Structure Elucidation

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Mechanism of the Asymmetric Hydrogenation of Exocyclic α,β-Unsaturated Carbonyl Compounds with an Iridium/BiphPhox Catalyst: NMR and DFT Studies**

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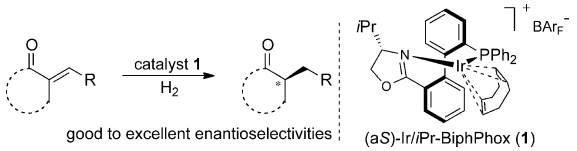
Abstract: *The mechanism of the asymmetric hydrogenation of exocyclic α,β-unsaturated carbonyl compounds with the (aS)-Ir/iPr-BiphPhox catalyst was studied by NMR experiments and DFT computational analyses. Computed optical yields of the asymmetric hydrogenation proceeding by an iridium(I)/iridium(III) mechanism involving a transition state stabilized through two intramolecular hydrogen bonds are in good accordance with the experimental ee values.*

Metal-catalyzed asymmetric hydrogenation is a well-established method of longstanding interest because of its high efficiency for preparing enantiomerically enriched compounds.[1–4] Recently, Ir/P,N complexes have attracted much attention because of their ready availability, high reactivity, and high enantioselectivity in asymmetric hydrogenation reactions.[3,4] However, the mechanism of the iridium-catalyzed asymmetric hydrogenation has not been studied in sufficient detail[5] when compared to the corresponding ruthenium-[6] and rhodium-catalyzed[7] reactions. Pfaltz et al. described the quantitative formation of solvate dihydrides upon hydrogenation of an iridium catalytic precursor at low temperatures.[5a,g] Computationally the hydrogenation of unfunctionalized olefins was studied by Andersson and co-workers and Burgess and co-workers using DFT computations, thus revealing an interplay of iridium(III) and iridium(V) intermediates,[5b,e,f,h] and the possibility of an iridium(I)/iridium(III) mechanism was discussed and supported by Chen et al.[5d,i,l] In view of the numerous successful iridium-catalyzed hydrogenations of various functionalized olefins and heterocycles reported recently,[3,4] it is important to understand the factors governing enantioselection in these reactions.

As the (a*S*)-Ir/*i*Pr-BiphPhox complex **1** demonstrated excellent results in the iridium-catalyzed asymmetric hydrogenation of exocyclic α,β-unsaturated carbonyl compounds[8] (Scheme 1), we decided to use it in our mechanistic study.



Scheme 1. Asymmetric hydrogenation of exocyclic α,β-unsaturated carbonyl compounds catalyzed by (a*S*)-Ir/*i*Pr-BiphPhox. BAr_F = tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate.

A solution containing 17 mg of **1** in 0.5 mL of CD_2Cl_2 was hydrogenated at −40 °C for 10 minutes.[9] The 1,5-cyclooctadiene ligand of **1** is immediately hydrogenated to cyclooctane upon introduction of hydrogen, even at decreased temperatures. The initial spectrum contained several species. After storage of the sample for a week in a freezer (−18 °C), its ^{1}H NMR spectrum (Figure 1) at 203 K contained two diastereomers of a pentahydride complex (**2a,b**) with three bridging hydride ligands in a 5:1 ratio (see the Supporting Information). A broadening of the peaks of the minor **2b** was observed when the temperature was increased. Even upon a slight rise in temperature from 203 K to 213 K the peaks of **2b** broadened dramatically and became difficult to distinguish.

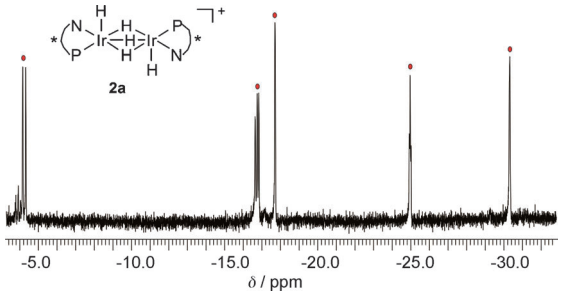


Figure 1. Section plot of the ^{1}H NMR spectrum (700 MHz, CD_2Cl_2, 213 K) for the five hydrides of the dimer **2a**.

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[**] Computational results in this research were obtained using the supercomputing resources at the Information Synergy Center, Tokyo Institute of Technology. This work was partially supported by the National Natural Science Foundation of China (21172143 and 21232004), Nippon Chemical Industrial Co., Ltd, Shanghai Jiao Tong University, and CAMPUS Asia Program of Tohoku University. BiphPhox = 2-(2′-(diphenylphosphino)-[1,1′-biphenyl]-2-yl)-4,5-dihydrooxazole.

