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Synthesis and structure of dinuclear [(2-*tert*-butyl-4,5,6-trimethylphenyl)$_2$Sn-Co(η^2-ethene)(η^5-Me$_5$C$_5$)] and its thermal conversion to trinuclear [{(2-*tert*-butyl-4,5,6-trimethylphenyl)$_2$Sn}$_2$Co(η^5-Me$_5$C$_5$)] (Co–Sn$_2$)

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Abstract

The title compounds **4** and **12** are prepared by reacting bis{(η^2-ethene)}(η^5-pentamethylcyclopentadienyl)cobalt(I) **3** with Weidenbruch's stannylene bis[bis{6-*tert*-butyl-2,3,4-trimethylphenyl}tin] (**1**) employing different thermal reaction conditions. Compounds **4** and **12** are rare examples of transition metal complexes of **1**. According to an X-ray crystal structure determination, **4** displays a half-sandwich structure with trigonal planar coordinated Co atom and a subvalent Sn(II) center. The Co–Sn bond length in **4** is 2.3926(4) Å and represents one of the shortest reported so far. A comparison of relevant bonding parameters of **4** and several related Co–Sn half-sandwich compounds containing low valent SnR$_2$ fragments reveals comparable steric and electronic effects of the stannylenes towards the 16 e {(η^2-ethene)(Me$_5$C$_5$)Co} fragment in these complexes. In contrast to the isostructural ethene/stannylene complex bis{methyl(trimethylsilyl)}stannio(η^2-ethene)(η^5-cyclopentadienyl)cobalt **6** containing Lappert's bis(stannanediyl) **2**, **4** is inert towards H$_2$O and does not activate water by an oxidative addition reaction to give a mixed hydroxo hydrido complex. At elevated temperatures, **4** reacts via ethene dissociation and ligand redistribution to form the trinuclear cobalt bis stannylene half sandwich complex Bis[bis{6-*tert*-butyl-2,3,4-trimethylphenyl}]stannio(η^5-pentamethylcyclopentadienyl)}cobalt(I) **12** in moderate yields. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Cobalt; Tin; Stannylene; Ethylene; Half-sandwich

1. Introduction

Unbridged metal–metal bonds exhibit a high reactivity especially when the M–M bonds are polarized. By choosing an appropriate combination of a transition metal and a main group metal, the bond polarity M–M′ can be tuned, thus allowing creation of chemical reactivity of such a bond mainly by bond polarization effects. The concept of bond polarity is not so readily applicable to M–M bonds (M = transition metal) [1], thus making the chemistry of heteronuclear M–M′ combinations (M = transition metal, M′ = main group metal) interesting to pursue in more depth. Our interest in this area has focused on heterodinuclear organometallic complexes containing a reactive M–M′ bond (M = transition metal; M′ = group 12, 13 or 14 metal), particulary those with an unbridged M–Sn bond like **6–10** which possess a metal bonded :SnR$_2$ stannylene fragment (Fig. 1, [2]).Complexes **6–10** offer ideal prerequisites for the linkage of novel metal–element bonds by insertion or addition reactions [2a,d]. Especially interesting features with regard to reactivity are the three-fold coordinated sub-valent Sn(II) center and the existence of an additionally labile bonded ethene ligand in the cobalt and iron complexes **6–10**. Thus, these compounds offer two distinct different sites for chemical reactivity.

