

Account / Revue

^{119}Sn NMR spectroscopic and structural properties of transition metal complexes with terminal stannylene ligands

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Abstract

The coordination effect of transition metal TML_n ($L = \text{co-ligand}$) on stannylenes R_2SnB_n ($B = \text{base}$, $n = 0-2$) has been examined analysing ^{119}Sn NMR data and X-ray molecular structures from the literature up to 2008.

Coordination deshielding $\Delta\delta$ (^{119}Sn) and chemical shift δ (^{119}Sn) of $\text{B}_n\text{R}_2\text{Sn-TM}(\text{CO})_n$ complexes, linearly correlate with δ (^{119}Sn) of R_2Sn . Slope, intercept and typical regions are interpreted through different ratios of σ/π -back bonding and impact of TM, R and B_n . Hybridisation changes explain dependencies of $^1J_{\text{Sn-TM}}$ coupling constants on L, R, B_n and TM gyromagnetic ratios γ_{TM} .

The Sn–TM bond lengths follow a parabolic profile along the TM period, fine-tuned by R, B and L_n . Electronic modifications on carbonyl complexes classify R_2Sn as poor π -acceptors, while shortening of Sn–R and widening of angles R–Sn–R correspond to increased s-character of the Sn–TM bond. A “coordinative Lewis base radius” $r_{\text{coord}}(\text{SnR}_2)$ of 1.18 Å is proposed. **To cite this article:** D. Agustin, M. Ehses, C. R. Chimie 12 2009.

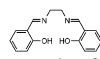
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Résumé

La coordination de métaux de transition TML_n ($L = \text{co-ligand}$) sur des stannylènes R_2SnB_n ($B = \text{base}$, $n = 0-2$) est examinée à travers les données RMN ^{119}Sn et les structures moléculaires obtenues par cristallographie.

Le déblindage de coordination $\Delta\delta$ (^{119}Sn) et le déplacement chimique δ (^{119}Sn) des complexes $\text{B}_n\text{R}_2\text{Sn-TM}(\text{CO})_n$ corrélient linéairement avec δ (^{119}Sn) de SnR_2 . La pente, l'ordonnée à l'origine et des régions particulières sont interprétées à travers différents rapports de liaisons σ/π , ainsi qu'avec TM, R et B. Des changements d'hybridation expliquent les relations entre constante de couplage $^1J_{\text{Sn-TM}}$ et L, R, B_n , et le rapport gyromagnétique γ_{TM} .

Abbreviations: Cp, cyclopentadienyl, C_5H_5 ; Cp^{Me} , methylcyclopentadienyl, $\text{C}_5\text{H}_4\text{Me}$; Cp^* , pentamethylcyclopentadienyl, C_5Me_5 ; CSD, Cambridge Structure Database; dppb, diphenyldiphosphinobutane; dppe, diphenyldiphosphinoethane; dppm, diphenyldiphosphinomethane; dppp, diphenyldiphosphinopropane; dipe, 1,2-bis(di-isopropylphosphino)ethane; e.s.d., estimated standard deviation; Fc, ferrocenyl, $(\eta^5\text{-C}_5\text{H}_4)_2\text{Fe}$; HOMO, highest occupied molecular orbital; LUMO, lowest unoccupied molecular orbital; L, 2-electron donor ligand; MNDO, modified neglect of differential overlap; MO, molecular orbital; NHC, N-heterocyclic carbene; NMR, nuclear magnetic resonance; ppm, parts per million; SalenH_2 ,

; ^tBu, tert-butyl; TM, transition metal; UV–vis, ultraviolet/visible spectroscopy; VE, valence electrons; $L_n\text{TM}$, transition metal complex fragment (co-ligand L); OTf, triflate (O_3SCF_3).

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Les longueurs de liaison Sn–TM suivent un profil parabolique sur une période de TM, selon R, B et L_n . Les modifications observées sur $R_2\text{Sn-M}(\text{CO})_n$ classent $R_2\text{Sn}$ comme faible accepteur π , raccourcissement de Sn–R et ouvertures d'angles R–Sn–R correspondant à une augmentation du caractère s de la liaison Sn–TM. Un rayon de coordination $r_{\text{coord}}(\text{SnR}_2)$ de 1.18 Å est proposé.

