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Chirality and the Metal-alkene Bond; Distortions in the Solution and Solid-state Structures of η^2-Ethene Rhodium *bis*-Oxazolinylmethane Complexes

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Abstract : The X-ray crystal structure of N,N,-Bis-[2-((4S)-(methyl)-1,3-oxazolinyl)]methane-bis(η^2ethene)rhodium(I) has been determined, and demonstrates a specific distortion from ideal bonding geometry of the alkenes which maintains C_2 symmetry. This distorted structure is shown to be maintained in solution for this complex and the (4S)-(1-methylethyl) analogue by ^{1}H NMR studies particularly nOe. Extended Hückel calculations have been carried out on a simple model, and demonstrate the relative ease of some (RhC=C) bending modes in which C_2 symmetry is maintained.

Development of asymmetric homogeneous catalysis has been largely an empirical process, not least because of the apparent complexity associated with the attendant catalytic cycles, and the small energetic differences involved in discrimination between diastereomeric pathways leading to the enantiomers of product[1]. In most cases this discrimination arises from differential steric effects, not yet well understood, and rationalisation has depended on models which lack experimental verification. Part of the problem is that the structures of key transition states are unknown and perhaps inaccessible. In rhodium asymmetric hydrogenation, which has been the most widely studied of all catalytic mechanisms[2], both the resting state of the catalyst and a late reactive intermediate have been characterised in solution and the former has been subjected to X-ray analysis[3]. An obvious way to discover the details which are not amenable to direct experiment is by a combination of molecular mechanics and quantum chemical calculations[4]; this is being actively pursued.

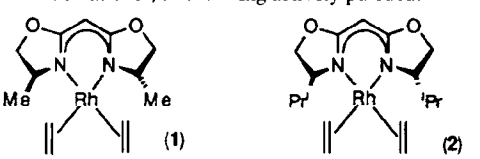

Figure 1. Rhodium bis-oxazoline complexes

Like many other important catalytic reactions, rhodium asymmetric hydrogenation involves a coordinated alkene, and the way in which its geometry responds to the ligand which controls the stereochemical outcome is important. The typical ligands for rhodium asymmetric hydrogenation are chelating diarylphosphines, in which the backbone, or less frequently the aryl rings, carries an appropriate stereogenic centre or axis. The precursor complex for catalysis is most frequently a cycloocta-[1,5]-diene or bicyclo[2,2,1]hepta-2,5-diene diphosphine rhodium cation salt, and about twenty five X-ray structures are recorded for such complexes. Distortions in the alkene geometry with respect to the P-Rh-P plane are frequently observed[5], typically a twist of the diene unit orthogonal to that plane to reduce the intracomplex steric demand. Kyba[6] has pointed out that the sense of this twist correlates with the stereochemical course of asymmetric hydrogenation of dehydroamino acids. In crystallographically characterised complexes of the enamide complexes themselves[3], the alkene has rolled around the coordination sphere so as to maintain near-equal C-Rh distances to C_α and C_β but C_α becomes coplanar with the N-C=O unit of the coordinated amide. These limited examples indicate that the ideal structure of a square-planar d^8-alkene complex orthogonal to the coordination plane and symmetrically disposed about it, is readily

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distorted. Questions remain as to the ease of that distortion and its response to elements of asymmetry in the coordination sphere. For this reason the structure of a model compound (**1**) was evaluated, guided by the recent successes of Pfaltz and co-workers in applying these and related ligands in the homogeneous catalysis of cyclopropanation, allylic alkylation and related reactions[7]. The bis-oxazolines are sufficiently simple, and sufficiently well-defined in space, to be accessible to ab initio MO treatment. The intention was then to define the structure of an appropriate complex, discover the distortions of the η^2-alkene structure induced by the chirality of the ligand, and compare theory and experiment. At this stage the experimental work has been completed and the theoretical calculations are in progress[8]; a simple MO model can give insights into the observed results, however, and is the subject of this preliminary Communication.

Synthesis of the rhodium complex (**1**) proved to be straightforward by direct reaction of the lithium salt of the alanine-derived bis-oxazoline with di-μ-chlorotetrakis(η^2-ethene)dirhodium(I), giving yellow plates of the desired compound ; the valine-derived analogue (**2**) was prepared similarly. The ^{1}H NMR spectrum of the complex indicated several interesting features. Firstly, by comparison with the corresponding pentanedionate complexes[9], the rotation of the ethene units about the centroid of the Rh-alkene bond is slow, such that there are four distinct sharp proton resonances. The chemical shift of one of these is at unusually high field [δ 0.80 vs. 2.7-3.4 ppm], and its location relative to the CHMe-stereogenic centre of the oxazoline was determined by difference nOe and COSY experiments. Recrystallisation was effected from freshly distilled, degassed pentane in a septum-sealed ampoule. The solution was stored at room temperature and after a period of three weeks the solvent had slowly evaporated through the septum. Two crystalline forms resulted: at the bottom and sides of the vessel the compound had crystallised as plates whilst at the top of the vesssel it had crystallised as needles. Both of these forms provided crystals suitable for X-ray analysis, which refined readily to R-factors of 4 % and 3 % respectively. The differences between the two were minor and the latter structure, in which H atoms were located, is considered in subsequent discussion. The basic geometry is shown in Figure 2; the Me-groups are in axial positions in an approximately C_2 symmetrical molecule. The most interesting feature is that the alkene is considerably distorted from the "ideal" arrangement with its C=C bonds orthogonal to and bisected by the complexation square plane. One pair of carbons is approximately in the plane, and the alkenes have rolled to maintain C-Rh equidistance whilst remaining orthogonal; there is no evidence of the twisting distortion expected on the precedent of diolefin complexes[5]. With this structure in hand the anomalous ^{1}H chemical shifts were shown to be associated with the pair of inner hydrogens, which are close to the NRhN coordination plane.