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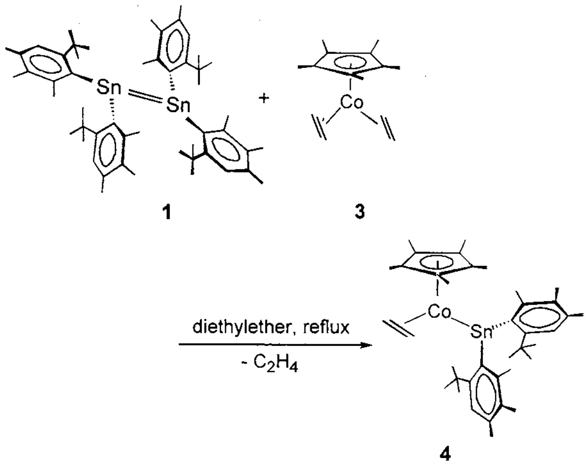
The coordination of :SnR_2 stannylene or stannanediyl fragments to low valent transition metal centers is already known for a number of transition metal fragments, mostly containing strong donor–acceptor substituents like e.g. CO [3]. Examples for the coordination of :SnR_2 fragments to pure hydrocarbyl transition metal fragments are still rare. With respect to the nature of M–Sn bonding in such complexes, relevant bond distances M–Sn are usually found to be significantly shorter in pure (hydrocarbyl)transition metal stannylene complexes than in heteroelement—especially CO—substituted ones [4]. This fact results from a distinct M–Sn double bond character for the former complexes as judged from their binding parameters and we are interested in finding new examples exhibiting such short M–Sn bonding.

Herein we report on our studies towards synthesis, structure and unusual thermal reactivity of a new stannylene cobalt complex containing an unbridged short Co–Sn bond. In particular, we present the introduction of the :SnR_2 hydrocarbyl stannylene bis{2-*tert*-butyl-4,5,6-trimethylphenyl}tin derived from the bis(bis(hydrocarbyl)-stannylene (**1**), as ligand in organocobalt chemistry and report on the distinct altered chemical and thermal reactivity of the new cobalt stannylene complex **4** compared to its isostructural analogues **6** and **7** containing the Sn{$(CH(SiMe_3)_2)$}$_2$ fragment derived from Lappert's bis(stannanediyl) **2**.

2. Results and discussion

The reaction of bis[{2-*tert*-butyl-4,5,6-trimethylphenyl}$_2$tin] (**1**) with [$(\eta^5\text{-}Me_5C_5)Co(\eta^2\text{-}C_2H_4)_2$] **3**, first at room temperature and then at reflux temperature in ether leads to dissociation of one ethene ligand and substitution by an SnR_2 fragment generated from **1**, and results in formation of the mixed mono(ethene/stannylene)cobalt complex **4** (Eq. (1)).

(1)



Ethene substitution in **3** already stops after one ethene ligand is replaced by a SnR_2 unit even when an excess of stannylene is present. This situation is maintained even when **3** is already formed but is still further

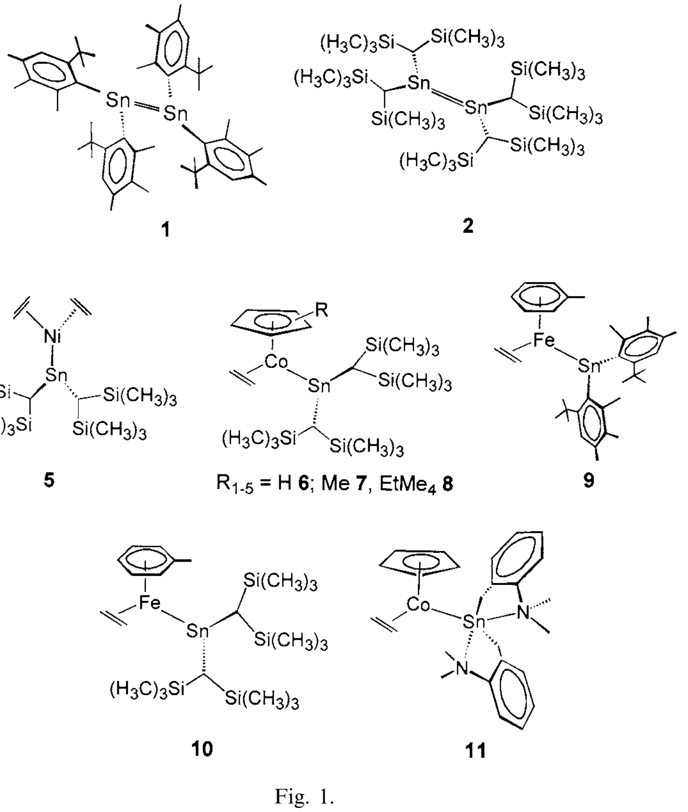
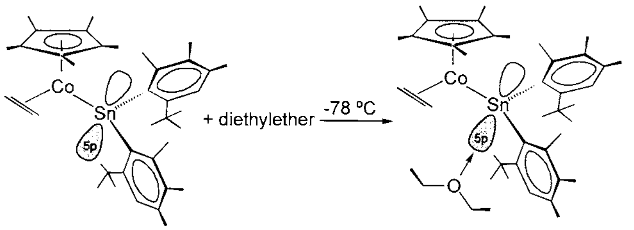


