

FA4-MS06-O1

Structure and Reactivity in Homogeneous Catalyst Model Systems. Stefanus Otto^a, Peter N. Bungu^a. ^a*Sasol Technology Research & Development, Sasolburg, South Africa.*
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X-ray crystallography was used extensively to obtain structural information on a series of bicyclic ligands of relevance in modified Co hydroformylation. [1] In addition the steric- and electronic nature of these ligands was further investigated through their respective phosphine selenides. [2, 3]

The oxidative addition of MeI to [Rh(bid)(CO)(L)] (bid = mono anionic bidentate ligand; L = phosphine ligand) is well known to be sensitive to the nature of the phosphine ligand. [4] Oxidative addition, to form the metal alkyl, is typically favored by an increase in electron density on the metal centre while steric hindrance would have a negative impact. The subsequent migratory insertion step, to form the metal acyl, is favored by both increased electron density and steric hindrance. These systems can be considered as convenient model systems to study both metal alkyl and acyl formation, as relevant in many catalytic processes, but at ambient temperature and pressure. Structure and reactivity relationships are presented based on X-ray crystallography, ³¹P NMR, IR and UV-vis measurements.

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Metals and DNA: Crystallography as an Essential Tool in Bioinorganic Chemistry. Bernhard Spingler^a, Philipp M. Antoni^a, Alfredo Medina-Molner^a. ^a*Institute of Inorganic Chemistry, University of Zurich, Switzerland.*
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Our research group is interested in mono- and dinuclear metal complexes that interact with the rare left-handed Z-DNA. [1, 2] The temporary formation of Z-DNA during transcription could be exploited as a new target for rapidly replicating cells. This could lead to a completely novel strategy in the fight against cancer.

We are searching for metal complexes that can discriminate between the prevalent right-handed B-DNA and Z-DNA. The presentation will summarize our recent research efforts, mainly in the area of azamacrocyclic complexes. It will be shown for several cases that the ability to crystallize and study important intermediate and final products was essential for the progress of our research. [3]

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FA4-MS06-O3

A New Stable Monomeric Lead(II) Complex Pb(SCH₂CH₂NMe₂)₂: Structure and Dynamic Behaviour in Solid State. Victor N. Khurstalev^a, Rinat R. Aysin^a, Ivan V. Glukhov^a, Irina V. Borisova^b, Larissa A. Leites^a, Nikolai N. Zemlyansky^b. ^a*A.N.Nesmeyanov Institute of Organoelement Compounds of RAS, Moscow, Russia.* ^b*A.V.Topchiev Institute of Petrochemical Synthesis of RAS, Moscow, Russia.*
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In continuation of our investigations on the relative contributions of different factors to the stabilization of divalent Group 14 (E¹⁴) compounds, we report here the results of experimental and theoretical studies of a new stable lead(II) complex Pb(SCH₂CH₂NMe₂)₂ (**1**). The molecular structure of **1** was studied by single-crystal X-ray diffraction analysis at 100 and 290 K and variable-temperature (93-303 K) Raman spectroscopy in solid state. The electronic structure of **1** was elucidated by quantum-chemical calculations within the DFT approach.

The X-ray diffraction study has shown that **1** is a monomer stabilized by two intramolecular coordination N→Pb bonds with the formation of two five-membered rings, both having the usual *envelope* conformations. In the crystal of **1** at 100 K, the only asymmetrical conformer with the two five-membered rings differing in the positions of the cap-carbon atoms was observed (Fig. 1a). In contrast, at the same conditions the Ge(II) (**2**) and Sn(II) (**3**) analogs of **1** have symmetrical structures, in which the conformations of both five-membered rings are identical (Fig. 1b) [1]. However, the X-ray crystal structure analysis at 290 K has revealed that **1** exists both as the asymmetrical and symmetrical conformers in the 7:3 ratio, respectively; the minor symmetrical conformer has the same structure as those of **2** and **3** (Fig. 1c). It is interesting to note that only one of the two five-membered heterocycles in **1** (in the conformation unobserved in **2** and **3**) undergoes the transformation upon heating. The most striking feature of the Raman spectra of **1** is a doublet at 885/896 cm⁻¹, which is absent in the spectra of **2** and **3**. This doublet evidently reflects the presence of two different conformations of the five-membered rings and is explained by rotational isomerism about the ordinary C-C bond. The reasons of the phenomenon found for **1** are currently under investigation.