Carbonyliron complexes containing Fe–Sn bonds are readily available by various synthetic methods [1]. The reaction of Fe(CO)₅ with organotin compounds appears to be particularly convenient, since the product distribution depends critically on the reaction conditions. In the case of methyltin compounds, major products (4, 5, 7) which could be crystallized were finally characterized by X-ray analysis [2]. Although these results appear to be conclusive, there is some doubt about the correct assessment of all major species present in the reaction solution. We have now repeated some of the reactions between organotin compounds and Fe(CO)₅ and have applied ¹¹⁹Sn NMR in order to get more information on the composition of the reaction solutions. Furthermore, we wanted to determine one-bond coupling constants $J(¹¹⁹Sn^{57}Fe)$ and to compare the magnitude of geminal coupling constants $²J(¹¹⁹Sn¹¹⁹Sn)$ across Fe in non-cyclic and cyclic compounds. For these purposes we have studied compounds 1 to 7.

Results and Discussion

With the exception of compounds 3 and 6, all complexes were prepared following known procedures [1]. Compound 3 was obtained as white fibrous solid from the reaction between Fe(CO)₅ and Me₂SnCl₂ after 16 h at 120 °C, followed by the usual work-up procedure. For the synthesis of 4a and 5–7, we started from Fe(CO)₅ and Me₂SnCl₂, as described [1]. The complexes 4 and 7 could be separated by column chromatography, whereas the minor products 5 and 6 always formed a mixture (ca. 40:60) which could not be separated as yet. Interestingly, the presence of 6 had not been detected in previous studies. The divinyl derivative of 6 was reported as a minor product of the reaction between (CH₂=CH)₂Sn[O(O)CCF₃]₂ and Na₂[Fe(CO)₅], as proposed on the basis of IR and mass spectroscopic data [2]. The exchange reaction according to eq. (1) also afforded a mixture of the compounds 5 and 6.
NMR data ($\delta^{119}$Sn and coupling constants) are given in Table I.

**Coupling constants $^1J(^{119}$Sn$^{57}$Fe)**

In the case of compound 1, the conditions for observing $^1J(^{119}$Sn$^{57}$Fe) in the $^{119}$Sn($^1$H) NMR spectrum (Fig. 1) are ideal since all other couplings to $^{119}$Sn are readily obtained from $^{13}$C NMR spectra and assigned in the $^{119}$Sn NMR spectrum. The situation for the other compounds can be much more complicated: The relative intensities of $^{57}$Fe (natural abundance 2.19%) and $^{13}$C satellites may be similar and the two types of satellites may severely overlap because of the comparable magnitude of $^3J(^{119}$Sn$^{13}$C) and $^1J(^{119}$Sn$^{57}$Fe) values. In addition, the $^{13}$C satellites may be broadened owing to dynamic processes. This becomes already apparent in Fig. 2 for compound 4a. The coupling constant $^1J(^{119}$Sn$^{57}$Fe) = 64 Hz could only be deduced from the $^{119}$Sn($^1$H) NMR spectrum (measured at 10 °C in order to slow down intramolecular scrambling of the carbonyl groups) after the five different values $^1J(^{119}$Sn$^{13}$C$^a$), $^2J(^{119}$Sn$^{13}$C$^b$) and $^3J(^{119}$Sn$^{13}$C$^c$) values had been determined under the same conditions by $^{13}$C NMR. In the cases of the compounds 2, 3 and 4b, the $^{119}$Sn NMR signals were too broad for an accurate assignment of all satellite signals and in the mixtures containing the compounds 5 and 6 severe overlap with $^{13}$C satellites (see Fig. 3) prevented the unambiguous assignment of $^{57}$Fe satellites. Rapid scrambling of all 16 carbonyl groups in complex 7 leads to an averaged coupling $^2J(^{119}$Sn$^{13}$C$^d$) = 42 Hz. This facilitates the assignment of $^{57}$Fe satellites in the $^{119}$Sn NMR spectrum of 7 on the basis of their intensity (ca. 50% of the intensity of the $^{13}$C satellites) to give $^1J(^{119}$Sn$^{57}$Fe) = 36 Hz. Although it proved
possible to determine several coupling constants \( J(119\text{SnFe}^{119}\text{Sn}) \) for the first time, the data set is too limited for further discussion, in particular in the absence of sign information on these couplings.