Fig. 1.

refluxed with an excess of the bis(stannanediyl) (**1**) in ether. Complex **4** is highly soluble in pentane and ether. From the latter solvent, **4** can be obtained at −20°C as deep purple to black crystals which are stable at room temperature.

Interestingly **4** cannot be crystallized at −78°C from diethylether during several months, possibly indicating a reversible ether solvent coordination to the sub-valent Sn(II) center in **4**. At higher temperatures (> −30°C), dissociation of the ether ligand might occur which lowers the solubility of **4** and in turn allows crystallization of **4** within a few days as deep purple to black crystal chunks. The plausible coordination of the ether solvent at temperatures > −30°C can be understood by a donation of the oxygen lone pair of the ether solvent into the low lying vacant 5p π-orbitals of the subvalent three-fold coordinated Sn(II) center (Eq. (2)). A similar solvent coordination behavior has been found for Lappert's bis(stannanediyl) [{Sn{CH(SiMe$_3$)}$_2$}$_2$] (**2**) [6] and the Ni complex [(η^2-C$_2$H$_4$)$_2$Ni-Sn{CH(SiMe$_3$)$_2$}$_2$] (**5**) derived therefrom [7]. To the best of our knowledge, such a behaviour is reported here for the first time for a transition metal complex containing a pure bis(hydrocarbyl)stannylene :SnR$_2$ like [(2-*tert*-butyl-4,5,6-trimethylphenyl)$_2$Sn:].



4 **4** x (diethylether) (2)

3. NMR characterization of 4

According to the results of the ^{1}H- and ^{13}C-NMR analysis of **4**, both aryl ligands at tin are chemically inequivalent. As already observed for the related Co–Sn complexes **6–8**, as well as the isoelectronic Fe–Sn complexes **9** [2c] and **10**, the protons of the ethene ligand of **4** appear as broad resonances (Table 1). Compared to the (ethene)Co–Sn complex **11** containing penta-coordinated tin [8], the proton signals of the π coordinated ethene of **4** are significantly shifted to lower field ($\Delta\delta = 1$ ppm) indicating the missing π-back-bonding acceptor ability of the penta-coordinated Sn in **11**, which is due to the two additional N donor atoms present in **11** compared to the situation at the trivalent Sn in **4**, still containing a low lying vacant 5p π-orbital. The NMR assigments for **4** were substantiated by a C–H COSY experiment.

