# Molecular Structure, Solution Dynamics and Reactivity of Group-6 Stannylene Complexes

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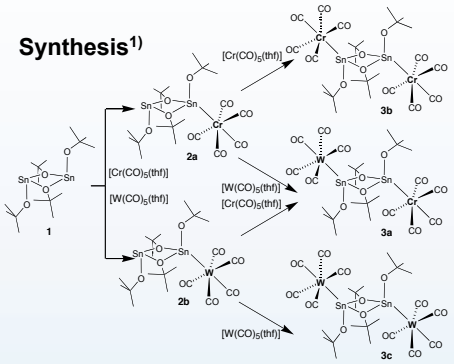
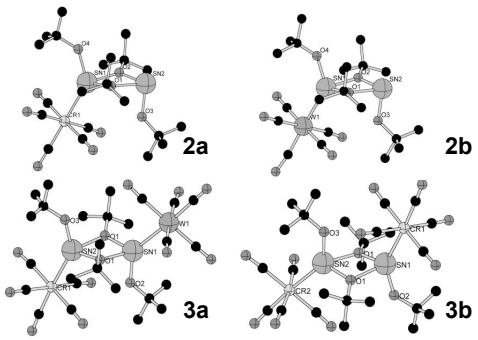
## Motivation[1)]

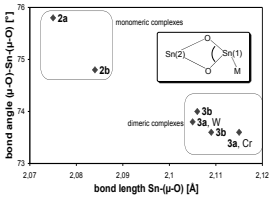
Renewed interest in stannylene complexes[3)] has risen to stabilise heteroleptic stannylenes, heterobimetallic complexes or clusters and stabilise stannylene complexes with low coordination numbers.[4-6)]
Our aim was to develop new single-source precursors for the preparation of mixed group-6-tin phases. In this report, we present the characterisation of new chromium and tungsten-stannylene complexes. We report on their molecular structure and dynamic behaviour in solution and compare their properties with that of the free ligand.

## Synthesis[1)]

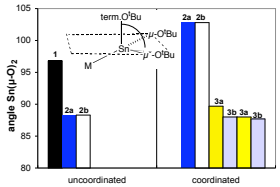



## X-ray Crystallography[1)]



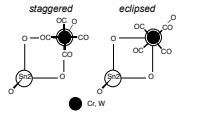




The regular **$Sn_2O_2$ ring** in **1** is distorted upon co-ordination with one transition metal:
The Sn-O bonds to the co-ordinated tin atom become shorter, the (μ-O)-Sn-(μ-O) bond angle increases.



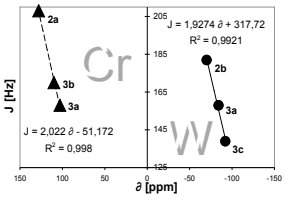

The **angle between Sn(μ-O)$_2$ plane - terminal O$^t$Bu depends** on the no. of co-ordinated transition-metal fragments.

| [Å] | 2a/2b | 3a | 3b |
|---|---|---|---|
| $Cr_{staggered}$-Sn | 2.575(2) | 2.61(2) | 2.60(4) |
| $Cr_{eclipsed}$-Sn | - | - | 2.62(3) |
| $W_{staggered}$-Sn | 2.721(1) | - | - |
| $W_{eclipsed}$-Sn | - | 2.740(1) | - |

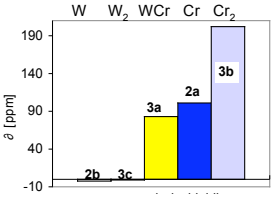



The **Sn-metal distance** depends on *number* of co-ordinated fragments *and orientation* of CO-groups with respect to term. O$^t$Bu.

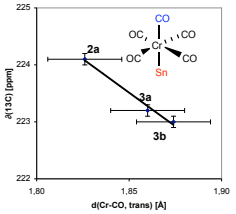
## NMR Spectroscopy[1)]



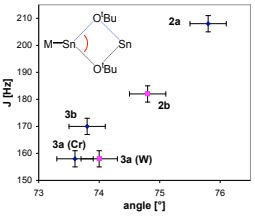

For a given transition metal, the coupling $^2J_{Sn\text{-}Sn}$ correlates with the chemical shift ∂($^{119}$Sn) of the co-ordinated tin atom.




