Experimental and Theoretical Investigations on the Synthesis, Structure, Reactivity, and Bonding of the Stannylene-Iron Complex Bis{{bis(2-*tert*-butyl-4,5,6-trimethyl-phenyl)}Sn}Fe(η^6-toluene) (Sn-Fe-Sn)

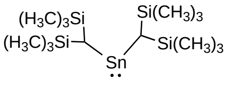
Jörg J. Schneider,*[a] Norbert Czap,[a] Dieter Bläser,[a] Roland Boese,[a] Jürgen Ensling,[b] Philipp Gütlich,[b] and Christoph Janiak[c]

Abstract: The π-(arene)bis(stannylene) complex bis{{bis(2-*tert*-butyl-4,5,6-trimethylphenyl)}Sn}Fe(η^6-toluene) (Sn-Fe-Sn, **15**) is accessible in high yields by a metal-atom-mediated synthesis between iron atoms, toluene, and the stannylene [{bis(2-*tert*-butyl-4,5,6-trimethylphenyl)}Sn] (**3**). Complex **15** has a half-sandwich structure with short Fe–Sn bonds (2.432(1) Å) and a trigonal-planar coordination at both the Fe and Sn atoms. The distance between the two Sn centers is 3.56 Å. Complex **15** is stable under ambient conditions and displays a π-arene lability, so far rarely observed for (arene)iron complexes; this leads to an irreversible substitution of the arene and formation of fivefold-coordinated zerovalent iron complexes. The π-arene lability of the title compound is a result of the Fe–Sn bonding situation, which can be interpreted, on the basis of an extended Hückel molecular orbital calculation, as being solely a donation of the 5σ lone-pair of Sn into empty or half-filled acceptor d orbitals on Fe. As the calculations reveal, there is little backbonding from the iron to the tin, and the strong σ donation leads to an increased occupation of the π-antibonding orbitals of the η^6-arene, which are mainly responsible for the experimentally observed arene lability. Fe and Sn Mössbauer spectra support the polar character of $Sn^{\delta+} \rightarrow Fe^{\delta-}$ with strong σ donation from tin to iron, but significantly low iron-to-tin π backdonation.

Keywords: arenes · half-sandwich complexes · iron · metal–metal interactions · stannylenes

Introduction

Stannylenes or stannanediyls, :SnR$_2$, are unique ligands with respect to their ability to stabilize low-valent transition metal centers. In addition to Lappert's stannylene **1**,[1a] there are a number of other SnR$_2$ systems that bear different R ligands (compounds **2**–**8**). Their ability to bond to transition metal centers is often ambivalent: they can act as donors (through their filled 5σ orbital) or as acceptors (through their empty 5p orbitals) towards a transition metal center. We have found that the creation of subvalent tin centers at Co- or Fe-ligand fragments in combination with an additional labile ethene ligand, as found in **9**–**12**, leads to an enhanced reactivity.[2–4] In **9**–**12**, the stannylenes SnR$_2$ are more strongly bound than the ethene ligands, since the loss of ethene occurs quite easily in these complexes, to give highly reactive [(L)Fe(Co)(SnR$_2$)] fragments (L = Cp or arene), which are amenable to further reactions. This fact might point towards a strong Co(Fe)–Sn σ bond, probably strengthened by significant Co(Fe)-π backdonation into empty 5p-π orbitals on tin in these complexes. Such bonding is presumably present in the Ni- and



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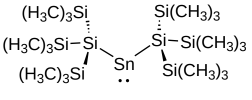
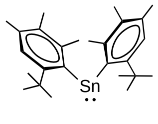


2[1i]



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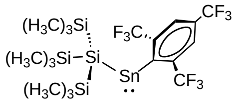

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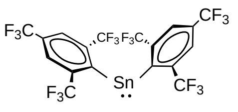
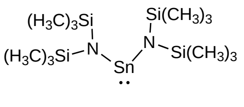


5[1g]



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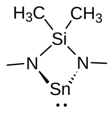
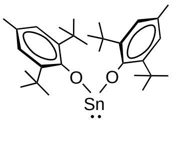


7[1j,k]



8[1d]

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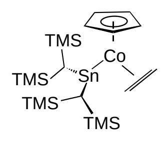
[a] Priv.-Doz. Dr. J. J. Schneider, Dr. N. Czap, D. Bläser, Prof. R. Boese
Institut für Anorganische Chemie der Universität GH-Essen
Universitätsstrasse 5–7, 45117 Essen (Germany)
Fax: (+49) 201-184-4195
E-mail: joerg.schneider@uni-essen.de

[b] Dr. J. Ensling, Prof. P. Gütlich
Institut für Anorganische und Analytische Chemie
der Universität Mainz, Staudingerweg 9, 55099-Mainz (Germany)

[c] Prof. C. Janiak
Institut für Anorganische und Analytische Chemie
der Universität Freiburg, Albertstrasse 21, 79104-Freiburg (Germany)



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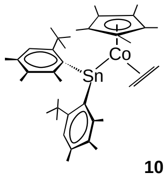

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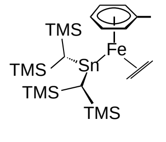

