

## Theoretical studies of organometallic processes: scientific visualization

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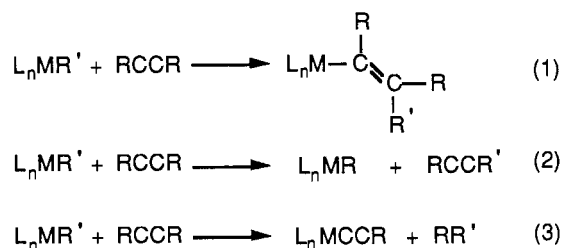
The results of *ab initio* electronic structure calculations, molecular mechanics and dynamics calculations, and literature single crystal X-ray diffraction structural studies are presented to validate the theoretical methodology used and to help elucidate the mechanisms of reactions at organotransition metal centers. We find steric interactions to be an important contribution to reactions at scandium cyclopentadienyl complexes. We find dynamics to be important in understanding an osmium complex and  $\pi$  stacking to be important in determining the regioselectivity of Pt(II) asymmetric hydroformylation catalysts.

### INTRODUCTION

The two major contributors to barriers of chemical reactions are electronic effects and steric effects. These two effects are conveniently studied by the complementary theoretical techniques of *ab initio* quantum mechanical electronic structure calculations and classical molecular mechanics. In this work we discuss application of both techniques to reactions at scandium, osmium, and platinum centers with a primary focus on the platinum(II) catalyzed hydroformylation reaction. In the Scandium Cyclopentadienyl Complexes section we discuss recent results wherein we assess the steric contribution to the acetylene insertion reaction at scandium. In the Diosmacycle Dynamics section we report an observation regarding the ring puckering dynamics of a diosmacyclobutane complex. In the Platinum Hydroformylation section we present results supportive of an important role for  $\pi$  stacking in determining the regiochemistry of the hydroformylation of aryl olefins.

### SCANIUM CYCLOPENTADIENYL COMPLEXES

We recently reported the results of an *ab initio* electronic structure study of the acetylene insertion reaction at  $\text{Cl}_2\text{ScH}$  (ref. 1). Three pathways are possible, the classical  $\beta$  insertion reaction (1),  $\sigma$  bond metathesis (2), or  $\sigma$  bond metathesis exchange (3) resulting in C-C bond formation.



Experimentally (ref. 2) paths (1) and (3) are observed to occur competitively. Computationally we found the classical  $\beta$  insertion reaction (1) to be significantly favored due to the energetic gain associated with intermediate  $\pi$  complex formation. The steric difference between the chloride ligands used in the calculation and the permethylcyclopentadienyl ligands ( $\text{Cp}^*$ ) used experimentally was assessed for the  $\pi$  complexation step using molecular mechanics. The atoms in the equatorial plane were held fixed at the *ab initio* coordinates for the scandium hydride as well as the complexed acetylene species. Substitution of Cl by Cp resulted in a 1 kcal/mol decrease in the binding energy of the acetylene, suggesting the steric demand of Cl and Cp are comparable. Substitution of Cl by  $\text{Cp}^*$ , however, decreased the binding energy of acetylene by 11 kcal/mol, suggesting that for  $\text{Cp}^*$  complexes the acetylene will not form a bound  $\pi$  complex.

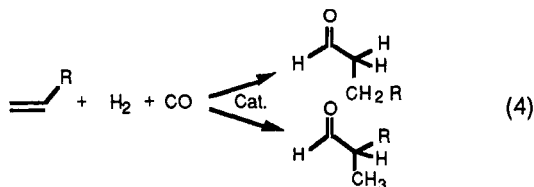
### DIOSMACYCLE DYNAMICS

In an extensive series of experiments Norton and coworkers (ref. 3) synthesized the diosmacyclobutane  $\text{Os}_2(\text{CO})_8(\text{C}_2\text{H}_4)$  **1**, established the utility of **1** as a vibrational model for surface bound olefins, have demonstrated the stereospecific exchange of olefins by **1**, determined the solid state structure of **1** by X-ray and neutron diffraction, and determined the solution phase structure of **1** by liquid crystal  $^1\text{H}$  NMR. **1** was observed to have a puckered ring structure in the solid state but gave a single sharp  $^1\text{H}$  NMR signal down to  $-90^\circ\text{C}$  consistent in solution with an effective  $\text{C}_{2v}$  symmetry structure. By  $^{13}\text{C}$  labeling and detailed analysis of the liquid crystal  $^1\text{H}$  NMR, including coupling to  $^{13}\text{C}$  label, Norton and Bender established that a correct analysis and detailed fit to the liquid crystal  $^1\text{H}$  NMR requires inclusion of two interconverting  $\text{C}_2$  puckered ring structures.