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Keywords: Tin; Transition metal complexes; Stannylenes; ^{119}Sn NMR; Coupling constant; X-ray crystallography; Molecular structure

Mots-clés : Étain ; Complexes de métaux de transition ; Stannyliènes ; RMN ^{119}Sn ; Constante de couplage ; Cristallographie RX ; Structure moléculaire

1. Stannylenes $R_2\text{Sn}$ as ligands

1.1. Electronic structure of stannylenes $R_2\text{Sn}$

Stannylenes (“stannanediyls”) are divalent tin compounds which show electron deficiency with respect to the Xe electron configuration. The nomenclature had been used for the first time during the 1960s even if Sn(II) compounds are known for more than 150 years [1]. It logically fits into the column of low valent group-14 species like carbenes (“methylenes”), silylenes, germylenes and plumbylenes. As opposed to the lighter homologues, stannylenes have been characterised in solution and the solid state quite early. The tin species are electrochemically more stable (standard reduction potential $\text{Sn}^{4+} \rightarrow \text{Sn}^{2+}$: 0.15 V; $\text{Sn}^{2+} \rightarrow \text{Sn}^0$: –0.141 V [2]) than their lighter congeners. They can be isolated as monomers if the appropriate sterically or electronically stabilising substituents are chosen.

The electron distribution around the low valent tin atom is highly asymmetric as seen by the non-linear arrangement of the substituents. Two descriptions of the electronic ground state are usually discussed: sp^2 hybridisation as found with carbene species (for the singlet state), with an idealised R–Sn–R bond angle of 120° . However, hybridisation is getting more and more unfavourable with heavy elements. Hence, an unhybridised model with an R–Sn–R angle of 90° view is preferred to describe the orbital distribution around Sn(II). In real structures, angles between 90° and 100° are generally found, favouring the unhybridised view with widening of the angle due to steric factors. The inclusion of $(n-1)d$ -orbitals has found not to be necessary to best describe the physico-chemical properties by various calculation methods (Fig. 1) [3].

In the sp^2 -hybridised view, the lone pair of electrons is situated in one of the sp^2 lobes and points away from the substituents. In the unhybridised model, the electron pair is distributed spherically around the

tin atom. Common to both models is the empty p-orbital perpendicular to the plane formed by the $R_2\text{Sn}$ moiety.

It is the presence of the lone pair of electrons that makes these compounds potential ligands in transition metal (TM) complexes. Prominent valence isoelectronic ligands are e.g. carbenes and carbon monoxide, CO. They are at the same time isolobal [4] to phosphines, PR_3 . All those ligands are formally able to accept π -back bonding from symmetry adapted filled TM orbitals (Fig. 2).

To reduce the lack of electron density, Sn(II) compounds easily accept Lewis bases perpendicular to the SnR_2 plane. In absence of donor solvents, this leads to aggregation forming oligo- and polymers. Coordination of such aggregates to TMs leads to lower aggregation grades. However, the tendency away from intra- to intermolecular Lewis bases increases upon TM coordination. The majority of stannylene complexes form base adducts.

Stabilisation of divalent species by the help of TM complexes is in the focus of the present review. This feature-rich chemistry has been the subject of several reviews [5–9], many of which are mentioning TM coordination as one aspect of stannylene chemistry. Others focus on specific stannylene ligands or special aspects like synthesis and reactivity. The most

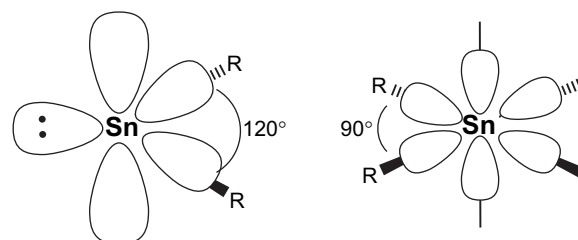


Fig. 1. Alternative hybridisation models for Sn(II) compounds: sp^2 hybridisation (left) with filled sp^2 lobe versus unhybridised model (filled s-orbital not shown).

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