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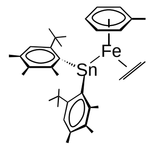

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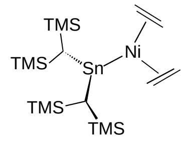

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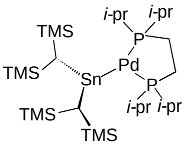

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Pd(ethene)(stannylene) complexes **13** and **14**. Their short Ni(Pd)–Sn distances were interpreted with respect to the formation of a Ni(Pd)=Sn bond.[2, 3] However, the widespread argumentation that significantly shortened bonds are the ultimate diagnostic criteria for a bond order >1 for π multiple bonds has been questioned, especially with respect to metal–metal bonds of heavier elements.[5]

In light of the recent discussion of polar effects in heterobimetallic metal bonds[6] and in an attempt to learn how a homoleptic stannylene substitution at an iron(0) center affects π-arene reactivity, we synthesized the title compound **15** and report herein on our experimental studies (synthesis, reactivity, structure, Mössbauer studies) and semiempirical extended Hückel molecular orbital calculations.

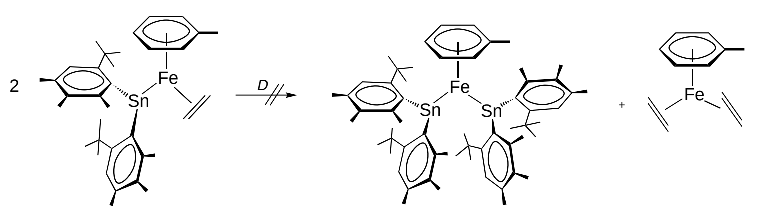
Results and Discussion

Very recently we reported on the synthesis, structure, and reactivity of the stannylene ethene iron complex **12**.[4b] This compound appeared to us to be a promising starting compound in order to generate **15** by simple elimination of ethene (Scheme 1). We have observed a similar reaction for the isolectronic Co-stannylene complex **10**, which looses ethene upon heating to give trinuclear bis{{bis(2-*tert*-butyl-4,5,6-trimethyl-phenyl)}-Sn}Co(η^5-Me$_5$Cp) (**16**).[4c]

Synthesis of 15: Solutions of **12** in diethyl ether did indeed loose ethene when warmed from $-10\,^\circ$C to room temperature. The loss of ethene was accompanied by a characteristic color change from purple to brown. However, apart from the elimination of ethene, we did not observe any clear indication of the formation of **15**. Therefore, we turned our attention to the metal-vapor synthesis technique. This technique is known to be able to generate chemically labile 14 e [(η^6-toluene)Fe] fragments under very mild conditions from the bis(arene)iron sandwich [(η^6-toluene)Fe(η^4-toluene)] (**17**).[7] However, **17** can decompose autocatalytically above $-50\,^\circ$C with liberation of toluene and decomposition into finely divided particles of elemental iron, the surfaces of which are often covered by traces of hydrocarbons. This material is known to be reactive in a number of catalytic transformations.[8] Nevertheless, careful preparation and isolation techniques allow the storage and handling of arene solutions of **17** without significant decomposition, that is, by the use of standard Schlenk techniques below $-50\,^\circ$C. Thus, these solutions are valuable, highly reactive sources of 14 e [(η^6-toluene)Fe)] fragments. This indicates that **17** can be used as the ultimate candidate for our further preparative studies.[4c]

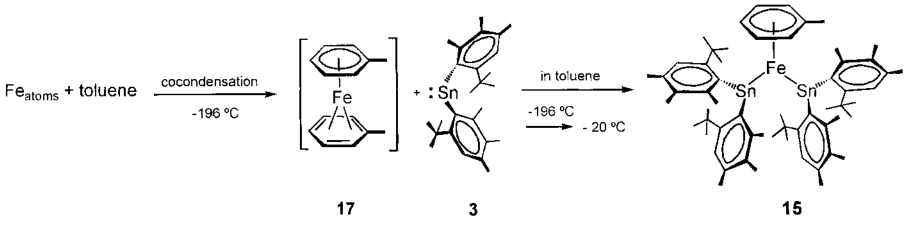
Complex **17** was treated with Weidenbruch's tertraaryldistannene (**3**)$_2$ between $-78\,^\circ$C and 20 °C to give the title compound **15** in 65 % yield. Complex **15** was formed by the substitution of one toluene ligand from **17**, which is known to be the sole primary product from our two-step reaction sequence (Scheme 2, step 1).

One arene ligand in **17** is weakly coordinated and can easily be substituted by the 2 e stannylene donor **3** (Scheme 2, step 2). Complex **15** is thermally robust, but highly air-sensitive in solution. The ^{1}H NMR of **15** is complex. Due to the asymmetric substitution pattern on each of the four phenyl rings, the local symmetry at the central iron atom is low (C_1). Therfore three sets of arene signals arise: two signals from four σ-bonded aryls on tin and one for the η^6-bonded toluene ligand. The ^{119}Sn NMR spectrum shows a single high-field signal shifted by 457 ppm from $\delta = 1130$ (**3**, 298 K)[9] to $\delta = 673$ (298 K). This is out of the range typically observed for SnR$_2$ centers with twofold coordination and is shifted towards the region for three-coordinate tin; this is in accord with an association process.[9]



12 15

Scheme 1. Attempt to synthesize the bis(stannylene) complex **15** from complex **12**.



