_2\text{Cl}_2]$ (**11b**)

The preparation of **11b** was carried out in an identical manner to **7b**. $\text{Me}_2\text{Sn}(\text{C}_5\text{Me}_4\text{H}-1)_2$ (**5**) (1.00 g, 2.56 mmol) and $[\text{NbCl}_4(\text{THF})_2]$ (0.94 g, 2.56 mmol). Yield: 0.85 g, 83%. Anal. Calc. for $\text{C}_{18}\text{H}_{26}\text{Cl}_2\text{Nb}$: C, 53.22; H, 6.45. Found: C, 52.94; H, 6.39%.

4.19. Synthesis of $[\text{Nb}(\text{C}_5\text{Me}_4\text{SiMe}_3)_2\text{Cl}_2]$ (**12b**)

The preparation of **12b** was carried out in an identical manner to **7a**. $\text{Me}_2\text{Sn}(\text{C}_5\text{Me}_4\{\text{SiMe}_3\}-1)_2$ (**6**) (1.00 g, 1.86 mmol) and $[\text{NbCl}_4(\text{THF})_2]$ (0.69 g, 1.86 mmol). Yield: 0.63 g, 61%. Anal. Calc. for $\text{C}_{24}\text{H}_{42}\text{Cl}_2\text{NbSi}_2$: C, 52.36; H, 7.69. Found: C, 52.00; H, 7.60%.

4.20. X-ray structure determinations of $\text{Me}_2\text{Sn}(\text{C}_5\text{Me}_4\text{H}-1)_2$ (**5**) and $\text{Me}_2\text{Sn}(\text{C}_5\text{Me}_4\{\text{SiMe}_3\}-1)_2$ (**6**)

Data were collected on a Bruker SMART CCD-based diffractometer operating at 50 kV and 100 mA, using $\omega/2\theta$ scan-technique. The structure was solved using the SHELXS-97 software by direct methods and refined by full-matrix least-squares methods on F^2 [17,18]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions, and refined in the riding mode. Weights were optimized in the final cycles. Crystallographic data are given in Table 7.

Table 7
Crystal data and structure refinement for **5** and **6**

	5	6
Formula	C ₂₀ H ₃₂ Sn	C ₂₆ H ₄₈ Si ₂ Sn
<i>F</i> _w	391.15	535.51
<i>T</i> (K)	100(2)	100(2)
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	8.7564(1)	14.9483(2)
<i>b</i> (Å)	13.4869(1)	9.5901(1)
<i>c</i> (Å)	16.8979(2)	20.2146(2)
α (°)	82.884(1)	
β (°)	86.808(1)	103.149(1)
γ (°)	75.670(1)	
<i>V</i> (Å ³)	1917.95(3)	2821.90(6)
<i>Z</i>	4	4
<i>D</i> _{calc} (g cm ⁻³)	1.355	1.260
μ (mm ⁻¹)	10.515	8.067
<i>F</i> (000)	808	1128
Crystal dimensions (mm)	0.30 × 0.25 × 0.20	0.35 × 0.30 × 0.12
θ Range (°)	2.64–70.47	4.49–70.55
<i>hkl</i> Ranges	–10 ≤ <i>h</i> ≤ 10, –16 ≤ <i>k</i> ≤ 16, –20 ≤ <i>l</i> ≤ 20	–18 ≤ <i>h</i> ≤ 16, –11 ≤ <i>k</i> ≤ 11, –24 ≤ <i>l</i> ≤ 24
Data/parameters	6613/399	2595/229
Goodness-of-fit on <i>F</i> ²	1.040	1.056
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0445, <i>wR</i> ₂ = 0.1181	<i>R</i> ₁ = 0.0286, <i>wR</i> ₂ = 0.0721
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0479, <i>wR</i> ₂ = 0.1214	<i>R</i> ₁ = 0.0287, <i>wR</i> ₂ = 0.0722
Largest difference in peak and hole (e Å ⁻³)	2.137/–2.081	0.951/–0.896

$$R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}; wR_2 = \frac{[\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)]]^{0.5}}$$

5. Supplementary material

CCDC 634216 and 634217 contain the supplementary crystallographic data for **5** and **6**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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