In order to obtain an estimate for the height of the barrier connecting the two  $\text{C}_2$  structures and to assess the importance of including a dynamical interconversion contribution to the dipolar coupling constants, we report *ab initio* electronic structure calculations on the  $\text{C}_2$  structure as well as the  $\text{C}_{2v}$  saddlepoint. The barrier we obtain (1 kcal/mol) is to determine the four fold torsional parameter about the Os-Os bond for use in the molecular mechanics force field. The resulting forcefield is used in a constant temperature (300K) molecular dynamics simulation. We find that the dipolar coupling constants we obtain from a 20 ps molecular dynamics simulation are in agreement with the coupling constants obtained experimentally and from the two site model used by Norton and Bender.

### PLATINUM HYDROFORMYLATION

The hydroformylation reaction or Oxo process is the reaction of alkenes with synthesis gas ( $\text{CO} + \text{H}_2$ ) to produce aldehydes. The reaction is catalyzed by a number of transition metal complexes (ref. 4,5). The process was first discovered for a cobalt catalyst (ref. 5), though all group 8,9, and 10 transition metals show catalytic activity. Cobalt based catalysts are the most used for the commodity scale production of *n*-butanal, though rhodium-based catalysts (ref. 6) have received increased attention due to their greater selectivity under milder reaction conditions.



The use of platinum complexes has been, until recently, hampered by the lower reaction rates and the tendency for the substrate to undergo competitive hydrogenation (ref. 7-9).

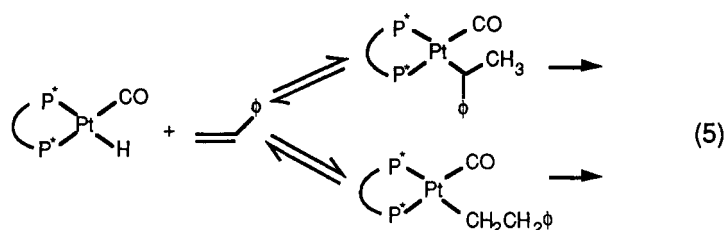
When a monosubstituted olefin is used as substrate there are two isomeric products formed, a branched aldehyde (potentially chiral), and a straight chain or normal aldehyde. A disparity exists between commodity scale industrial hydroformylation and the specialty chemical scale use of hydroformylation in asymmetric synthesis. In commodity scale industrial hydroformylation the normal (linear) aldehyde (*n*-butanal) is the desired product, whereas in asymmetric synthesis the branched product is desired due to its potential chirality. Cobalt catalysts generally have high normal to branched ratios ranging from 4 to 7, and  $\text{HRh}(\text{CO})(\text{PPh}_3)$  hydroformylates propene to give predominately *n*-butanal with a normal to branched ratio of 9.

Until recently, only moderate enantiomeric excess had been realized in hydroformylation reactions using rhodium and platinum catalysts. Through the use of chelating chiral diphosphine ligands rhodium catalysts have been used to catalyze the hydroformylation of styrene to hydrotropaldehyde in 25-30% ee (ref. 9-11). In a number of reactions, the optical yields were observed to be dependent upon the temperature and partial pressures of carbon monoxide and hydrogen, as expected.

The use of platinum complexes in asymmetric hydroformylation has been more problematic due to the generally lower reaction rates and the tendency for the substrate olefin to undergo competitive hydrogenation (ref. 7 and 8). In addition, relatively low branched to normal ratios have been observed in the hydroformylation of monosubstituted alkenes. Recent work (ref. 7), however, on  $\text{L}_2\text{PtCl}_2/\text{SnCl}_2$  catalyst precursors and preformed  $\text{L}_2\text{PtClSnCl}_3$  achieved enantiomeric excesses at nearly an acceptable level (~80% ee) providing the opportunity for establishing this reaction as being viable for asymmetric synthesis. A key feature of this work was the trapping of the formed aldehyde by triethyl orthoformate as the chiral aldehyde formed was observed to racemize under reaction conditions without trapping reagent.

Successful asymmetric hydroformylation of olefins requires the control of regiochemistry (n/b ratio) as well as the control of absolute stereochemistry (ee) of the branched product. Previous efforts directed towards understanding asymmetric hydroformylation have focused on developing an understanding of the chiral induction step; control of the regioselectivity has been rarely studied for asymmetric catalysts and is the focus of the present work.