17 3 15

Scheme 2. Synthesis of **15** via the bis(arene)iron sandwich complex [(η^6-toluene)Fe(η^4-toluene)] (**17**).

Molecular structure of 15:[10] Figures 1 and 2 show the molecular structure of **15** in the solid state. Complex **15** displays a typical half-sandwich structure with trigonal-planar coordination at the iron atom as well as at both tin centers. The Fe–Sn bond lengths (2.433(1) Å) are comparable with those of the isoelectronic mixed (ethene)(stannylene)-(toluene)iron complex **12**, which contains one SnR_2 ligand (Fe–Sn 2.4362(10) Å).[2b] Evidently, there is no additional steric impact imposed on the molecule by the introduction of the second bulky SnR_2 fragment in **15**. The ethene and the SnR_2 ligand seem comparable in their bonding towards the {(η^6-toluene)iron} fragment; at least a difference is not reflected in the Fe–Sn bond length. The η^6-bonded toluene ligand is planar and shows no out-of-plane bending of the outermost ring carbon atoms such as that found in related Co and Ni complexes of the type [(η^6-arene)M(L_2)] (M = Co, Ni).[11] The distances between Fe and the ring carbon atoms lie between 2.08 and 2.10 Å and are in good agreement with those of related (η^6-toluene)iron half-sandwich complexes, such as [(η^6-toluene)Fe(η^2-ethene)] (2.08–2.15 Å),[12] [(η^6-toluene)-Fe(η^2-bipyridine)$_2$] (2.08–2.15 Å),[13] and [(η^6-toluene)Fe(η^2-diazadiene)$_2$] (2.081–2.101 Å).[14] The four aryl ligands, grouped into two pairs, are oriented nearly orthogonally to each other; this results in an in-plane (*endo*) or out-of-plane (*exo*) orientation of each pair (Figure 2).

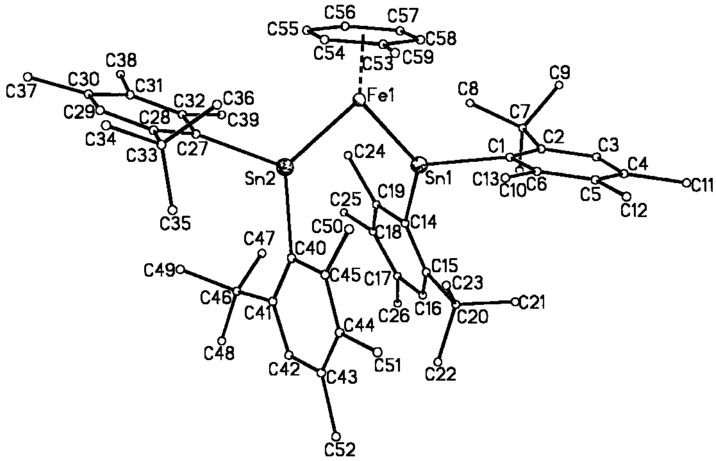


Figure 1. Crystal structure of **15** in the solid state as a stick-and-ball representation (hydrogen atoms have been omitted for clarity). Selected bond lengths [pm] and angles [°]: Fe1–Sn1 243.2(1), Fe1–Sn2 243.4(1), Sn–Sn 356, Sn1-Fe1-Sn2 94.0(1), C1-Sn1-C14 104.4(2), C27-Sn2-C40 114.2(2).

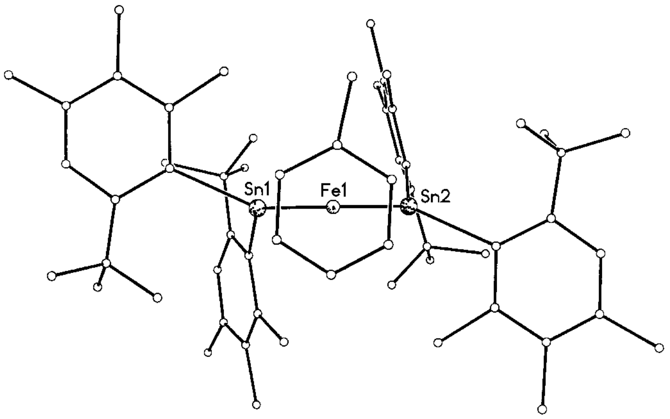


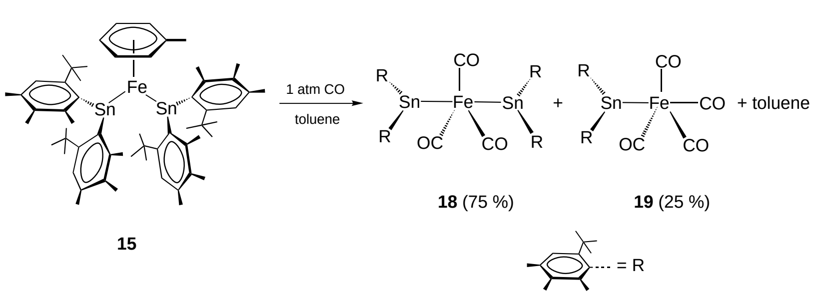
Figure 2. Structure of **15** viewed from above the η^6-toluene ligand to show the two pairs of aryl ligands and their *exo* and *endo* arrangements.