**Coupling constants** \( J(119\text{SnFe}^{119}\text{Sn}) \)

An inspection of Table I shows that there are two ranges of magnitude for \( |J(119\text{SnFe}^{119}\text{Sn})| \) values, one between 300 and 350 Hz (3, 2 [4]), and the other one between 1400 and 1800 Hz. The latter range is always associated with the cyclic compounds 4 to 6 (see also Figs 2 and 3). Although two equivalent coupling pathways are present in the complexes 4, 5 and 6, the increase in the magnitude of \( |J(119\text{Sn}^{119}\text{Sn})| \) exceeds by far the expected range predicted by the additivity of coupling pathways, a concept which is frequently valid [5]. The X-ray analyses of 4a [2a] and 5 [2b] have revealed rather short distances \( d_{\text{SnSn}} \approx 330 \text{ pm} \), just somewhat longer than in metallic \( \beta \)-Sn (302, 318 pm). Therefore, tin-tin interactions can be proposed as a third and apparently efficient coupling pathway. The smaller value of \( |J(119\text{Sn}^{119}\text{Sn})| \) in 4b as compared to 4a is in agreement with other coupling data if SnMe groups are replaced by SnBu groups [6].

**Chemical shifts** \( \delta^{119}\text{Sn} \)

The \( \delta^{119}\text{Sn} \) value of compound 1 is almost identical with the value reported in the literature [7]. However, the literature data given for 4a (\( \delta^{119}\text{Sn} +257 \)) cannot be correct; we find \( \delta^{119}\text{Sn} +88 \) for 4a instead. It appears that compound 3 (\( \delta^{119}\text{Sn} 258.5 \))

<table>
<thead>
<tr>
<th>Compound Nr.</th>
<th>Solv.</th>
<th>( \delta^{119}\text{Sn} )</th>
<th>( 2J(119\text{Sn}^{13C\text{CO}}) )</th>
<th>( 2J(119\text{Sn}^{119}\text{Sn}) )</th>
<th>( 1J(119\text{Sn}^{57}\text{Fe}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C6D6</td>
<td>+ 144.1</td>
<td>132.0</td>
<td>–</td>
<td>42.7</td>
</tr>
<tr>
<td>2</td>
<td>C6D8</td>
<td>+ 80.4</td>
<td>101.0, 65.0, 33.0</td>
<td>349.8</td>
<td>&lt;40</td>
</tr>
<tr>
<td>3</td>
<td>C6D6</td>
<td>+ 258.5</td>
<td>n.m.</td>
<td>302.0</td>
<td>n.m.</td>
</tr>
<tr>
<td>4a</td>
<td>C6D6</td>
<td>+ 87.8</td>
<td>86.0, 48.0, 28.0</td>
<td>1798.0</td>
<td>n.m.</td>
</tr>
<tr>
<td></td>
<td>C6D6</td>
<td>+ 88.2</td>
<td>86.0, 45.0, 34.0</td>
<td>1728.0</td>
<td>64.0</td>
</tr>
<tr>
<td>4b</td>
<td>C6D6</td>
<td>+ 86.5</td>
<td>83.0, 44.0, 30.0</td>
<td>1403.5</td>
<td>n.m.</td>
</tr>
<tr>
<td>5</td>
<td>C6DCl2</td>
<td>+ 123.8</td>
<td>n.m.</td>
<td>1580.0</td>
<td>40.0</td>
</tr>
<tr>
<td>6</td>
<td>C6DCl2</td>
<td>+ 101.5</td>
<td>n.m.</td>
<td>1710.0</td>
<td>n.m.</td>
</tr>
<tr>
<td>7</td>
<td>C6DCl2</td>
<td>+ 953.0</td>
<td>n.m.</td>
<td>1710.0</td>
<td>n.m.</td>
</tr>
</tbody>
</table>

