

**PSEUDO VASKA-TYPE COMPLEXES: SOLID STATE AND SOLUTION BEHAVIOUR AS MODEL HOMOGENEOUS CATALYSTS**

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The Rh Vaska-type complexes, trans-[Rh(CO)(Cl)(YR<sub>3</sub>)] (Y=Group 15 atom; R=aryl or alkyl), analogues of the well-known Vaska's complex, trans-[Ir(CO)(Cl)(PPh<sub>3</sub>)], are well behaved model systems for various catalytic systems. They readily undergo a variety of reactions e.g., iodomethane oxidative addition, typically forming alkyl species as intermediates, e.g., [Rh(Cl)(CO)(CH<sub>3</sub>)(I)(YR<sub>3</sub>) ~], reductive elimination, substitution, insertion, etc. These Rh(I) complexes are easy to synthesize, and in conjunction with their Pd(II) and Pt(II) analogues, are potential homogeneous catalysts to also investigate structurally due to favorable thermal stability, while the CO and PR<sub>3</sub> ligands render IR and <sup>31</sup>P NMR spectroscopy as powerful tools to evaluate different ligand effects.

These complexes were used to quantify electronic and steric effects of different tertiary group 15 donor ligands (P, As, Sb) [1], including PPh<sub>2</sub>Fc (ferrocenyl-diphenylphosphine), and PTA (1,3,5-triaza-7-phosphaadamantane) enabling correlations between IR, <sup>31</sup>P NMR and X-ray crystallographic data. Selected four-, five- and six-coordinate pseudo Vaska-type complexes are presented, illustrating structural aspects and reactivity, equilibria and thermodynamics of these with regard to iodomethane oxidative addition/ ligand substitution.

**References**

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**Keywords:** VASKA-TYPE COMPLEXES, OXIDATIVE ADDITION, STIBINES

**STRUCTURE OF PLATINUM, ZINC AND CADMIUM 8-HYDROSELENO-L-QUINOLINATES**

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New compounds: platinum (I), zinc (II) and cadmium (III) 8-hydroseleñoquinolates have been synthesized in order to elucidate the nature of the chemical bond metal-selenium in the five-membered metal-containing rings. The complete X-ray diffraction analysis of the complexes I-III has been performed.

8-Hydroseleñoquinoline acts as bidentate (Se, N-) ligand in the I-III. The central atom is coordinated by two ligands forming planar five-membered rings. The coordination polyhedron of platinum and cadmium is a centrosymmetrical trans-square, that of zinc- distorted tetrahedron. In III the intermolecular contacts (Cd...Se 2.998(1) Å) connect the central atom with two selenium atoms in two neighbour molecules, and coordination polyhedron of cadmium is an elongated octahedron. The determined lengths of coordination bonds are: Pt-Se 2.405(2) Å, Pt-N 2.041(3) Å, Zn-Se 2.368 Å, Zn-N 2.055 Å, Cd-Se 2.6475(5) Å, Cd-N 2.369(5) Å.

The comparison of the obtained bond length values with the sum of corresponding covalent radii shows that the strength of the M-Se bonds is decreased in the complexes I-III in the succession Pt-Se, Zn-Se, Cd-Se, but the decrease of the M-N bond strength is not so distinct. The decrease of the chelate angle SeMN values is inverse proportional to ratio of covalent radii of central atoms Zn < Pt < Cd.

The bond length dynamics in the analogous five-membered metal-containing rings with Se, S, O atoms (8-hydroseleño-, 8-mercapto- and 8-hydroxyquinolate) has been evaluated quantitatively for the first time. The M-X bond strength shows a nonlinear increase in the mentioned complexes and this increase follows the succession M-O, M-S, M-Se. This phenomenon is especially expressed in platinum 8-hydroseleño- and 8-mercaptoquinolates. The shortening of the bond can be explained by the increment of additional direct donor-acceptor bonding.

**Keywords:** CRYSTAL STRUCTURE, COORDINATION COMPOUNDS, 8-HYDROSELENOQUINOLINATE

**BRIDGING THE 16-MEMBERED Z- MACROCYCLE : CONSEQUENCES FOR CONFORMATION AND REACTIVITY.**

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The saddle conformation for 16-membered Jager-type metallomacrocycles contains a cavity suitable for the binding of small molecules such as dioxygen to the metal centre. The efficacy of such reactions is dependant on cavity geometry and the interactions with the surrounding structure [1]. Those structures determined thus far have the methyl substituents on the macrocycle bound to the same side (*cis* isomer) 1. Bridges of varying lengths and constituents have been connected over the metal centre to vary the cavity size and shape. The recently discovered *trans* isomer with a Z-type conformation [2] appears alongside the well-established saddle species 1 in the reaction mixture. Recently we determined structures of bridged compounds of the *trans* isomer, 2, looking at the conformation of the macrocycle ring and the position of the bridge relative to the metal centre. What's the difference in cavity size and conformation between the *cis* and *trans* bridged compounds? What are the consequences for reactivity?

This work has answered these questions in conjunction with ESR and theoretical studies.

**References**

1. D.H. Busch and N.W. Alcock, Chem. Rev., 1994, 94, 585 (and refs. therein)
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**SYNTHESIS, PROPERTIES AND STRUCTURE OF SOME BITHIOPHENE COMPLEXES OF CHROMIUM, TUNGSTEN, MANGANESE AND IRON**

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The mono- and biscarbene complexes of chromium, tungsten, manganese and iron with a bithiophene spacer were synthesized using the classical Fischer method. The reaction of lithiated bithiophene with chromium hexacarbonyl [Cr(CO)<sub>6</sub>], followed by treatment with triethyloxonium tetrafluoroborate (Et<sub>3</sub>OB<sup>+</sup>F<sub>4</sub><sup>-</sup>) yielded a monocarbene complex [Cr{C(OEt)C<sub>4</sub>H<sub>2</sub>SC<sub>4</sub>H<sub>2</sub>S}(CO)<sub>5</sub>], and the biscarbene complex [(CO)<sub>5</sub>Cr{C(OEt)C<sub>4</sub>H<sub>2</sub>SC<sub>4</sub>H<sub>2</sub>SC(OEt)}Cr(CO)<sub>5</sub>], as well as bisbithienyl-1,2-dione organic byproduct 2',2'-bisbithienyl-1,2-dione. Similarly, treatment with [W(CO)<sub>6</sub>] yielded the related tungsten monocarbene and biscarbene products. Reaction with cyclopentadienyl iron dicarbonyl iodide [FeCp(CO)<sub>2</sub>I] resulted in the formation of the stable diiron bithienylene complex: Cp(CO)<sub>2</sub>Fe{C<sub>4</sub>H<sub>2</sub>SC<sub>4</sub>H<sub>2</sub>S}Fe(CO)<sub>2</sub>Cp]. The influence of the carbene moiety on the electronic distribution around the rings is clear from the <sup>1</sup>H and <sup>13</sup>C NMR data collected. Almost all the NMR signals are shifted downfield of those of the free ligand due to deshielding by the electronegative carbene moieties and, in some cases, the electron-withdrawing ester groups. X-ray crystallographic studies indicated that the presence of substituents on the bithiophene ring system forces the rings to align in the same plane and in the *trans* configuration with respect to the sulphur atoms, to aid in the flow of electrons through the molecule.

**Keywords:** BITHIOPHENE CARBENE TRANSITION METALS