Table 1
^{1}H- and ^{13}C-NMR data for **4** and **12**

^{1}H-NMR (C$_6$D$_6$, 27°C, δ (ppm)):	
4:	7.19, 7.12 (2s, 2H, =CH$_{aryl}$) 3.27, 3.15, 2.10, 2.08, 2.03 (2s, 6H; s, 6H; s, 6H; all CH$_3$-aryl) 2.43, 2.20, 2.12, 1.93 (4m, vbr, 4H, C$_2$H$_4$) 1.71 (s, 15H, Me$_5$C$_5$)
4:	7.32, 7.09 (2s, 4H, =CH) 2.49, 2.25, 2.11. 1.76, 1.67 (2s, 9H, s, 18H, 2s, 9H, CH$_3$-aryl) 1.58, 1.52 (2s, 36H, C(CH$_3$)$_3$) 1.41 (s, 15H, Me$_5$C$_5$)
^{13}*C-NMR (C$_6$D$_6$, 27°C, δ (ppm)):*	
12:	160.5, 158.6, 153.3, 153.2, 142.0, 141.9, 136.1, 135.8, 134.1, 133.9 (sp$_2$C$_{aryl}$) 127.6, 127.2 (sp$_2$C$_{aryl}$–H) 89.6 (Me$_5$*C*$_5$) 37.2, 36.8 (*C*(CH$_3$)$_3$) 34.8, 28.2 (C$_2$H$_4$) 32.6, 32.4 (C(*C*H$_3$)$_3$) 23.5, 22.6, 21.5, 16.0, 15.9 (CH$_{3aryl}$) 10.7 (*Me*$_5$C$_5$)
12:	168.2, 164.0, 154.7, 152.1, 148.4, 144.6, 135.7, 135.6, 133.8, 133.5 (sp$_2$C$_{aryl}$) 127.2, 125.6 (sp$_2$C$_{aryl}$–H) 92.5 (Me$_5$*C*$_5$) 34.1, 33.6 (*C*(CH$_3$)$_3$) 33.1, 32.8 (*C*(*C*H$_3$)$_3$) 37.5, 36.8, 21.4, 21.3, 16.0, 15.1 (CH$_{3aryl}$) 9.2 (Me$_5$*C*$_5$)

EI–mass spectroscopy of **4** reveals an easy loss of the ethene ligand giving the [M–C$_2$H$_4$]$^+$ fragment ion as highest *m*/*e* signal in the mass spectrum.

4. Molecular structure of 4

X-ray quality crystals of **4** were obtained from concentrated diethylether solutions at −20°C over several days. Its molecular structure is depicted in Fig. 2 [9]. The tin atom displays an ideal trigonal structure reflected by the sum of the bond angles (359.9°). If Me$_5$C$_5$ is considered to occupy three coordination sites and the σ-bonded :SnR$_2$ and the ethene ligands occupy two sites, **4** corresponds to a five coordinated compound. The bonding parameters of the {(η^2-ethene)(Me$_5$C$_5$)Co} fragment are virtually in agreement with the closely related complexes **6** and **7** containing Lappert's stannylene [2a].

The Co–Sn distance is 2.3926(4) Å for **4**, and well below the sum of the covalency radii of Co and Sn (2.55 Å) and in good agreement with the Co–Sn bond distance found in **6** (2.396(1) Å) [2a] and **7** (2.386(2) Å) [2d] as well as in the related isoelectronic complex bis{(2-*tert*-butyl-4,5,6-trimethylphenyl)}stannio(η^2-ethene)(η^6-toluene)iron **9** containing a Fe–Sn bond (2.4362(10) Å) [2c]. It is intriguing to compare the

Co–Sn atom distances with the Ni–Sn distance of 2.387(1) Å, which is found only insignificantly shorter in the bis(ethene)nicke-(stannylene) complex **5** [7a]. For **5** significant double bond character of the Ni–Sn bond is discussed according to Ni_{dp}–$Sn_{p\pi}$ backbonding contributions based on a modified Duncanson–Chatt model [7a,b]. Support of this interpretation comes from shortened Sn–C_{sp3} bond distances in the Ni–Sn{CH($SiMe_3$)}$_2$ fragment in **5** compared to the relevant Sn–C_{sp3} distances in the 'free' [{Sn(CH($SiMe_3$)$_2$}$_2$] bis(stannanediyl) **2** [6a,b]. Such a shortening, however, is not found in the cobalt complexes **6–8**. Relevant Sn–C_{sp3} bond distances in **6–9** are only insignificantly shorther compared to the 'free' bis(stannanediyls) **1** and **2** (**1**: 2.218(5) and 2.189(5) Å) [5], **2**: 2.22 Å [6c]). The same holds true for the Sn–$C_{ipso(aryl)}$ distances in the isoelectronic Fe–Sn complex **9** (2.252 Å) containing Weidenbruch's stannylene [bis{(2-*tert*-butyl-4,5,6-trimethylphenyl)}-Sn:] [2c]. Hence a 'partial oxidation' caused by significant π-donor capability of the subvalent Sn atoms towards the Co or Fe atoms in **4** as well as in **6–9** is not reflected in these data and is in contrast to the Ni–Sn compound **5**. Nevertheless, a M_{dp}–$Sn_{p\pi}$ contribution seems to be reasonable in view of the close resemblance of the overall very short M–Sn bond lengths in **4** and **6–9**. An in depth discussion of M–Sn bonding in these transition metal/stannylene half-sandwich complexes must await future work.