Reactivity studies of 15: Regarding the reactivity of **15**, several scenarios are possible. On one the hand, the Fe–Sn bonds may be susceptible towards bond cleavage, which would result in the generation of a 14 e (η^6-toluene) iron fragment or a 16 e [(η^6-toluene)(SnR_2)] fragment if only one SnR_2 ligand is cleaved off. On the other hand, the toluene ligand may be labile and thus can be substituted by various ligands. The latter reactivity pattern is especially interesting, since it would open up three coordination sites on the iron that might allow access to an enhanced reactivity at the iron center.

Reaction of **15** with H_2O, PEt_3, and CO (1 atm) reveal that the Fe–Sn bond is stable and not prone towards attack by these molecules. However, CO attacks the Fe–arene bonds and is able to replace toluene smoothly; even at room temperature the reaction occurs within minutes, as indicated by a color change from brown to intense red. The main product of the reaction is the bis(stannylene) compound [$(CO)_3Fe\{SnR_2\}_2$] (**18**) (Scheme 3).[4b] The synthesis of **18** is accompanied by the formation of [$(CO)_4Fe{-}SnR_2$] (**19**). This indicates that cleavage of the Fe–Sn bond does occur to some extent upon treatment of **15** with CO gas. The bis(stannylene) complex **18** is prone towards the loss of a stannylene ligand in benzene solution. NMR monitoring of a benzene solution of **18** indicated the formation of **19** over the course of several days, even when the sample is stored at $T < 0\,°C$.

In agreement with a local D_{3h} symmetry, a strong ν_{CO} band is found at 1879 cm^{-1} for **18**, whereas the monostannylene complex **19** is characterized by a three-band pattern according to a local C_{4v} symmetry (ν_{CO} = 2029(s), 1968(m), 1910(vs) cm^{-1}). The structures are thus in accordance with those expected for complexes of composition ML_3 and ML_5.[15]

Stoichiometric amounts of CO were used in an attempt to replace the arene ligand selectively. This did not result in the



15

18 (75 %)

19 (25 %)

Scheme 3. Replacement of the labile toluene ligand by CO.

formation of pure **18**. Formation of **18** is still accompanied by moderate amounts of the monostannylene complex **19**.

The observed lability of the η^6-coordinated arene ligand in the bis(stannylene) complex **15** is one out of only three rare cases reported so far in which arene lability has been observed in organoiron chemistry.[4b, 16]

Theoretical investigations of 15: In order to gain insight into the nature of the electronic as well as the steric situation present in this of trinuclear half-sandwich complex, we conducted a semiempirical extended Hückel molecular orbital (EHMO) study. The aim of this study was twofold. Firstly, we hoped to obtain information as to what extent the significant iron – metal d backbonding into the 5p-π orbitals on tin is responsible for the evidently short Fe – Sn bond distances. Secondly, in spite of the recently questioned validity[6e] of various EHMO studies,[6] we were interested in obtaining reliable and still interpretable (by well-established chemical paradigms), semiqualitative information on the bond polarity of the unbridged Fe – Sn bonds in **15**. To strengthen our conclusions regarding the latter point, we have provided support for our calculations by ^{57}Fe and ^{119}Sn Mössbauer studies, which provide information about the valence state (oxidation and spin state) as well as the coordination environment (see below).

For our theoretical studies we used the geometrical parameters obtained from the X-ray crystal structure analysis as a point of reference and discuss model systems on which the theoretical work was performed.

From an EHMO study on the model complexes $[(\eta^6\text{-}C_6H_6)Fe(SnMe_2)_2]$ and $[(\eta^6\text{-}C_6H_6)Fe(SnPh_2)_2]$, the following electronic situation in **15** emerged. When the toluene ligand is replaced by benzene and the substituted aryl ligands of **15** are replaced either by Me (CH_3) or phenyl (C_6H_5), the overall electronic situation does not change to a significant extent, in particular the Fe – Sn and the $[(\eta^6\text{-}C_6H_6)Fe]$ bonding situation. The role of the substituted aryl ligands on Sn in **15** is merely steric. The main Fe – Sn interaction is of σ type (see Figure 3). Double bonding contributions are negligible.

