

**STRUCTURES OF DIRHODIUM BIS ( $\mu$ -GUANIDINATE) DERIVATIVES**R.A. Baber A.G. Orpen

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We report an investigation of the crystal structures of a series of dirhodium ligand bridged complexes. These organometallic complexes are used in redox reactions, which often result in mixed valence species. The work builds on chemistry developed by Professor N. G. Connelly on the synthesis of mixed valence species that are able to sustain intermolecular electron transfer reactions. Ligands such as the acetamido and triazenido (see below) have been used to obtain dinuclear metal complexes with chemically accessible oxidation potentials. This research reports the study of the molecular structure of complexes such as the 1,2,3-triphenylguanidinate bridged species such as  $[\text{Rh}_2(\text{L})_2(\text{CO})_4]$  (see below). Comparisons are made of the intramolecular and supramolecular structures of these complexes and those of analogous  $[\text{Rh}_2]^{III}$  and related species with bis(triazenido), bis(acetato), and bis(amidinato) ligands that we have previously reported.

**Keywords: ORGANOMETALLIC REDOX****STRUCTURAL STUDIES OF BIS(PHOSPHOLANE) COMPLEXES**K.M. Heslop A. G. Orpen

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Molecular design has become an important tool of research and is attracting increasing interest in the field of homogeneous catalysis. The objective is to design ligands that will confer desirable properties (e.g. selectivity, stereospecificity) on their metal complexes. This rests on building an understanding of the fundamental properties of existing ligands. Methods of obtaining this understanding involve determination of individual molecular structures and molecular modelling. Here we report structural and conformational analyses conducted on bis(phospholane) (bDuP) complexes used in the asymmetric hydrogenation of enamides, as shown below. The complexes studied, shown below, have a cyclopentane backbone, which fixes the 5-membered chelate ring in either a  $\lambda$  or  $\delta$  conformation. This is in comparison to the analogous BPE ligand, which has a  $-\text{CH}_2-\text{CH}_2-$  backbone and interconverts between the  $\lambda$  and  $\delta$  conformers. Results of hydrogenation of amide substrates with  $\text{Rh}(\text{bDuP})$  species show that  $\delta > \text{BPE} > \lambda$  in stereoselectivity. For  $\text{R}=\text{H}$  the observed selectivity is 98, 85 and 77% e.e for  $\delta$ , BPE and  $\lambda$  respectively and for  $\text{R}=\text{Ph}$ , 95, 91 and 73% e.e. In all cases the R-product is formed. Conventional quadrant analysis predicts that the product formed should be the S-enantiomer. As this is not the case, the expected Halpern mechanism cannot be operating. Molecular mechanics calculations have been carried out on adducts of the complexes with amide substrates in an attempt to elucidate the mechanism of hydrogenation and the origin of the enhancement of stereoselectivity with the  $\delta$ -chelate.

**Keywords: PHOSPHINES HOMOGENEOUS CATALYSIS MOLECULAR MODELLING****METAL ION COORDINATION: TOWARDS A DATABASE FOR PROTEIN CRYSTALLOGRAPHERS**J.P. Glusker A.K. Katz P. George C.W. Bock

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We are analyzing structural information on the coordination numbers and interatomic distances in metal-ion complexes in order to set up a database that will aid in investigations of the roles of metal ions in biological macromolecules. Metal ions under consideration are monovalent Li, Na, K, divalent Be, Mg, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn and trivalent Al, Cr, Fe, Co and Mn. Small-molecule crystal structures are accessed by a detailed study of data from the Cambridge Crystallographic Database. The metal-ion coordination number is confirmed by checking the original publication and viewing the structure by computer graphics. Results are then compared with those in crystal structures in the Protein Databank. Ligand preferences (with respect to oxygen, nitrogen and sulfur) as a function of coordination number and metal ion oxidation state are recorded on triangular graphs. The effects of another metal ion in close proximity, and the orientation of water molecules binding to the metal ion in each valence state, are also analyzed. In addition, *ab initio* molecular orbital and density functional calculations are used to determine the energetic consequences of ionizing a metal-ion bound ligand (water, ammonia, hydrogen sulfide) and also of moving this ligand from one metal-ion coordination sphere to another. The overall aim is to assess the spatial characteristics in ligand binding and the modes of action in enzymatic catalysis of each of these metal ions.

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**Keywords: METAL ION COORDINATION METALLOENZYMES DATABASES****IS THE TRANS EFFECT AN APPLICABLE CONCEPT IN DI- AND POLYNUCLEAR METAL COMPLEXES?**F.J. Lahoz S.E. Ruiz J.A. Lopez M.V. Jimenez E. Sola L.A. Oro

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It is nowadays very clear that the reactivity of mononuclear metal complexes is not affected in the same manner by all co-ordinated ligands: that ligand occupying the trans position to the reactive site makes the greatest contribution to the result of a reaction. This fact constitutes the basis of the well known trans effect (or trans influence). The applicability of this useful concept has been successfully extended to most co-ordination geometries, but its use has been restrained to the chemistry of monometallic complexes. Interested on the understanding of the co-operative reactivity of metal centres in dinuclear and polynuclear compounds where the intermetallic separations are large enough to exclude any direct metal-metal bond or interaction, we have investigated the molecular structures of a series of related bridged diiridium complexes with long intermetallic separations. These structural data have shown that in these complexes the co-operation pathways between metals do not involve concerted actions of various metals on a substrate, but the transmission of electronic information from one metal to the other. Starting from these structural studies, we have also accumulated theoretical and chemical (reactivity) information to evidence the existence of a dinuclear trans effect. The transmission of this structural trans effect is manifest when a direct metal-metal bond is present in the molecule or when an electronic communication could be established through the bridging ligands. The obtained results illustrate the potential relevance of the dinuclear trans effect concept in the understanding of both structure and reactivity of dinuclear compounds.

**Keywords: TRANS EFFECT DINUCLEAR COMPLEXES STRUCTURE REACTIVITY**