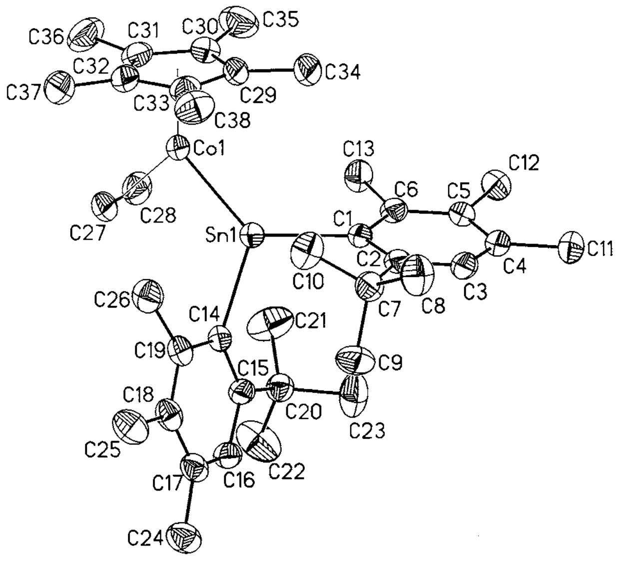


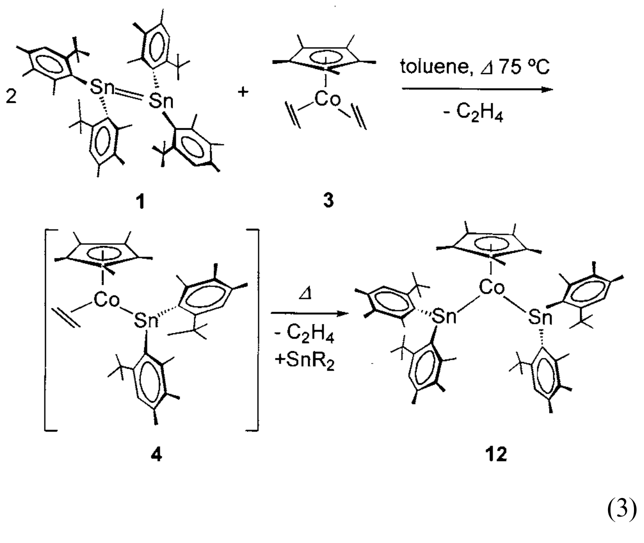
Fig. 2. Molecular structure of **4** in the solid state as determined by X-ray crystallography. Selected bond length (Å) and angles (°): Sn–Co 2.3926(4), Sn–C1 2.228(3), Sn–C14 2.228(3), Co–C27 2.001(3), Co–C28 2.024(3); C14–Sn–Co 122.94(7), C1–Sn1–C14 106.44(10), C1–Sn–Co 130.61(6).

5. Reactivity studies of 4

As we have shown recently, the stannylene complexes **6–8** bearing Lappert's stannnanediyl ligand [:Sn{CH($SiMe_3$)$_2$}$_2$] display a high reactivity towards alkynes or chalcogenes [2a,10] Reactions of **6–8** with alkynes are initiated by an initial loss of the π bonded ethene ligand, further reaction steps in the sequence are alkyne coordination, followed by catalytic or stoichiometric transition metal centered C–C and C–Sn coupling reactions, leading to homo (alkynes); or mixed alkyne/stannylene cyclotrimerization leading to cobalt(stannacyclopentadienyl) products [10].