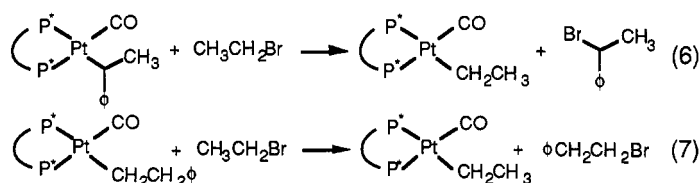
The direction of insertion of the alkene into the metal hydride bond almost certainly determines the n/b ratio of aldehydes. Olefin insertion/ $\beta$  elimination reaction pairs are in general reversible, establishing a pair of competing equilibria prior to the rate limiting steps of each pathway.



As a first step in the theoretical characterization of the importance of steric factors for both the regioselectivity and enantioselectivity of a class of platinum(II) hydroformylation catalysts ( $L_2Pt(CO)X$ ), we have augmented the Dreiding forcefield to include square planar platinum(II), have benchmarked the forcefield on a pair of Pt(II) complexes (an alkyl and an acyl-like methoxycarbonyl), and have examined the differential stabilization of the initially formed platinum alkyl complexes resulting from styrene insertion into a Pt-H bond to form either the primary phenethyl product (leading to normal or linear product) or the secondary  $\alpha$ -methyl styryl product (leading to branched product). The four chelating chiral diphosphine ligands chosen for initial study include (+)-2*S*,3*S*-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane [DIOP], *N*-(*tert*-butoxycarbonyl)-(2*S*,4*S*)-4-(diphenylphosphino)-2-[(diphenylphosphino)methyl]pyrrolidine [BPPM], and the dibenzophosphole [DBP-DIOP and DBP-BPPM] analogues. Experimentally (ref. 7), DBP-DIOP and DBP-BPPM give b/n ratios greater than 3. DIOP and BPPM give b/n ratios of 1.3 and 0.5. The theoretical results are presented below in the [Results and Discussion](#) section and the force field used described in the [Theoretical Details](#) section.

**Results and Discussion.** In order to address the large number of conformational degrees of freedom available in the complexes studied, the minimized trial structure for each complex was subjected to 5 cycles of annealed dynamics from 0 to 600K with a temperature ramp of 1° per 1fs. Each structure from the resulting collection of structures was minimized using a Fletcher-Powell minimization procedure.

To minimize errors in the theoretical methodology used we calculate the energetics for a pair of isodesmic reactions (ref. 10) (6) and (7) for the branched and normal intermediates, respectively. The energetics found from (6) and (7) are used to assess the relative stabilizing interactions between the aryl ligand and the chelating phosphine.



For process (6) we find a significant stabilization of the  $\alpha$ -methyl styryl substituent when the DBP phosphines are used. For both the DIOP and BPPM systems the  $\alpha$ -methyl styryl DBP complex is preferentially stabilized by 1 to 1.5 kcal/mol. When the energetics for reactions (6) and (7) are compared for BPPM and DBP-BPPM we find that the branched,  $\alpha$ -methyl styryl, product is preferred over the normal, phenethyl, product for DBP-BPPM by 3 kcal/mol. For BPPM the reverse preference is found, the normal, phenethyl, product is preferred by 3 kcal/mol. The 6 kcal/mol differential found for the two paths in (5) is consistent with the experimental b/n ratios of 0.5 and 3 for BPPM and DBP-BPPM, respectively. The BPPM catalyst preferentially forms the normal product, whereas DBP-BPPM due to the favorable interaction between the phenyl ring of the alkyl ligand and the dibenzophosphole substituent of the phosphine forms the branched product.

These energetic differentials can be explained in terms of the non-bonded interactions visually observed in the molecular mechanics derived structures of the complexes. The corresponding structures for the DBP-BPPM phenethyl **2** and  $\alpha$ -methyl styryl **3** complexes are shown in Fig. 1. The arrows indicate the lack **2** and occurrence **3** of a  $\pi$  stacking interaction.

