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^{119}Sn and ^{57}Fe Mössbauer Studies of some Stannylene and Tin Ylid Complexes of Iron Carbonyl Derivatives

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Organo-tin compounds containing an Sn–N bond can be added in some cases to metal coordinated carbonyl groups forming a carbenoid ligand. This was shown by example with tin amides of tin(IV) (*1*) and tin(II) (*2*) when these compounds are allowed to react with iron pentacarbonyl [1].

In contrast to analogue reactions involving aluminum and titanium amides [2, 3], all Sn–N bonds are cleaved to generate Sn–O bonds.

In addition to this chemistry *2* can act as a σ-donor towards transition metal carboyl complexes similar to tertiary phosphines according to the non-bonding pair of electrons at the tin atom, thus forming a stannylene complex [4]. Both types of reactions are realized when *2* is treated either with $M(CO)_6$ (M = Cr, Mo, W) or $Fe(CO)_5$. The more electrophilic carbonyl carbon atoms of $Fe(CO)_5$, however, favour the additional reaction. Some reactions we investigated in our laboratory are collected in Scheme 1.

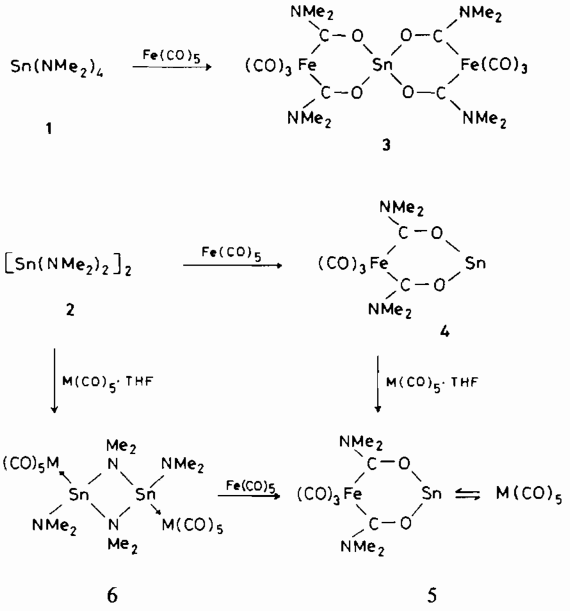
The formal oxidation numbers of the tin and iron atoms can be considered to remain unchanged during these procedures. The reaction of *2* with $Fe(CO)_5$ yield the new complex *4* containing a lone pair of electrons, which can be used as a starting material for the preparation of *5* when treated with photochemically produced $M(CO)_5 \cdot THF$ complexes. Compound *5* is also available from *6* by subsequent reaction with $Fe(CO)_5$.

The tetrahedral coordinated *1* gives *3* and the spectroscopic data are in agreement with a symmetric structure involving chemically equivalent $Fe(CO)_3$ moieties.

TABLE I. ^{57}Fe and ^{119}Sn Mössbauer Parameters[a] [in mm sec^{-1}].

Compound	Fe		Sn		Ref.
	I.S.	Q.S.	I.S.	Q.S.	
2			2.72	2.07	14
3	0.25	0.54	1.56	1.60	this work
5	0.25	0.53	2.17	2.84	this work
4	0.25	1.11	3.02	3.11	this work
6			1.89	2.22	this work

[a] Recorded at 77 K rel. to $Na_2[Fe(CN)_5NO] \cdot 2H_2O$ (iron) [10] and at 77 K *versus* $Ba^{119}SnO_3$ (tin) [13].



Scheme 1.

The purpose of the present investigation was to obtain more information on the bonding and electronic structure with the help of the Mössbauer spectroscopy on the ^{119}Sn and ^{57}Fe nuclei.

^{119}Sn Mössbauer Data

According to various Mössbauer effect studies of tin(II) compounds and their transition metal complexes, it becomes apparent that the estimation of the formal oxidation state on the bases of the isomer shift (I.S.) is not possible [5]. Some empirical trends are found concerning the question of a participation of the 5s electron lone pair in bonding.

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Recent studies have shown that coordination of 'stannylenes' or base-stabilized Sn II compounds to transition metal acceptors give rise to lower I.S. values [6]. These findings are in agreement with our experimental results. The transformation of complex *4*, which can formally be considered as a 'stannylene', into *5* by the acceptor $Cr(CO)_5 \cdot THF$ causes a drastic decrease of the I.S. value from 3.02 to 2.17 mm sec^{-1}. This effect is connected with an increase of the quadrupole splitting Q.S. from 2.31 to 2.84 mm sec^{-1}. The same tendencies are found when going from complex *2* to *6*, *e.g.* compounds whose coordination numbers have increased relative to *4*/*5* by one unit.

The complexes *5* and *6* exhibit I.S. values of about 2.1 ± 0.2 mm sec^{-1} (Table I), similar to those recorded by comparable complexes containing tin(II) ligands. These values are practically independent from the number and the nature of the substituents as shown by other authors [6, 7].

Due to the change of the I.S. value from *4* to *5* it can be deduced that *4* does not contain an Sn–Sn interaction which could arise from a possible dimerisation in order to stabilize the tin atom with the unfavoured coordination number two. This kind of stabilization proceeds with tin II compounds bearing bulky substituents [8]. Formation of a transition metal complex using these compounds leaves the I.S. values unchanged [5].