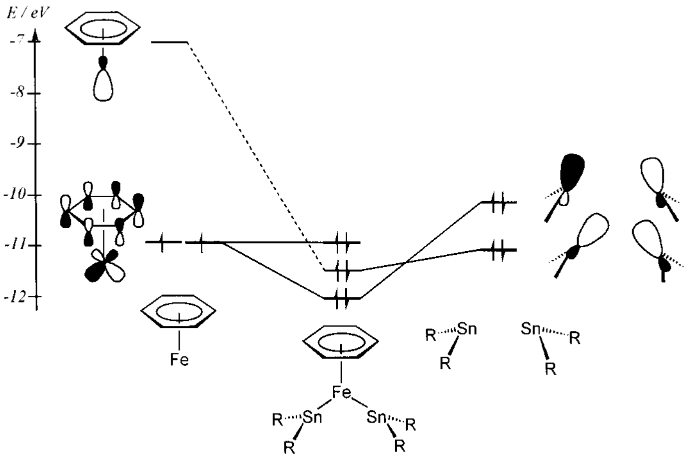


Figure 3. Schematic interaction diagram between the fragment orbitals of $[(\eta^6\text{-}C_6H_6)Fe]$ and $(SnR_2)_2$ (R = Me, Ph). The Fe – Sn interaction is invariant towards a change in R as well as towards rotation around the Fe – Sn bond. From the degenerate $[(C_6H_6)Fe]$ antibonding π set of the $[(\eta^6\text{-}C_6H_6)Fe]$ fragment, only the relevant orbital is drawn.

The Fe – Sn and the $(\eta^6\text{-}C_6H_6)$ – Fe interactions do not change as the SnR_2 group rotates around the Fe – Sn bond. The corresponding orbital energies and reduced overlap populations (as a measure of bond strength) remain essentially invariant: Fe – Sn 0.66, Fe – C_{arene} 0.070 – 0.079. (The slight deviation in the latter is the result of the low symmetry of the system and therefore varies somewhat from one carbon atom to the next.) The experimentally observed rotation/distortion is solely the result of the steric repulsion of the aryl rings on tin. This could be demonstrated with an induced rotation on the model system $[(\eta^6\text{-}C_6H_6)Fe(SnPh_2)_2]$.

The Fe – Sn bond can be interpreted as a donation of the Sn 5s lone-pair electrons into empty or half-filled acceptor d orbitals on iron. There is little iron-to-tin backbonding. The electron donation leads to an increased occupation of $[(\eta^6\text{-}C_6H_6)Fe]$ π-antibonding orbitals. The reduced overlap population of the Fe – C_{arene} bond (as a measure of bond strength) drops from 0.103 in the $[(\eta^6\text{-}C_6H_6)Fe]$ fragment to 0.070 – 0.079 in the model complexes $[(\eta^6\text{-}C_6H_6)Fe(SnMe_2)_2]$ and $[(\eta^6\text{-}C_6H_6)Fe(SnPh_2)_2]$. Consequently, the arene ligand will be bound more weakly to the iron center. This theoretical finding is nicely reflected in the observed π-arene exchange lability described above. Figure 3 shows a schematic interaction diagram to illustrate the Fe – Sn and $[(\eta^6\text{-}C_6H_6)Fe]$ bonding situation in **15**. The HOMO is mainly Fe-based in character. The metal – metal bonds display strong polar contributions. The metal charges in the individual fragments are Fe -0.48 in $[(\eta^6\text{-}C_6H_6)Fe]$ and Sn $+0.7$ in SnR_2. Upon interaction of the fragments they change to Fe -1.64 and Sn $+1.4$ (it should be emphasized here, that the trend is important, not the actual numerical values). Experimentally a $Sn^{\delta+} \rightarrow Fe^{\delta-}$ polarization has been substantiated in a rather general way for a series of organotin transition metal complexes by means of Mössbauer spectroscopy.[17]

^{57}Fe and ^{119}Sn Mössbauer studies of 15:[18] Complex **15** contains two active Mössbauer nuclei, so that this technique can provide valuable information about valence state and geometry in coordination compounds. ^{57}Fe and ^{119}Sn Mössbauer spectra of **15** were recorded at 80 K on crystalline samples of **15** (Figures 4 and 5, respectively) resulting in two symmetrically split doublets for the iron and the tin nuclei with

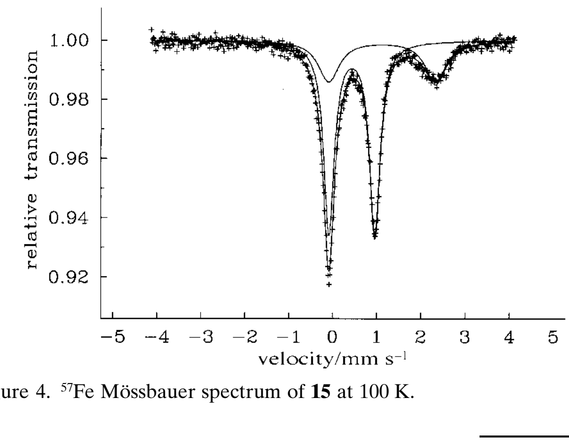


Figure 4. ^{57}Fe Mössbauer spectrum of **15** at 100 K.

