are due to propyl torsions, features also noted in the spectra of *n*-propylbenzene and 4-*n*-propyltoluene. The observation of only three origins also substantiates the conclusion derived from the data on the ethylbenzenes that $\tau_1 = 90°$.

These results show (a) supersonic molecular jet spectroscopy is capable of observing specific molecular conformations which have very low barriers to conformational interchange, (b) aromatic ring methyl groups in the *p*- and *m*-xylenes can be considered as independent, nearly free rotors in S_0 and S_1, (c) the aromatic ring methyl groups in *o*-xylene are considerably more hindered in S_0 and S_1, and for S_1, cross kinetic and potential terms must be introduced, (d) the barriers for rotation are greater in S_1 than S_0, (e) the dynamic nature of the motion of the ring methyl groups is contrasted by a more static, locked-in character of the aromatic ethyl and *n*-propyl substituents, (f) aromatic *n*-alkyl substituents have their first C–C torsion perpendicular to the plane of the aromatic ring, and (g) aromatic *n*-propyl substituents exist in anti and gauche conformations, as observed in these TOFMS/DE experiments.

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Potential Energy Profile of a Full Catalytic Cycle of Olefin Hydrogenation by the Wilkinson Catalyst

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It is only in the last few years that for elementary reactions of organotransition-metal compounds the transition-state geometry can be optimized and the potential energy profile can be obtained from ab initio molecular orbital calculations.[2] Elementary reactions thus studied include oxidative addition/reductive elimination,[3] olefin insertion/β-elimination,[4] carbonyl insertion,[5] thermolysis of ketene complexes,[6] and isomerization of metallacycle to an alkylidene–olefin complex.[7] Despite such success, a study of an entire cycle of a catalytic process, consisting of several elementary reactions, has been a challenge to theoreticians.

We communicate here the results of the first such study, on homogeneous olefin hydrogenation by the Wilkinson catalyst.[8] We concentrate on the dominant catalytic cycle of the mechanism proposed by Halpern.[8b-d] The model of the cycle we adopted, shown in Scheme I, consists of oxidative addition of H_2, coordination of ethylene, ethylene insertion, isomerization, and reductive elimination of ethane. In the present study we use PH_3 as L,[9] and neglect the effect of solvent proposed in the Halpern mechanism for **1**, **2** and **5**.

The geometries of the intermediates, **1–5**, and the transition states connecting them have been optimized with the Hartree–Fock energy gradient method,[10] and some important geometries are

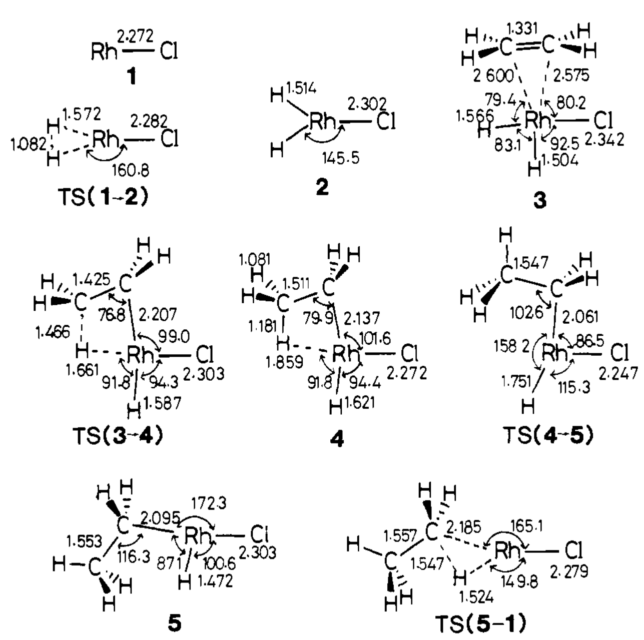
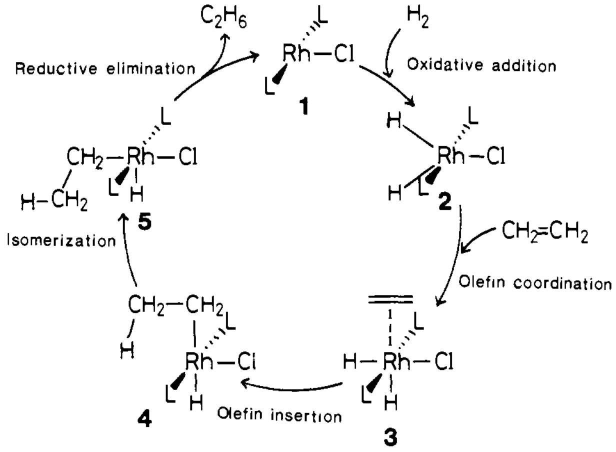


Figure 1. Optimized geometries of some important species in angstroms and degrees. TS(1→2), for instance, denotes the transition state connecting **1** and **2**. Though practically all the geometrical parameters were optimized, only essential values are shown. Two PH_3's, one above and one below the plane of the figure, are omitted for clarity.

Scheme I



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[9] We are aware of the fact that the actual catalysis takes place with L = PPh_3, and we plan to examine in the future the role of the phenyl group.