Most recently we have found that the cobalt stannylene complex **6**, after ethene loss is able to activate water by an oxidative addition reaction at room temperature giving an unusual hydroxo hydrido complex [11]. In sharp contrast to these findings **4** is completely inert towards H_2O under identical reaction conditions. Stirring etheral solutions of **4** with a 50 fold excess of H_2O for several hours, allows to recover **4** nearly quantitatively. These findings point towards a distinct alteration of chemical reactivity of **4** versus **6** when changing the {CH_3($SiMe_3$)$_2$} fragments against the {(2-*tert*-butyl-4,5,6-trimethylphenyl)arene} fragments as ligands at tin.

Complex **4** is thermally stable under refluxing conditions in diethylether (see Section 2). However prolonged heating at elevated temperatures (75°C, toluene) causes a color change of the initial clear deep purple to a clear brown solution within a few hours and is accompanied by evolution of ethene. After workup and crystallization at −30°C for several weeks, brown crystals of the trimetallic bis(stannylene)cobalt complex **12** could be isolated in moderate yield (Eq. (3)).



(3)

6. Spectroscopic characterization of 12

Under electron impact mass spectroscopic conditions (70 eV), only the characteristic SnR_2 stannylene ligand fragment is observed as main fragmentation pattern. However, under fast atom bombardment conditions (fab) the characteristic molecular ion $[M]^+$ *m/e* 1130 as well as the fragment ion $[M-SnR_2]^+$ *m/e* 663 as base peak and various distinct other fragment ions are observed for **12** (see Section 8).

The ^1H- and ^{13}C-NMR data confirm that the four aryl ligands are pairwise inequivalent and therefore show two sets of relevant signals, one for the two *endo*-2-*tert*-butyl-4,5,6-trimethylphenyl ligands and one for the two *exo*-2-*tert*-butyl-4,5,6-trimethylphenyl ligands (Table 1). This assignment is further substantiated by our recent synthesis of an isolobal bis(stannylene) iron complex, derived from a reaction of **1** with solvated iron atoms [12].

In contrast to **4** a similar, thermally induced rearrangement of the closely related (Cp)(ethene)cobalt–stannylene derivative **6** containing Lappert's stannylene is not observed. Instead, treatment of **6** under electron impact mass spectroscopic conditions (EI MS) (10^{-3} torr, 70 ev) results in ethene dissociation and gives a signal in the EI MS of nominal composition $C_{38}H_{86}Co_2Si_8Sn_2$ [2a].

The different reactivity of **4** and **6** in the thermal rearrangement behaviour as well as the reactivity with water points towards distinct different electronic effects of the SnR_2 fragments as ligands to the $[(\eta^2\text{-ethene})(\eta^5\text{-Cp}^R)Co]$ fragment.

7. Conclusions

It was shown that the $:SnR_2$ hydrocarbyl stannylene ligand bis{6-*tert*-butyl-2,3,4-trimethylphenyl}tin derived in solution from the bis(stannanediyl) **1** is able to substitute either one or two ethene ligands in bis(η^2-ethene)(η^5-pentamethylcyclopentadienyl)cobalt **3** to form the di- and trimetallic cobalt stannylene halfsandwich complexes **4** and **12** representing rare examples of transition metal complexes of this stannylene. The X-ray structure of **4** reveals a short Co–Sn bond, indicating a distinct Co to Sn π-backbonding contribution in addition to the Co–Sn single bond.

8. Experimental

8.1. General experimental information

All reactions were carried out under an atmosphere of dry nitrogen gas with standard Schlenk techniques. **1**, **2** and **3** were synthesized according to the literature [3a,13]. Microanalysis were performed by the microanalytical laboratory of the Chemistry Department of the University/GH-Essen. All solvents were dried appropriately and were stored under nitrogen. The NMR spectra were recorded on a Bruker AC 300 spectrometer (300 MHz for ^1H, 75 MHz for ^{13}C) and referenced against the remaining protons of the deuterated solvent used. NMR samples were prepared by vacuum transfer of predried, degassed solvents onto the appropriate amount of solid sample, followed by flame sealing of the NMR tube. EI-MS spectra were recorded on a MAT 8200 instrument using standard conditions (EI, 70 eV). A fractional sublimation technique was used in the EI spectra for compound inlet. IR spectra were recorded in KBr with a Nicolet 7109 FT- instrument.