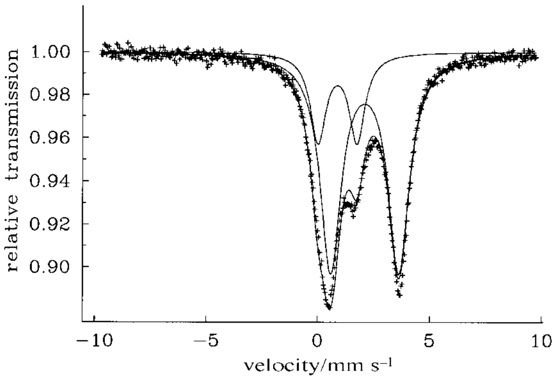


Figure 5. ^{119}Sn Mössbauer spectrum of **15** at 100 K.

characteristic Mössbauer parameters: ^{57}Fe (relative to α-iron): $\delta_{IS} = 0.53$ mm s^{-1}, $\Delta E_Q = 1.04$ mm s^{-1}; ^{119}Sn (relative to $CaSnO_3$): $\delta_{IS} = 2.11$ mm s^{-1}, $\Delta E_Q = 3.04$ mm s^{-1}. In addition to these major doublets, both spectra display one additional symmetrically split doublet as a minor component with the following Mössbauer parameters: ^{57}Fe (relative to α-iron): $\delta_{IS} = 1.23$ mm s^{-1}, $\Delta E_Q = 2.42$ mm s^{-1}, 31 % intensity; ^{119}Sn (relative to $CaSnO_3$): $\delta_{IS} = 0.90$ mm s^{-1}, $\Delta E_Q = 1.74$ mm s^{-1}, 23 % intensity. The origin of these signals is not yet clear; however, they most probably result from impurities introduced by the decomposition of the very air-sensitive **15** during our sample preparation procedure. The major, symmetrically split ^{119}Sn doublet (Figure 5) is in agreement with two equivalent tin centers in the solid state.

Regarding the ^{57}Fe parameters for **15**, the values are in good agreement with a pseudotrigonal coordination on the iron(II) center, assuming that one coordination site on the iron is occupied by the η^6-bonded toluene and the other two by SnR_2 ligands. Mössbauer parameters comparable with those of **15** are found for the $\eta^6-\eta^4$ benzene sandwich complexes $[(\eta^6\text{-}C_6H_6)Fe(\eta^4\text{-}C_6H_4)]$ and $[(\eta^6\text{-}C_6H_6)Fe(\eta^4\text{-}C_6H_8)]$, which display a rather similar coordination of the iron center, assuming that one coordination site on iron is occupied by the η^6-bonded benzene and the remaining two by the η^2-ene coordination ($\delta_{IS} = 0.64$ mm s^{-1}, $\Delta E_Q = 1.04$ mm s^{-1} and $\delta_{IS} = 0.49$ mm s^{-1}, $\Delta E_Q = 0.92$ mm s^{-1}).[19]

The complex $[(\eta^6\text{-toluene})Fe(H_2)(SiCl_3)_2]$,[7i] which has a half-sandwich structure as in **15** and iron in the formal oxidation state +4, has a considerably smaller $\delta_{IS} = 0.25$ mm s^{-1}, but a rather similar $\Delta E_Q = 0.91$ mm s^{-1} (298 K).[7i] With respect to Sn^{II}, the observed parameters for **15** show a slight, although significant, deviation from the values of Lappert's distannene $(\mathbf{1})_2$ ($\delta_{IS} = 2.16$ mm s^{-1}, $\Delta E_Q = 2.31$ mm s^{-1}),[20] which may serve as a "point of reference" for the discussion, since there are, as yet, no Mössbauer parameters available for Weidenbruch's distannene $(\mathbf{3})_2$. This seems warranted, since both stannylenes are strictly monomeric in solution and X-ray crystallography shows both compounds to have a related dimeric structure with a bent double bond.[1h] It is evident that $(\mathbf{1})_2$ and **15** have drastically lowered δ_{IS} values compared with those from pure inorganic or even organometallic systems that contain Sn^{II} and have typical values of $\delta_{IS} = 3-4$ mm s^{-1}. Examples for the latter are halogenostannates(II)[21] or sandwich complexes $[(\eta^5\text{-RCp})_2Sn^{II}]$ (R = alkyl).[20, 22] In these compounds the 5s orbital on tin, which contains the lone pair, retains its high σ-s character compared with $(\mathbf{1})_2$ and **15**. Thus, the relatively large differences in the δ_{IS} values for $(\mathbf{1})_2$ and **15** relative to these compounds are indicative of a certain amount of p character in the Sn–Sn $(\mathbf{1})_2$ and Sn-Fe-Sn (**15**) bonding; this is induced by rehybridization of the 5s lone pair on Sn. In this process s electron density is lost, both in donation to the transition metal as well as by rehybridization.[23, 24] The quadrupole splitting for **15** is in agreement with that which would be expected for a trigonal configuration on tin. Work in other systems shows that trigonal three-center coordination as in **15** gives similar ΔE_Q values.[23] Most convincing here is a comparison with the Mössbauer parameters for $[R_2Sn\text{-}M(CO)_5]$ (R = $CH(SiMe_3)_2$, M = Cr, Mo)[20] which are in the same range and for which a trigonal-planar coordination at tin has also been derived from crystallographic work.[1c]