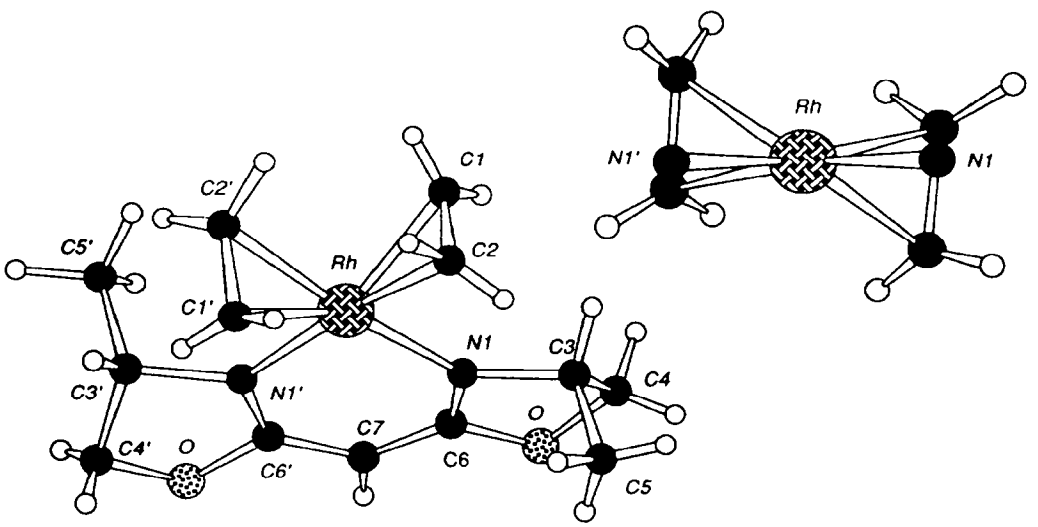

Figure 2. X-ray crystal structure of complex (1); the inset shows a view through the N-Rh-N plane towards the alkenes and demonstrates the distortion from structural ideality. Crystal data : tetragonal, $P4_1$. a = 9.724, b = 9.724, c = 15.106; α= β = γ = 90.000°; Main bond lengths (Å) and angles (°): Rh-C1 2.075(7), Rh-C2 2.080(6), Rh-C1' 2.080(6), Rh-C2' 2.133(8), Rh-N1 2.056(8), Rh-N1' 2.060(6), C1-C2 1.347(8), C1'-C2' 1.384(10), N-Rh-N1' 88.8(3), C1-Rh-N1' 150.4(3), C2-Rh-N1' 171.8(3), C1'-Rh-N1 152.0(3), C2'-Rh-N1 171.8(3).

A theoretical investigation was carried out with the aim of separating the electronic and steric factors present in complex (**1**). To this end, four C_2 distortions of a model complex, (**3**), were examined at the Extended Huckel level (EHT)[9,10] Since EHT is known to be poor at reproducing experimental bond-lengths[11] idealised bond-lengths and angles which led to overall C_2 symmetry were used throughout, and the starting geometry was assumed. The total energy of each system at eight or more points during the four pure C_2-symmetric distortions of (**3**), labelled α–δ (Figure 3), was computed and the important contributions to the energy change assessed. This was carried out at a fragment molecular orbital (FMO) level[12] with the aid of correlation diagrams.

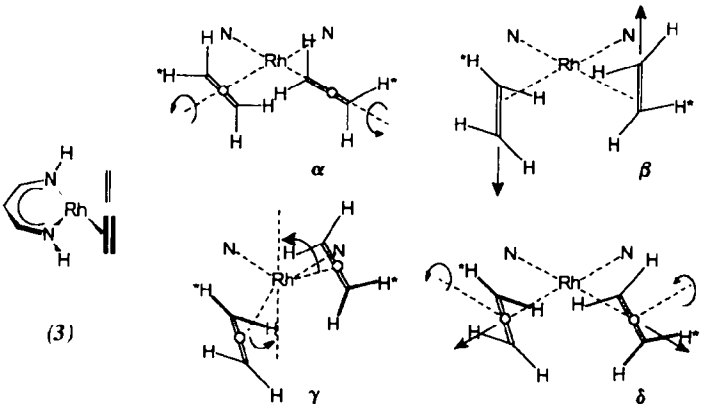

Figure 3. - Model complex (3) and pictorial representations of distortions of (3), α–δ.