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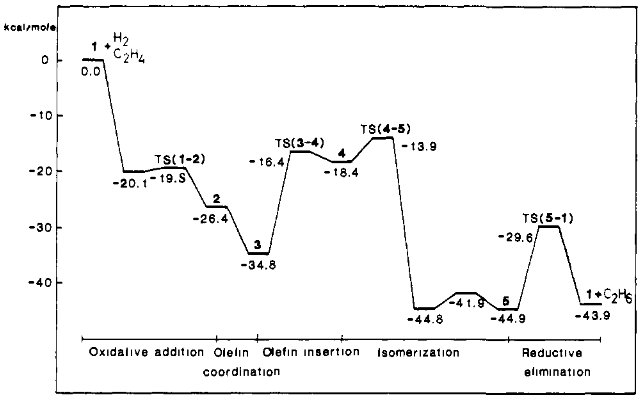

Figure 2. Potential energy profile of the entire catalytic cycle, in kilocalories per mole.

shown in Figure 1. The potential energy profile for the full cycle is shown in Figure 2. The energy difference between both ends of the profile corresponds to the energy of the reaction H_2 + $CH_2{=}CH_2 \rightarrow CH_3{-}CH_3$.[11] We find in Figure 2 that the potential energy profile is smooth, without excessive barriers and without too stable intermediates. This is, of course, the way it has to be for any good catalytic process, but it is heartening to find it out in a theoretical calculation.

The first two reactions, oxidative addition of H_2 and coordination of olefin, are found to be exothermic with little or no activation barrier. Olefin insertion, followed by isomerization of the trans ethyl hydride complex **4** to a cis complex, is the rate-determining step with a barrier height of about 20 kcal/mol. These two reactions, exothermic overall, may actually take place as one combined step with little stability in the trans intermediate **4**.[12] The final step of reductive elimination of ethane from the cis complex **5** is nearly thermoneutral with a substantial barrier (~15 kcal/mol).

Some specific features of the geometries and the energetics of the intermediates and the transition states may be noted in Figures 1 and 2. In the oxidative addition of H_2, formation of an H_2 complex is followed by a transition state, noted as TS(**1**→**2**), with a very small barrier (<1 kcal/mol). TS(**1**→**2**) is very late, with the Rh–H distances nearly as short as in the product **2**. The barrier being small, these two steps should be considered to take place as a combined step without a barrier. Olefin prefers to coordinate to the Y-shaped (trigonal bipyramidal) intermediate **2** from the HRhCl end, rather than from the HRhH end, to give **3** without a barrier. The Rh–C bond is long in **3**, probably due to the strong trans influence of the hydride as well as the electronic and steric effect of the chloride. The intermediate **3** is in a valley of the potential energy profile and may be detectable experimentally. The olefin insertion product **4** shows signs of a very strong agostic interaction, with a small RhCC angle (~80°), a short Rh···H distance, and a long CH bond (1.18 Å compared to normal 1.08 Å) interacting with Rh. The isomerization of the trans complex **4** to a cis complex, from which the reductive elimination can take place, has several possible routes and intermediates. Among them, the hydride migration from **4**, followed by the chloride migration to give **5**, seems to be the most favorable. The large exothermicity of the hydride migration brings the potential energy profile down, and the chloride migration takes place with a small (~3 kcal/mol) barrier. The ethyl migration which leads **4** directly to **5** has a higher barrier (not shown) and is unfavorable.

Detailed analysis of the geometries and the energetics of reactants, intermediates, and transition states, as well as a comparison with similar reactions studied previously, will be published elsewhere. The study of the solvent effect on the potential energy profile is also in progress.

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(10) The use of the Hartree–Fock method is justifiable for all the present complexes, where at least two phosphines and a chloride stabilize the closed-shell ground state. We use a valence double-ζ basis set for Rh with a relativistic effective core potential, the 3-21G set for hydrides and hydrocarbons, and the STO-2G set for the spectator ligands Cl and PH_3.

(11) The experimental value from the standard heat of formation is 32.7 kcal/mol,[11a] compared with the present HF/3-21G value of 43.9 kcal/mol. The 6-31G* RHF and MP2 calculations have given 44.0 and 41.1 kcal/mol, respectively.[11b] (a) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *J. Phys. Chem. Ref. Data, Suppl. 2* **1982**, 11. (b) *Carnegie-Mellon Quantum Chemistry Archive*; Whiteside, R. A., Frisch, M. J., Pople, J. A., Eds.; Carnegie-Mellon University: Pittsburgh, 1983.

(12) An electron correlation (MP2) calculation with a larger basis set at the optimized geometries of Figure 1 gives the energy of **4** higher than that of TS(**3**→**4**).

Cocomplexation of Urea and UO_2^{2+} in a Schiff Base Macrocycle: A Mimic of an Enzyme Binding Site

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The single-crystal X-ray structure of the ternary complex of a Schiff base macrocycle **1** shows that the electrophilic uranyl cation and urea both complex cooperatively in the cavity of the macrocycle.

As part of our work on the complexation of neutral molecules by macrocyclic ligands,[1] we are particularly interested in the complexation of urea. We have shown that urea can form complexes with (aza-)18-crown-6[2,3] but the association constants of these complexes in water are very small (18-crown-6–urea, log $K_s = 0.1$).[4]

Protonation of urea effects stronger binding especially when the crown ether is sufficiently large to form an encapsulated complex (e.g., the complex benzo-27-crown-9–urea–$HClO_4$).[5] Protonation of the weakly basic urea (pK_a = 0.1, water, 25 °C) requires strongly acidic conditions and to avoid this we have introduced a covalently linked carboxylic group in the cavity of the macrocycle. A strong hydrogen bond of urea with 2-carboxyl-1,3-xylyl-30-crown-9 resulted in an encapsulated complex.[6]

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