With regard to the result of our theoretical study and the question of bond polarity, it should be recalled that the Fe–Sn bond has polar character $Sn^{\delta+} \rightarrow Fe^{\delta-}$ with strong tin-to-iron σ donation, but it has significantly low π-bonding interaction. The experimental quadrupole splitting $\Delta E_Q = 3.05$ mm s^{-1} for **15** is in good agreement with the theoretical results, since significant dπ–pπ backbonding from Fe to Sn would need a population of the 5π orbitals on tin perpendicular to the two $\{(SiMe_3)_2HC\}_2\}$Sn–Fe planes. This would result in a significant reduction of ΔE_Q, which is, however, not observed. A similar argumentation holds true for the above-mentioned complexes $[R_2SnM(CO)_5]$ (R = $CH(SiMe_3)_2$, M = Cr, Mo) with large ΔE_Q values similar to those measured for **15**.[20] It is interesting to note that a related bond polarity (Si → Mo) has been substantiated in molybdocene and tungstenocene derivatives of divalent SiR_2 silicon species recently described by Jutzi and co-workers.[25]

Conclusions

In this contribution we have described the reactivity of the divalent tin species [{(2-*tert*-butyl-4,5,6-trimethyl-phenyl)}$_2$Sn] **2** towards toluene-solvated iron atoms, $[(\eta\text{-toluene})_2Fe]$. Complex **2** is highly reactive towards these solutions which can be accounted for by i) its high donor capability and ii) the ready accessibility of reactive subvalent 14 e fragments $[(\eta^6\text{-toluene})Fe]$ generated from toluene solutions, which contain $[(\eta\text{-toluene})_2Fe]$ as the sole product. The title compound represents the first structurally characterized bis(stannylene) compound with two threefold-coordinated tin atoms. The Fe–Sn bonds in **15** are found to be short. They were characterized on the basis of EHMO calculations as highly polar with no significant p backbonding donation from iron to tin. Thus, the Fe–Sn interaction can be described as a "dative" coordination from the two tin atoms to the iron atom.

Experimental Section

General: The metal-atom reaction was conducted in home-built, all-glass, static metal–vapor reactors (6 L) based on the design published by Klabunde.[26] Elemental iron was 99 % pure. The metal was evaporated from resistively-heated alumina crucibles (Mathis Comp., USA). In metal – vapor reactions, ≈20% of the metal is typically lost because of the deposition of metal vapor outside of the reaction zone of the metal/toluene cocondensate. This was accounted for by determining the yields. With the excepttion of the metal – vapor synthesis, all reactions were carried out under an atmosphere of dry nitrogen gas with standard Schlenk techniques. Microanalyses 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 AC300 spectrometer (300 MHz for ^{1}H, 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. MS spectra were recorded on a MAT8200 instrument under standard conditions (EI, 70 eV) and the fractional sublimation technique for the compound inlet.

Theoretical studies: Qualitative MO computations were performed within the extended Hückel formalism[27] with weighted H_{ij}'s[28] with the CACAO program (Version 4.0).[29] Geometrical parameters were taken from the X-ray structural work of **12**. The atomic parameters were used as supplied by the CACAO program, in particular Fe (H_{ii} [eV], ζ) 4s: – 9.17, 1.9; 4p: – 5.37, 1.9; 3d: – 12.7, 5.35, 1.80 (double ζ expansion of the d orbitals with the coefficients 0.5366 and 0.6678); Sn (H_{ii} [eV], ζ) 4s: – 16.16, 2.12; 4p: – 8.32, 1.82.

Synthesis of [(η^6-toluene)Fe-{Sn-(*tert*-butyl-4,5,6-trimethylphenyl)$_2$}$_2$] (15): Iron vapor (1.21 g, 21.5 mmol) was codeposited with excess toluene (150 g) at – 196 °C and 10^{-2} Pa over a period of 2 h. The reaction mixture was filtered at – 78 °C through a pad of alumina (5 cm) to remove unreacted iron metal. A solution of [Sn(*tert*-butyl-4,5,6-trimethylphenyl)$_2$] (**3**$_2$) (2.5 g, 53 mmol) in ether (20 mL) was added at – 78 °C, and the resulting solution was warmed to room temperature under stirring for 12 h. All volatiles were removed in vacuo (10^{-2} Pa), and the brown solid residue was dissolved in diethyl ether. The resulting deep brown solution was filtered through a medium porosity glass frit, concentrated, and cooled to – 30 °C to give **15** (2.28 g, 1.97 mmol, 65%, based on added distannane (**3**)$_2$). ^{1}H NMR (300 MHz, C_6D_6, 27 °C): δ = 7.29, 6.98 (2s, 4H, =CH), 5.32, 5.10, 5.16, 4.84 (2t, 2H, *m*-H; m, 1H, *p*-H; m, 2H, *o*-H), 3.47, 3.35, 2.21, 2.19, 2.12, 2.07 (6s, 36H, CH_3-aryl), 1.43 (s, 3H, CH_3-toluene), 1.36, 0.85 (2s, 36H, *t*Bu); ^{13}C NMR (75 MHz, C_6D_6, 27 °C): δ = 164.3, 161.1, 151.9, 151.8, 141.9, 141.4, 135.7, 135.3, 133.8, 133.5 (C-aryl), 126.7, 125.1 (CH-aryl), 94.6, 83.4, 81.6, 81.4, 81.0, 80.0 (C-toluene), 37.3, 36.6 ($C(CH_3)_3$), 33.1, 32.1 ($C(CH_3)_3$), 25.3, 25.1, 21.5, 21.4, 16.4, 16.1 (CH_3-aryl), 21.6 (CH_3-toluene); ^{119}Sn{^{1}H} NMR (300.1 MHz, C_6D_6, 27 °C) δ = 673; IR (KBr) $\tilde{\nu}$ = 1392(s), 1383(s), 1375(s, all CH_3), 1278(m, *t*Bu), 808(w), 775(w) cm^{-1} (both η^6-toluene); MS (EI, 70 eV): decomposition; $C_{59}H_{84}FeSn_2$ (1160.84) found C 65.38, H 8.00, Fe 4.89; calcd 65.17, H 8.10, Fe 4.83; cyclovoltammetry in (CH_2Cl_2): – 1.3 V; completely irreversible reduction.