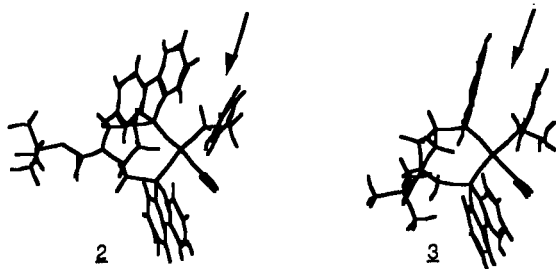


Fig. 1 Molecular mechanics structures for the DBP-BPPM phenethyl **2** and  $\alpha$ -methyl styryl **3** complexes.

For all four of the chiral diphosphine complexes studied, the  $\alpha$ -methyl styryl complexes are calculated to have a significant  $\pi$  stacking interaction between the phenyl ring of the aryl ligand and the aryl substituent of the phosphine ligand. The phenethyl ligands are calculated to not have a significant  $\pi$  interaction. The increased alkyl chain length effectively prevents the aryl substituent of the phenethyl ligand from interacting with an aryl substituent of the chiral phosphine ligand. For DBP-BPPM this favorable "steric" interaction is sufficient to overcome the steric repulsion between the methyl of the  $\alpha$ -methyl styryl and the adjacent carbonyl in the complex. For BPPM the steric repulsion between the methyl of the  $\alpha$ -methyl styryl and the adjacent carbonyl is large enough to make the phenethyl complex energetically preferred.

**Theoretical Details.** In a molecular mechanics calculation the energy of an arbitrary geometry for a molecule is usually written as a superposition of various two-body, three-body and four body interactions. The potential energy is expressed as a sum of bonded and nonbonded interactions:

$$E = E_R + E_\theta + E_\phi + E_\omega + E_{vdw} + E_{el} \quad (8)$$

The bonded interactions consist of bond stretching ( $E_R$ ), bond angle bending ( $E_\theta$ ), dihedral angle torsion ( $E_\phi$ ), and inversion terms ( $E_\omega$ ), while the nonbonded interactions consist of van der Waals ( $E_{vdw}$ ) and electrostatic ( $E_{el}$ ) terms. Recent applications of molecular mechanics to organometallic chemistry include a number of studies of cyclopentadienyl complexes (ref. 11-13) as well as a studies on olefin hydrogenation (ref. 14).

We have extended the Dreiding force field (ref. 15) to include square planar platinum and phosphorus coordinated to transition metal centers. The parameters for the remaining atoms are taken directly from the published Dreiding force field.

The bond stretching terms are harmonic force constants  $700 \text{ (kcal/mole)/\AA}^2$ . The distance is taken as a sum of the atomic radii for the atoms involved in the bond. For platinum a radius of  $1.35\text{\AA}$  is used; for the new phosphorus atom type a radius of  $1.05\text{\AA}$  is used (the original Dreiding phosphorus atom type has a radius of  $0.89\text{\AA}$ , a value appropriate for nucleic acids). These radii are used to determine the natural bond lengths for all platinum and coordinated phosphorus bonds, except bonds between platinum and the coordinated phosphorus. For this linkage, a coordinate covalent bond, we use a platinum radius of  $1.23\text{\AA}$ , resulting in a natural bond length between platinum and phosphorus of  $2.28\text{\AA}$ . A harmonic in theta expansion is used for the angle bend term. The natural angles are taken as only being dependent upon the nature of the central atom. For platinum a natural square planar angle of  $90^\circ$  is used, and for the new phosphorus atom type a natural tetrahedral angle of  $109.471^\circ$  is used (the original Dreiding phosphorus atom type has a natural angle of  $93.3^\circ$ , taken from  $\text{PH}_3$ ). The torsional terms for two bonds IJ and KL connected via a common bond JK is the usual fourier form. The rule based scheme as outlined in the Dreiding paper is used for the new phosphorus atom type, torsional terms involving platinum as one of the central atoms J or K are not included. Nonbonded interactions (van der Waals forces) are also included with a Lennard-Jones expression. Interactions are not calculated between atoms bonded to each other (1, 2 interactions) or which are involved in angle interactions (1, 3 interactions). The van der Waals parameters for the new phosphorus atom type are taken from the Dreiding paper (ref. 15). For platinum we use  $RE=2.97$  and  $DE=0.05$ . Electrostatic interactions are calculated using partial charges determined using the recently developed QEq charge equilibration scheme (ref. 16). Interactions are not calculated between atoms bonded to each other (1,2 interactions) or which are involved in angle interactions (1,3 interactions). A dielectric constant of 1 is used in the current work.