\[ a \text{ Measured at } 25 \text{ °C if not mentioned otherwise, } \delta^{119}\text{Sn} \text{ data with respect to external neat } \text{Me}_4\text{Sn, } \Xi(119\text{Sn}) = 37.290665 \text{ MHz, coupling constants in Hz} ; \]
\[ b \text{ data from Ref. } [4] ; \]
\[ c \delta^1\text{H} = 0.91 \text{ s, } \delta J(119\text{Sn}^1\text{H}) = 51 \text{ Hz} ; \]
\[ d \delta^1\text{C} = 5.7, 203.2, 205.0 ; \]
\[ e \delta^1\text{H} (D_2\text{-THF}) = 1.05 \text{ s, } \delta J(119\text{Sn}^1\text{H}) = 44.8, \]
\[ f \delta^1\text{C} (D_2\text{-THF}) = -2.8, 206.8, 209.2 ; \]
\[ g \text{ measured at } 10 \text{ °C, in agreement with } \delta J(119\text{Sn}^{13C\text{CO}}) \text{ data obtained from }^{13}\text{C NMR at } 10 \text{ °C} ; \]
\[ h \text{ Me}_2\text{Sn group, assignment confirmed by measurement of the }^1\text{H coupled spectra and by successful application of the INEPT pulse sequence} ; \]
\[ i \delta^1\text{C} = 209.0, \delta J(119\text{Sn}^{13C\text{CO}}) = 42.0 \text{ Hz} . \]
had been studied in Ref. [7] instead of 4a. We have confirmed the nature of 3 and 4a by obtaining consistent 1H and 13C NMR spectroscopic data (see footnotes to Table I). The change in the $\delta^{119}\text{Sn}$ data between 2 and 3 ($\Delta^{119}\text{Sn} 205$) is rather similar to that between Me$_2$Sn and Me$_3$SnCl ($\Delta^{119}\text{Sn} 164$). In the cyclic compounds 4 to 6 the $\delta^{119}\text{Sn}$ values are found in a narrow range between +85 and +125. In contrast, the $^{119}\text{Sn}$ nucleus linked to four Fe(CO)$_4$ groups in complex 5 becomes deshielded ($\delta^{119}\text{Sn} +287.7$). This deshielding is much more significant in 6 ($\delta^{119}\text{Sn} +953$), and $^{119}\text{Sn}$ nuclear shielding reaches a minimum in compound 7 ($\delta^{119}\text{Sn} +2330$). In general, increased paramagnetic contributions arising from $\mathbf{B}_0$-induced mixing of ground states and energetically low-lying excited states are responsible for reduced shielding of heavy nuclei [8]. In the case of the complexes 6 and 7, three-centre FeSnFe bonds involve non-bonding unoccupied MO's of low energy, and it is therefore conceivable that this type of bonding causes the extreme deshielding. Indeed, apart from monomeric dialkylstannylenes ($\delta^{119}\text{Sn} = +2330$ [9]), there is no other example of such deshielded $^{119}\text{Sn}$ nuclei, and, in comparison with other tin(IV) compounds, the $\delta^{119}\text{Sn}$ value of 7 is more than 1000 ppm outside of the normal range [6].

**Experimental**

All compounds were handled in an inert atmosphere (Ar), using carefully dried solvents. The complexes were prepared following literature procedures: 1 [10], 4 [11], 5 and 7 [12]. The mixtures obtained from prolonged heating at 120 °C of an excess of Fe(CO)$_5$ with Me$_3$SnCl contained 4, 5, 6, 7 and Fe$_3$(CO)$_4$ and were purified by chromatography on silica which also served to retain paramagnetic impurities. This method gave 4 and 7 as pure products whereas 5 and 6 were isolated as a 40:60 mixture.

**Bis(chlorodimethylstannyl)tetracarbonyliron (3)**

A mixture of 1 g of Me$_2$SnCl$_2$ (4.52 mmoles) in 30 ml of Fe(CO)$_5$ is heated to reflux (ca. 120 °C) for 16 h. Chromatography on silica with hexane affords product 3 from the first fraction. Recrystallization from hexane gives 1.42 g (58.5%) of 3 as a white fibrous material (m. p. 153 °C).

IR [cm$^{-1}$]: 2085 vs, 2034 s, 2014 s, 2002 vs; MS: $m/e$ (% ) = 537 (48), 205 (100) Me$_2$SnFe.

**Exchange reaction between [Me$_2$SnFe(CO)$_4$]$_2$ (4a) and Sn/Fe(CO)$_4$$_4$ (7)**

A 1:1 mixture of 4a and 7 in toluene is heated to reflux for 36 h and filtered through silica. The toluene is removed in vacuo, the residue is dissolved in CH$_2$C1$_2$. U$^{19}$Sn NMR shows that the complexes 5 and 6 are present (ca. 40:60) together with an excess of the starting materials.

IR [cm$^{-1}$]: 2096 m, 2071 s, 2054 s, 2045 vs, 2028 m, 2011 s, 1998 s, 1987 vs.

NMR spectra were recorded using Bruker AC 300 and AM 500 spectrometers equipped with multinuclear units and variable temperature units. If possible, $^{119}\text{Sn}$ NMR spectra were measured with the refocused INEPT pulse sequence [13] [1, 2, 3, 4a, 5 (SnMe$_2$), 6 (SnMe$_2$)]. By using an appropriate delay between experiments (ca. 16 s) effects of dielectric heating as a result of $^1$H decoupling were fully compensated, leading to very sharp $^{119}\text{Sn}$ resonances. For the central Sn atoms in 5, 6 and 7, the $^{119}$Sn resonances were recorded without $^1$H decoupling. IR spectra were obtained with a Perkin Elmer 983 G instrument.

El-Mass spectra (70 eV) were recorded with a Finnigan MAT 8500 spectrometer ($m/e$ data are based on the $^{120}\text{Sn}$ isotope).

We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for support of this work.
[1] a) M. C. Baird, Progr. Inorg. Chem. 9, 1 (1968);
   d) R. A. Burnham, M. A. Lyle, and S. R. Stobart, J. Organomet. Chem. 125, 179 (1977);
   b) R. M. Sweet, C. J. Fritchie, Jr., and R. A. Schunn, Inorg. Chem. 6, 749 (1967);