**The co-ordination deshielding**
$\partial_{metal\text{-}free} - \partial_{coordinated}$ increases with the difference (*no. chromium*) - (no of tungsten atoms) ($N_{Cr}$ - $N_W$).

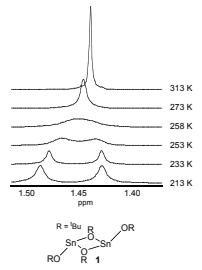



The carbonyl **$^{13}$C nuclei are shielded with increasing distance Sn-Cr(W)** (*decreasing π-backbonding*).

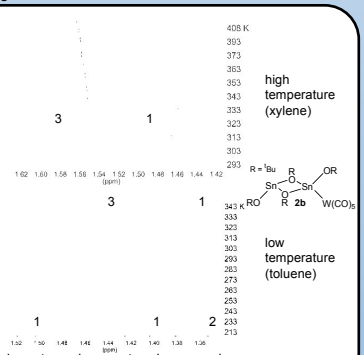



The **$^2J_{Sn\text{-}Sn}$ coupling constant increases with increasing angle (μ-O)-Sn-(μ-O)** (*higher s-character for Sn-O*).

## Dynamic NMR Spectroscopy: $^1$H[1, 2)]

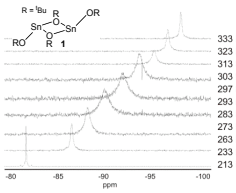



**1** shows coalescence of the signals for the bridging and terminal O$^t$Bu groups. The resonances show different temperature drifts.

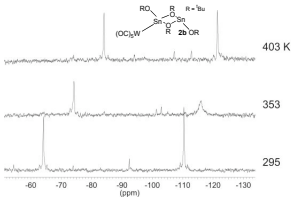



**2b** shows two subsequent coalescence phenomena:
At low temperature, one terminal O$^t$Bu exchanges with the bridging ones; at high temperature, all O$^t$Bu exchange.

## Dynamic NMR Spectroscopy: $^{119}$Sn{$^1$H}[1, 2)]

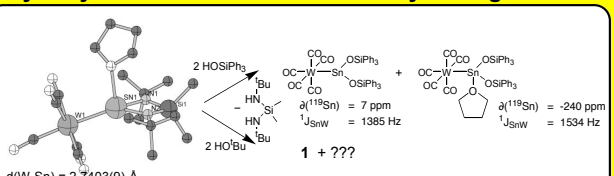



The singlet for **1** shows a linear temperature upfield drift and temperature dependence of the line width. The mechanism is under investigation.




The singlet for the metal-free Sn in **2b** shows the same behaviour as in **1**, whereas the co-ordinated Sn only shows a similar temperature drift.

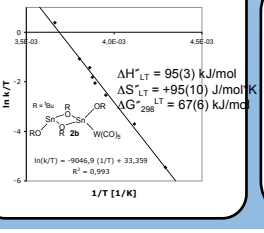
## Hydrolytic transformation of a stannylene ligand[7)]



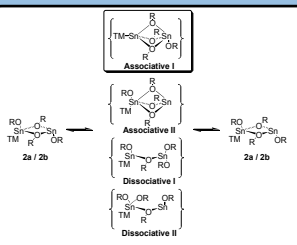

d(W-Sn) = 2.7403(9) Å
d(N-Sn) = 2.05(1) vs. 2.09 Å (*metal free ligand*)
∠ (N-Sn-N) = 75.0(4) vs. 73.3° (*metal free ligand*)

## Thermodynamics and Mechanism[1, 2)]

*Eyring-Plot after line shape analysis*




## Proposal for the low temperature mechanism of O$^t$Bu exchange




**Literature:**
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