

PS07.00.38 [Rh(LL)(CO)(PPh₃)] COMPLEXES AS MODELS FOR CATALYTIC PROCESSES: X-RAY^[1,2] vs ¹³P/¹³C NMR^[3] vs IODOMETHANE OXIDATIVE ADDITION REACTIVITY^[1] CORRELATIONS. A. Roodt, GJJ Steyn, L Damoense, JA Venter, SS Basson and W Purcell, Dept. of Chemistry, University of the Orange Free State, Bloemfontein 9300, South Africa, and YS Varshavsky, MR Galding, TG Cherkasova and LV Osetrova, Lebedev, National Rubber Institute, 1 Galspaskaja str., St Petersburg 198035, Russia.

X-ray structure determinations of ca. 20 complexes of the type, [Rh(LL')(CO)(PPh₃)], LL'-bid = symmetrical/unsymmetrical monocharged bi-dentate ligands [such as acac, Sacac, ox, cupf, dmavk (dimethylaminovinyl-ketionate), macsm (methyl (2-methylamino)-1-cyclopentene-1-dicarboxylate) etc.] containing different variations of oxygen, nitrogen and sulphur as coordinating atoms, were studied. These will be discussed briefly in terms of isomer distribution and bond strength manipulation in the Rh(I) coordination polyhedron.

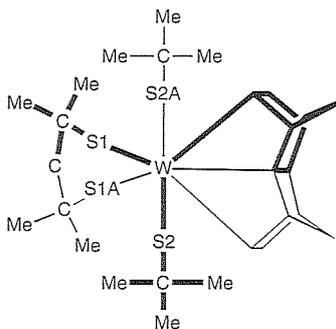
Next, a correlation between these structural results and ¹³P/¹³C data, relating to the Fermi contact term, will be presented and discussed.

Finally, an attempt to correlate both the above with the reactivity observed in these complexes in terms of both the formation of the [Rh(LL')(CO)(PPh₃)] complexes from the corresponding [Rh(LL)(CO)₂], as well as the stereochemistry and the reactivity of these complexes towards oxidative addition by iodomethane, forming Rh(III)-alkyl and Rh(III)-acyl products in the process, will be presented.

1. Steyn, GJJ; Roodt, A; Leipoldt, JG: *Inorg. Chem.* **1992**, 31, 3744.
2. Damoense, L; Purcell, W; Roodt, A: *Rhodium Express* **1994**, 5, 10.
3. Galding, MR; Cherkasova, TG, Varshavsky, YS, Osetrova, LV, Roodt, A: *Rhodium Express* **1995**, 9, 36, and refs within.

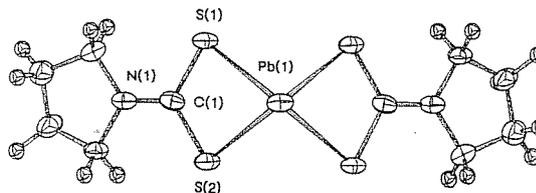
PS07.00.39 ORIENTATIONAL DISORDER IN THE X-RAY CRYSTAL STRUCTURE OF TRANS-[W(CO)₂(S(C₄H₉))₂(C₇H₈)]. Georgina M. Rosair, J. L. Davidson and B. J. Thiebaut, Dept. of Chemistry, Heriot-Watt University, Edinburgh, EH14 4AS, Scotland

The tungsten complex, [W(CO)₂(S(C₄H₉))₂(C₇H₈)] in Cmc₂1 is disordered with two orientations of the complex at the tungsten centre. This unusual form of disorder results from there being enough space in the crystal lattice for the molecule to be in two or more possible orientations at any given site. Orientational disorder has been observed in the tricyclic pleiadene. In the title compound, one molecule is generated from the other by a mirror plane (defined by the trans carbonyl ligands and two carbon atoms of the norbornadiene). The nature of the disorder will be discussed in more detail. The tungsten centre has distorted octahedral geometry [S(1)-W(1)-S(2) = 111.6(3)°], with the t-butyl thiol groups orientated with syn geometry with respect to one another.



PS07.00.40 STRUCTURE OF A LEAD COMPLEX USED IN FOOD ANALYSIS. M. Rossi, M-L. Chan, Department of Chemistry, Vassar College, Poughkeepsie, NY 12601 and F. Caruso, Istituto di Strutturistica Chimica, CNR, 00016 Monterotondo Stazione (Rome), Italy.

A method for determining the lead content in foods is by chelating lead with ammonium pyrrolidinedithiocarbamate. Crystal structure analysis of this lead complex shows an orthorhombic cell, *Pccn*, with *Z*=4, *a* = 13.839(14)Å, *b* = 14.058(16)Å, *c* = 7.763(6)Å. The structure is shown below.



The Pb—Pb intermolecular distance is 3.881(6)Å and the molecules stack along the *c* axis. Along the stacking direction, there are weak intermolecular interactions among the successive molecules and the Pb—S distances are 3.477(6)Å for Pb-S1 and 3.283(5)Å for Pb-S2. The results of this structure analysis will be contrasted to similar compounds.

PS07.00.41 NUCLEIC ACID-Hg(II) ION INTERACTIONS. STRUCTURE OF Hg(II) COMPLEXES WITH 1,3-DIMETHYLURACIL. Michal Sabat^{1*} Bernhard Lippert², Felix Zamora², and Richard D.S. Dixon¹, ¹Department of Chemistry, University of Virginia, Charlottesville, VA 22901, U.S.A., and ²Fachbereich Chemie, Universität Dortmund, 44221 Dortmund, Germany.

As a part of our study on the Hg(II) ion bonding to the carbon atoms of nucleic acid bases, three complexes of Hg(II) with 1,3-dimethyluracil (1,3-DimeU) have been synthesized and characterized by X-ray crystallography at -120°C. All the compounds contain Hg(II) ions bonded to C(5) atoms of 1,3-DimeU with the Hg—C distances ranging from 2.04 - 2.09 Å. Complex I has two 1,3-DimeU rings bound to Hg in a linear fashion. Complex II contains a Hg₃O moiety with the O atom bridging three Hg atoms.

Crystal data: (I) (1,3 DimeU)₂Hg₂, orthorhombic, *Fdd2*, *a*=14.185(4), *b*=25.275(7), *c*=7.924(2) Å *V*=2840(2) Å³, *Z*=8, *R*=0.020 for 563 reflections with *I*>3σ(*I*) (II) [(1,3-DimeU)Hg₃O]NO₃•2H₂O, triclinic, *P1*, *a*=13.859(4), *b*=19.655(6), *c*=9.879(2) Å, *α*=95.76(2), *β*=96.10(2), *γ*=99.23(2)°, *V*=2622(3) Å³, *Z*=4, *R*=0.053 for 4535 reflections with *I*>3σ(*I*) (III) 1(1,3-DimeU)Hg(Naph)NO₃, (Naph=naphthyridine C₈H₆N₂), triclinic, *P1*, *a*=10.735(3), *b*=10.915(2), *c*=6.966(2) Å, *α*=104.56(2), *β*=93.88(2), *γ*=79.18(2)°, *V*=775.8(4) Å³, *Z*=2, *R*=0.048 for 1867 reflections with *I*>3σ(*I*).