Published platinum forcefields have been used to study the binding interactions between Pt(II) and nitrogen donor ligands. In Hambley's work (ref. 17) the only interactions involving the Pt included are the Pt-N stretches. Pt-N bond distances of 2.01Å and 2.03 Å were used for Pt-amine and Pt-purine bond distances respectively. A Pt-N stretching force constant of 366kcal/molÅ<sup>2</sup> was reported. The corresponding Dreiding values are 1.99Å, 2.04Å, and 700 kcal/molÅ<sup>2</sup>. Angle bend interactions about the Pt center are approximated as 1,3 nonbonded interactions involving the ligands, electronic effects (rehybridization) at Pt are ignored. Van der Waals and electrostatic terms at the metal center are ignored. In the work of Lippard and coworkers (ref. 18) Pt-N stretch and N-Pt-N bend valence terms were included. A Pt-N distance of 2.00Å was used with a force constant of 201 kcal/molÅ<sup>2</sup>. The N-Pt-N angle was set at 90° with a force constant of 42 kcal/mol-rad.<sup>2</sup> Electrostatic interactions at platinum were included with the 2+ charge of Pt(II) distributed between the Pt and the adjacent nitrogen ligands (a residual charge of +0.278 was placed on Pt). The van der Waals parameters used on Pt were not reported.

As a benchmark for the forcefield molecular mechanics minimizations were carried out on a pair of square planar platinum complexes, 4 chloromethyl((+)-2S,3S-O-isopropylidene-2,3dihydroxy-1,4-bis(diphenylphosphino)butane)platinum(II) (ref. 19) and 5 (1,2-bis(Diphenylphosphino)ethane-P,P')bis(methoxycarbonyl)platinum(II) (ref. 20). The calculated and experimental Pt-X bond lengths and X-Pt-X bond angles for 4, and 5 calculated in a crystal environment are collected in Table I.

Table 1. Results of Crystal Minimization, Distances in Å, Angles in Degrees

Parameter	<u>4</u>		<u>5</u>	
	Calc.	X-ray	Calc.	X-ray
Pt-P <sub>1</sub>	2.32	2.32	2.29	2.29
Pt-P <sub>2</sub>	2.30	2.23	2.30	2.30
Pt-C <sub>1</sub>	2.13	2.17	2.04	2.06
Pt-Cl (C <sub>2</sub> )	2.35	2.32	2.05	2.06
P <sub>1</sub> -Pt-P <sub>2</sub>	98.	99.	86.	85.
C <sub>1</sub> -Pt-Cl (C <sub>2</sub> )	84.	82.	83.	90.
C <sub>1</sub> -Pt-P <sub>1</sub>	169.	168.	94.	90.
C <sub>1</sub> -Pt-P <sub>2</sub>	90.	92.	177.	175.
Cl(C <sub>2</sub> )-Pt-P <sub>1</sub>	89.	87.	173.	177.
Cl(C <sub>2</sub> )-Pt-P <sub>2</sub>	171.	174.	97.	94.

For 4 the Pt-P distance *trans* to carbon is in agreement with experiment but the Pt-P distance *trans* to chlorine is 0.07Å too long. The Pt-C bond distance is 0.04Å short and the Pt-Cl bond distance is 0.03Å too long. The valence angles are now within 3° of experiment.

For 5 the Pt-P bond distances are in agreement with experiment. The Pt-C(carbonyl) bond distances are 0.01Å and 0.02Å short of experiment. The C-Pt-C bond angle is 7° less than experiment. One of the C<sub>1</sub>-Pt-P cis bond angles is 4° larger than experiment, the other 3° larger than experiment. One of the C<sub>1</sub>-Pt-P trans angles is 3° smaller than experiment, the other 2° larger than experiment.

The agreement between calculated and experimental tertiary structure is quite good (see Figure 2).

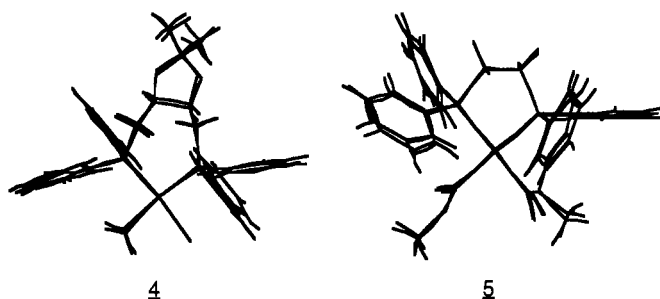


Fig. 2 Comparison of calculated and experimental solid state structures.

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