Descriptions of the four distortions are as follows: Distortion α is the conrotation of the alkenes about the axes defined by the Rh-alkene mid-point. Distortion β is the translation of the alkenes perpendicular to the plane **P** which is defined by the Rh and N atoms. Distortion γ is the rolling movement of the alkenes on the surface of a sphere centred on Rh, where the projection of the rhodium-alkene mid-point vector onto the plane **P** remains constant and all the rhodium-alkene distances stay constant. Finally, distortion δ is the rotation of the alkenes about the axes perpendicular to the rhodium-alkene mid-point and in the plane **P**, coupled with a small translation away from rhodium of the olefin along the rhodium-alkene mid-point (included to relieve compression of the Rh-C distances). The success of each distortion in relieving steric compression between the olefins and the chiral ligand was crudely measured by the distance moved by the two marked protons from their starting positions. The energy difference between the distorted molecules and undistorted (**3**) is plotted in Figure 4.

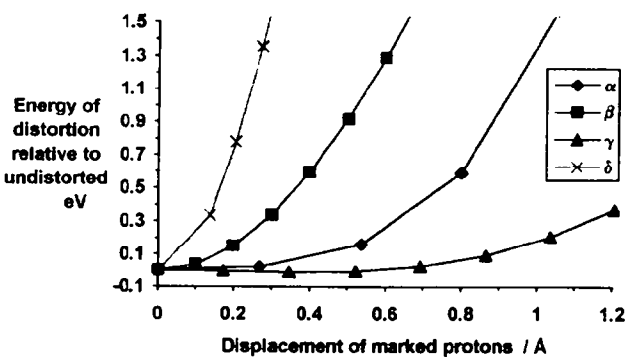

Figure 4.- Plot of change in energy for each distortion.

Even at a purely qualitative level, one can see that the major destabilising factor in play with all the distortions examined is attenuation of the back-bonding between the metal fragment and the alkene. This stabilisation of the d_{xy} and d_{xz} orbitals of rhodium (taking the C_2 axis as the z axis and **P** as the yz plane) is decreased in each distortion because of their symmetry with respect to the σ (yz) (both being anti-symmetric). Each of the distortions moves two or more of the alkene carbon atoms into this plane of symmetry and consequently into a

nodal plane of the two d orbitals, eliminating overlap. Three of the important molecular orbitals involved in the rhodium-olefin bonding are shown in Figure 5.

In the best case, γ, the reduction of orbital overlap between the more central alkene carbon atoms and the Rh d orbitals is counterbalanced by a concomitant increase in overlap of the other pair of alkene carbons with these d orbitals. This leads to a situation in which virtually no destabilisation occurs until the angle between the plane **P** and the Rh-alkene mid-point reaches 16°, corresponding to a displacement in the monitored protons of 0.7 Å. In the worst two cases, β and δ, the movement of two of the carbon atoms away from the rhodium centre reduces both the stabilisation of the d_{xy} and d_{xz} orbitals on rhodium by the alkene antibonding orbitals and that of the anti-symmetric combination of the olefin bonding orbitals by the rhodium d_{yz} orbital. In other words, both the electron donation from π to the metal and back-bonding to π* are drastically reduced. In case α the back-bonding is attenuated to almost the same extent as in β and δ, but the interaction between π and the metal d orbitals is little altered.

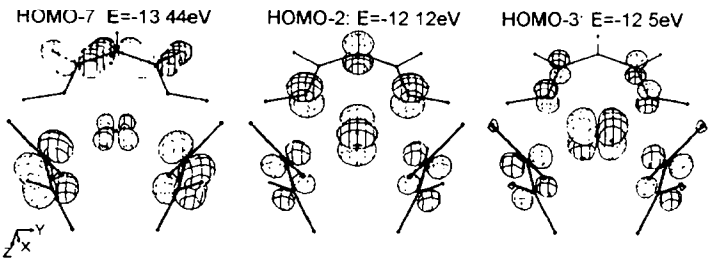

Figure 5.- Three of the main orbitals responsible for the rhodium-olefin bonding.

It can clearly be seen that the electronically favoured distortion is γ, in agreement with the observed structure. Although the absolute values of energy derived should be treated with caution, the conclusion that can be drawn is that the favoured distortion has little or no energetic electronic cost, provided that the movement of the olefinic protons is less than 0.7 Å. The distortion observed in the X-ray structure ca. 10°, corresponding to a movement of the marked protons of 0.45 Å - is well within this range.
Further work at an *ab initio* level of theory is underway in collaboration with Dr. A. Dedieu (Strasbourg) and will be reported in due course.

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