The formulation of *6* to be a dimer base-stabilized ylid complex is supported by the i.r. spectrum which is identical in the range of 1500 to 600 cm^{-1} with that of the free ligand *1* [9].

The Q.S. value, which is a measure of the deviation of the electronic environment at the tin nucleus from cubic symmetry, varies considerably with different metals and substituents in contrast to the I.S. values. In base-stabilized ylid complexes with a base molecule bonded to the tin atom a correlation between Q.S. and the base strength is discussed, the Q.S. value decreases with increasing base strength [7].

In the spectrum of *6* a remarkably small Q.S. value of 2.2 mm sec^{-1} is observed, similar to compounds with $\mu = PR_2$ or μ-AsR_2 bridged stannio complexes with the same coordination number four at the tin nucleus. The structure of *6* is the result of the concept that nitrogen ligands at the tin atom favour the formation of an Sn–N–Sn bridge instead of an 'internal' Sn–N interaction with a partial double bond similar to carbene complexes.

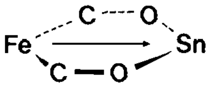
^{57}Fe Mössbauer Data

Few data are available in the literature of iron carbonyl complexes of the type $(CO)_4FeL$ in which the ligand L is bonded to the metal with a carbon atom (L = carbene, carbamoyl, alkoxycarbonyl, thiocarbonyl). From our measurements it has become apparent that the Q.S. values of these compounds are situated in a narrow range between 1.75 and 2.00 mm sec^{-1} [10]. In contrast to these results the corresponding data of the dicarbene complexes described in this paper are found to be much smaller. This can be interpreted as an increase of local symmetry at the iron nucleus.

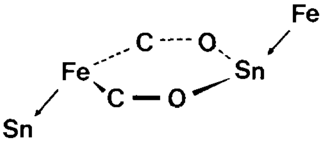
The structural unit $(CO)_3Fe[C(NMe_2)O]_2Sn$ is identical for the complexes *3*, *4* and *5* and should therefore exhibit similar Mössbauer parameters if no substantial change of the electronic environment occurs at the iron nucleus. This is the case for *3* and *5* within the experimental error, but not for *4* which shows a large increase of the Q.S. value. We interpret this unexpected difference as a participation of the iron atom at the coordination to the tin atom in complex *4*. Cryoscopic measurements of the mole mass have proved the monomeric character of *4* in solution connected with the unfavoured coordination number two for the tin atom.

Some tin(II) compounds with bulky ligands are found to be also monomeric in solution but compensate their electron deficiency by formation of an Sn–Sn bent double bond [8]. Such a stabilization in the solid state of *4* we have yet excluded from ^{119}Sn Mössbauer data; it should not affect the ^{57}Fe Q.S. value.

We therefore suppose an iron tin interaction at least in the solid state either on the bases of an intramolecular Fe → Sn transanular dative bond sketched in model A or the formation of a polymer (or dimer) with such a week bond cleaved from solvent molecules (model B).



A



B

The donor ability of an iron carbene complex with coordination number five and the formal oxidation state zero at the central atom is well known and proved by synthesis and crystal structure determination of $[(CO)_4FeC(O)NMe_2]_2Ni$ [11]. The participation of the iron atom at the coordination to the nickel cation is thereby accompanied by a drastic change of the Q.S. to a very similar value as recorded for complex *4* [10].

More information about this interesting bond system we hope to get from a single crystal determination which will be done if suitable crystals are obtained.

Experimental

The compounds *1* and *2* were prepared according to literature methods [9, 12]. *3–6* were synthesized as described previously [1, 4] and were handled with exclusion of air. The Mössbauer data were collected with usual methods [10, 13] at 77 K *versus* ^{57}Co-(Pd) (iron) or Ba^{119}SnO$_3$ (tin) sources, respectively.

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References

1 W. Petz and A. Jonas, *J. Organometal. Chem., 120,* 423 (1967).
2 W. Petz, *J. Organometal. Chem., 55,* C42 (1973).
3 W. Petz, *J. Organometal. Chem., 72,* 369 (1974).
4 W. Petz, *J. Organometal. Chem., 165,* 199 (1979).
5 J. D. Cotton, P. J. Davidson, M. F. Lappert, J. D. Donaldson and J. Silver, *J. Chem. Soc. Dalton,* 2286 (1976).
6 W.-W. Du Mont, J. L. Lefferts and J. J. Zuckerman, *J. Organometal. Chem., 166,* 347 (1979).
7 G. W. Grynkewich, B. J. K. Ho, T. J. Marks, D. L. Tomaja and J. J. Zuckerman, *Inorg. Chem., 12,* 2522 (1973).
8 D. E. Goldberg, D. H. Harries, M. F. Lappert and K. M. Thomas, *J. Chem. Soc. Chem. Commun.,* 261 (1976).
9 P. Foley and M. Zeldin, *Inorg. Chem., 14,* 2264 (1975).
10 J. Pebler and W. Petz, *Z. Naturforsch., 32b,* 1431 (1977).
11 W. Petz, C. Krüger and R. Goddard, *Chem. Ber., 112,* 3413 (1979).
12 K. Jones and M. F. Lappert, *J. Chem. Soc.,* 1944 (1965).
13 J. Lorberth, J. Pebler and G. Lange, *J. Organometal. Chem., 54,* 177 (1973).