

C,N-CHELATING LIGANDS IN ORGANOMETALLIC CHEMISTRY

ALEŠ RŮŽIČKA

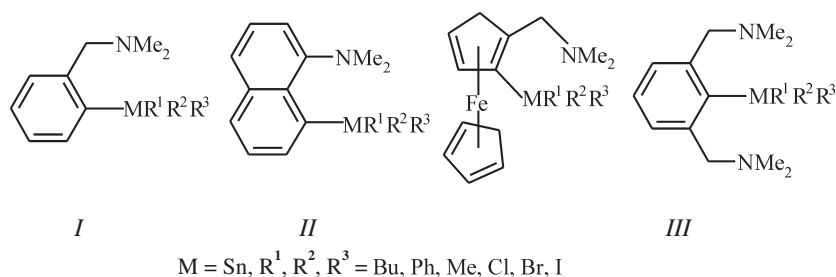
Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, nám. Čs. legií 565, 532 10, Pardubice, e-mail: ales.ruzicka@upce.cz

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Introduction

The organometallic compounds with the potentially di- or tridentate C,N-chelating ligands (see Scheme 1) are extensively studied due to their potential biological activity¹, enhanced reactivity² and very interesting structures^{2,3}. The central metal atom can interact with nitrogen donor centres from the other side(s) of ligand(s). The strength of this type of interaction is the most important criterion for estimation of the above mentioned advanced properties. In our work, we have concentrated us on the evaluation of this interaction using new and



Scheme 1

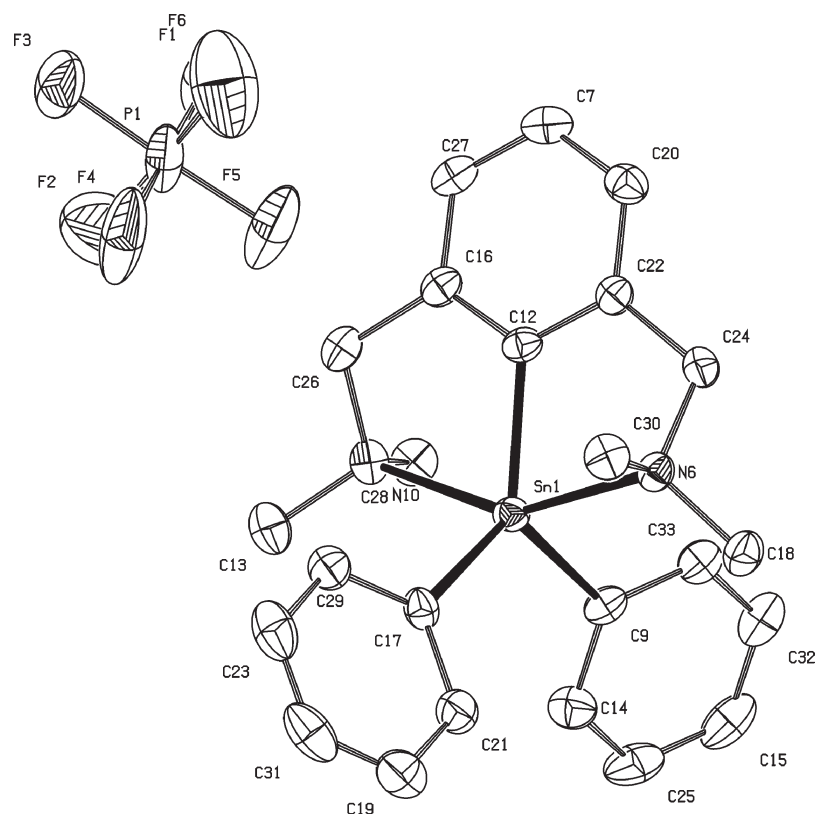


Fig. 1. Molecular structure of {2,6-bis[(dimethylamino)methyl]phenyl}diphenylstannylium hexafluorophosphate: $\{[(\text{CH}_3)_2\text{NCH}_2]_2\text{C}_6\text{H}_3\}(\text{C}_6\text{H}_5)_2\text{Sn}^+\text{PF}_6^-$, as an example of water soluble organotin(IV) compound

relatively easy methods. This text is a chronological survey of our work^{4–11}.

Results

The ¹¹⁹Sn, ¹⁵N, ¹³C and ¹H NMR spectra of {2-[(dimethylamino)methyl]phenyl}stannanes (*I*), [8-(dimethylamino)-1-naphthyl]stannanes (*II*) and {2,6-bis[(dimethylamino)methyl]phenyl}stannanes (*III*) (Scheme 1) were studied. The occurrence of intramolecular interaction between the nitrogen and tin atoms was demonstrated based on changes in the characteristic values of the NMR parameters of these nuclides ($\delta(^{119}\text{Sn})$, $\delta(^{15}\text{N})$, $J(^{119}\text{Sn}, ^{15}\text{N})$) and their interrelations, as well as on the relatively high values of the coupling constants $^3J(^{119}\text{Sn}, ^{13}\text{C}(\text{CH}_2))$ ^{4–6}.

The above mentioned results were compared with the same parameters in the solid state (CP/MAS NMR)⁶.

After these findings we concentrated on the possibility of evaluation of interaction strength by simple or advanced ¹H NMR measurements. Further work demonstrates the power of the gradient-enhanced proton-detected ¹H-¹¹⁹Sn Heteronuclear Multiple Quantum Correlation (HMQC) and *J*-HMQC in the detection and quantification of long range couplings between the ¹¹⁹Sn nucleus and the CH₂ and N(CH₃)₂ protons of the 2-[(dimethylamino)methyl]phenyl substituent. The strongly varying magnitude of the ⁶*J* coupling constants upon changing the substituents on tin demonstrates the existence of an intramolecular Sn-N donor-acceptor interaction of varying strength⁷.

During the study of donor-acceptor intramolecular interaction in {2,6-bis[(dimethylamino)methyl]phenyl}stannanes in solution and solid state, we have obtained some derivatives of the above mentioned moiety, which have very interesting structural, chemical, physical, and biological properties, above all a good water solubility of the prepared compounds, which is the main prerequisite for the use of organotin(IV) compounds as anticancer agents^{8–10}.

Conclusion

A relatively fast, easy and general method of measuring the magnitude of intramolecular donor-acceptor interaction tin-nitrogen in C,N-chelates was found. In the course of this investigation about 80 new compounds were prepared and

structurally characterised, with very interesting structural, acid-base and biological properties.

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A. Růžička (*Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, Pardubice*): **C,N-chelating Ligands in Organometallic Chemistry**

This paper briefly summarises recent investigation of the N-Sn intramolecular donor-acceptor interaction on three sets of compounds - {2-[(dimethylamino)methyl]phenyl}stannanes, [8-(dimethylamino)-1-naphthyl]stannanes and {2,6-bis[(dimethylamino)methyl]phenyl}stannanes using ¹¹⁹Sn, ¹⁵N, ¹³C and ¹H NMR spectroscopy in solution, ¹¹⁹Sn, ¹⁵N, ¹³C CP/MAS NMR spectroscopy, and solid-state X-ray diffraction techniques.