8.2. Synthesis of bis{2-tert-butyl-4,5,6-trimethylphenyl}stannio(η^2-ethene)(η^5-penta-methylcyclopentadienyl)cobalt(I) 4

A total of 0.27 g (1.1 mmol) **3** and 1.01 g (2.1 mmol) **1** were dissolved in 40 ml diethylether at room temperature. Stirring for 18 h at room temperature caused a color change to purple. Stirring was continued under reflux for three more hours. Removal of all volatiles in vacuum left a dark residue which was dissolved in 25 ml diethylether and filtered to give a clear deep purple colored solution from which 0.53 g (0.76 mmol, 71%) purple crystals of **4** separated within a few days at −20°C. MS(Ei, 70 eV) 662(1) $[M-C_2H_4]^+$, 469(1) $[SnAr_2]^+$, 222(10) $[M-SnAr_2]^+$. NMR data see Table 1. IR(KBr) 3041(s, =C–H), 2897(s, Me_5C_5), 2728(s, Ph^{tBuMe_3}), 1376 (m, Me_5C_5), 1176 (m, C_2H_4). Anal. Calc. for $C_{38}H_{57}CoSn$ (691.59) C 66.04, H 8.26. Found C 66.02, H 8.23.

8.3. Synthesis of bis{bis{2-tert-butyl-4,5,6-trimethylphenyl}stannio}(η^5-pentamethyl-cyclopentadienyl)-cobalt(I) 11

A total of 0.27 g (1.1 mol) **3** and 1.101 g (2.1 mmol) **1** were dissolved in 20 ml toluene and stirred for one hour at 75°C where upon the color changed from red brown to purple within a few minutes indicating initial formation of **4**. After one additional hour at 75°C, the purple color of the reaction mixture changed to a deep brown. Cooling to room temperature and removal of all volatiles in vacuum leaves a brown residue which was dissolved in ether, filtered and cooled to −30°C. This procedure afforded 198 mg (0.18 mmol, 16.3%) **11** as red brown microcrystalline material. MS(fab) 1130(3) $[M]^+$, 955(6) $[M-aryl]^+$, 779(5) $[M-2(aryl)]^+$, 663(100) $[M-Sn(aryl)_2]^+$. NMR data see Table 1.

Anal. Calc. for $C_{62}H_{91}CoSn_2$ (1132.88) C 65.73, H 8.10. Found C 65.84, H 8.05.

9. Supplementary material

X-ray crystallographic data for **4**: a single crystal with the approximate size $0.68 \times 0.56 \times 0.23$ mm^3, formula $C_{38}H_{57}CoSn$, (MG 691.46) was measured a Siemens-Smart CCD three circle diffractometer with Mo–K_α radiation at 183 K. Cell dimensions of the monoclinic system $a = 9.9156(1)$, $b = 30.8055(2)$, $c = 12.1535(1)$ Å, $\exists = 106.875(1)°$, $V = 3552.49(5)$ Å^3, space group $P2_1/n$ with $Z = 4$, $D_x = 1.293$ g cm^{-3}, $: = 1.19$ mm^{-1}, empirical absorption correction min/max transmission 0.55/1.00, R_{merg} before/after correction 0.0893/0.0415, 30891 intensities collected ($2\Theta_{\max} = 56.7°$), 7276 unique ($R_{\mathrm{int}}(F^2) = 0.0421$), 6649 observed ($F_o^2$ ($2\sigma(F^2)$)), structure solution (direct methods) and refinement (361 parameters, H atoms as riding groups, 1.2 fold isotropic U-values, 1.5 fold for methyl groups of the corresponding C-atoms) with Siemens-SHELXTL (Ver. 5.03), $R_1 = 0.0419$, wR_2 (all data) $= 0.1082$, GOF $=$ 1.089, residual electron density 1.83 e Å^{-3} at a distance of 1.64 Å from Sn1. Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCD-114510. Copies of the data can be obtained free of charge on application to: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44-1223-336-033; e-mail: deposit@chemcrys.cam.ac.uk].

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