Synthesis of [{(2-*tert*-butyl-4,5,6-trimethylphenyl)}$_2$Sn}$_2$Fe(CO)$_3$} (18), and [(2-*tert*-butyl-4,5,6-trimethylphenyl)}$_2$Sn-Fe(CO)$_3$} (19): Complex **15** (0.65 g, 0.55 mmol) was dissolved in toluene (20 mL). After three freeze and thaw cycles, CO gas was added at – 78 °C and the pressure of the solution was maintained at ≈1 bar for 12 h. All volatiles were removed in vacuo and the solid residue dissolved in diethyl ether and cooled to – 30 °C to give a 2:1 mixture (according to NMR spectroscopy) of **18** and **19**.

*Compound **18***: ^{1}H NMR (300 MHz, C_6D_6, 27 °C): δ = 7.18 (s, 1H, =CH), 3.11 (s, 3H, CH_3), 2.06 (s, 3H, CH_3), 1.98 (s, 3H, CH_3), 1.31 (s, 9H, *t*Bu); ^{13}C NMR (75 MHz, C_6D_6, 27 °C): δ = 219.1 (CO), 159.8, 152.6, 140.7, 136.8, 134.4, 127.5 (all aryl-C), 37.1 ($C(CH_3)_3$), 33.2 ($C(CH_3)_3$), 26.7, 21.3, 16.0 (all CH_3); ^{119}Sn{^{1}H} NMR (300.1 MHz, C_6D_6, 27 °C) δ = 1055.

*Compound **19***: ^{1}H NMR (300 MHz, C_6D_6, 27 °C): δ = 7.14 (s, 1H, =CH), 3.08 (s, 3H, CH_3), 2.16 (s, 3H, CH_3), 1.83 (s, 3H, CH_3), 1.41 (s, 9H, *t*Bu); ^{13}C NMR (75 MHz, C_6D_6, 27 °C): δ = 228 (CO), 162.5, 152.1, 142.0, 136.2, 134.3, 127.2 (all aryl-C), 37.5($C(CH_3)_3$), 34.4 ($C(CH_3)_3$), 27, 21.1, 15.7 (all CH_3); ^{119}Sn{^{1}H} NMR (300.1 MHz, C_6D_6, 27 °C) δ = 1059.

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[10] Crystal structure analysis of **15**: ($C_{59}H_{84}FeSn_2 \cdot C_4H_{10}O$); a dark brown crystal (0.42 × 0.30 × 0.12 mm), obtained from diethyl ether/acetonitrile, was measured on a Siemens SMART-CCD diffractometer, $Mo_{K\alpha}$ radiation at T = 298 K. Cell dimensions a = 1216.4(3), b = 1324.8(3), c = 1993.0(5) pm, α = 93.09(2), β = 104.74(2), γ = 105.13(2)°, V = 2973.3(11) × 10^6 pm^3, Z = 2, ρ_{calcd} = 1.296 g cm^{-3}, μ = 1.112 mm^{-1}, tri-

clinic crystal system, space group $P\bar{1}$, data collection of 11774 reflections, absorption correction with Siemens SADABS: R_{merg} before/after: 0.1344/0.0380, max/min equivalent transmission 1.00/0.31; 9612 independent reflections ($R_{\text{merg}} = 0.0398$, $1.82^\circ \le \Theta \le 28.28^\circ$), 6171 observed reflections $[F_o \ge 4\sigma(F)]$, structure solution with direct methods (SHELXS) and refined on F^2 (SHELXTL 5.03) (600 parameters). Hydrogen positions were calculated and refined as riding groups with 1.2-fold isotropic U values of the respective C atoms (1.5 for CH_3). The *tert*-butyl group (C34 to C36) was disordered, but could be resolved with ⅓ and ⅔ occupancy factors. A disordering of the atoms C53 to C59 was resolved with occupancy factors of 0.5 each, whereas the hydrogen atoms were inserted in their calculated positions. ($R1 = 0.0613$, $wR2$ (all data) $= 0.1735$, $w^{-1} = \sigma^2(F_o^2) + (0.0988\,P)^2$, with $P = [\max. F_o^2) + (2F_c^2)]/3$, maximum residual electron density 1.668×10^6 e pm^{-3}. Further details on the crystal structure determination may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (fax: (+49) 7247-808-666); e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-408895.

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