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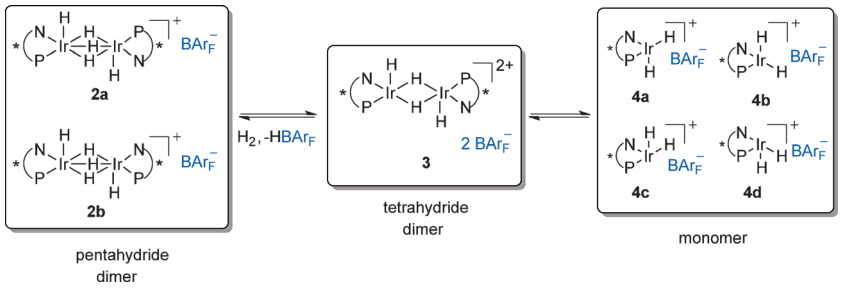

Scheme 2. Equilibrium of dimers found at low temperature.

Each isomer exhibited five hydride resonances in the δ range from -4 to -30 ppm. The relatively low-field hydrides of **2a** and **2b** resonated as a doublet and triplet with the $^1J_{Ir\text{-}H}$ coupling constants of 98 and 74 Hz, respectively. These data confirm the relative configuration of the two chelate cycles in **2a** and **2b** shown in Scheme 2. In total there are seven possible isomers of **2** and it is difficult to assign the structures of **2a,b** precisely by NMR spectroscopy alone. We hypothesize that the dimer pentahydrides **2a,b** have the structures shown in Scheme 2, and they are based on 2D NMR (^{1}H-^{1}H COSY, ^{1}H-^{1}H ROESY and ^{1}H-^{31}P HMBC) and computational data.[9] In recent reports similar structure was also found in rhodium-catalyzed hydrogenation.[10]

If the NMR spectrum was taken directly after low-temperature hydrogenation, other species were observed. Two major peaks at $\delta = -17.60$ ppm (d, $^1J_{Ir\text{-}H} = 41.3$ Hz) and at $\delta = -29.78$ ppm (br s) were seen in the hydride region of the ^{1}H NMR spectrum. Additionally, three sets of smaller signals of a similar shape, but lower intensity, were observed in close proximity to the two main signals. These observations correspond to the initial formation of several diastereomers of dinuclear iridium tetrahydrides (**3**) which are in equilibrium with the monomer solvate complexes **4**. Computational analysis showed that the formation of the dimers **3** from the monomers **4** is significantly exogonic. The symmetry of the spectrum of the major isomer of **3** corresponds well to the structure of the most stable among the computed structures of diastereomers. If the temperature of the hydrogenated sample was raised over 0 °C, a rapid loss of hydrogen accompanied by the decomposition of the catalyst occurred.

The addition of 1 equivalent of the prochiral substrate **5** to a solution containing **2** at -18 °C resulted in slow quantitative formation of the hydrogenation product **6** (Figure 2). The enantiomeric excess of **6** was determined to be 90 % (*S*), that is, of the same sign and value for the optical yield of the preparative hydrogenation of **5** catalyzed by **1** [93 % (*S*)]. We have thoroughly investigated, computationally, the possibility of a dimeric catalyst (either **2** or **3**) and were convinced that the steric repulsion strictly precludes coordination of the substrate in either case. Hence, we concluded that the hydrogenation is effectuated by the monomeric dihydride complexes **4**, and the formation of the pentahydrides **2** from tetrahydride dimers **3** is also reversible.

There are a total of sixteen possible ways in which a C_1-symmetric prochiral substrate can coordinate to a C_1-symmetric *cis* dihydride (each of the four diastereomers of *cis* dihydride can accommodate the substrate in four possible manners). However, it is a well-established fact in for transition metal catalyzed hydrogenations that the hydride *trans* to the phosphorus atom must be transferred in the migratory insertion stage.[5e] Therefore, we restricted our analysis to eight different pathways (four *S* and four *R*) initiated by the different modes of the substrate coordination coplanar to the P-Ir-H bond (Figure 2). In the consideration of an iridium(III)/iridium(V) mechanism,[5b,c,e,f,h,j] we have also tried to coordinate another molecule of dihydrogen to iridium either in the dihydride complexes or in the monohydride intermediates formed after the migratory insertion step. However, hydrogen invariably escaped during the computational optimizations. Hence, we were unable to confirm any involvement of a iridium(III)/iridium(V) mechanism in our case.

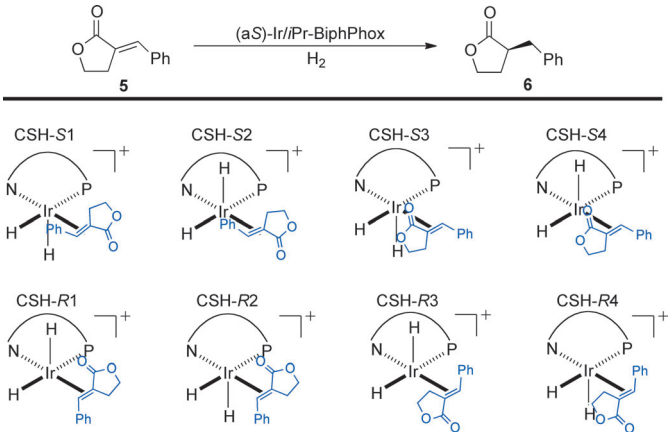

Figure 2. Eight possible pathways with the substrate **5** coordinated coplanar to the P-Ir-H moiety. CSH = catalyst/hydride/substrate complex.

The energies of the transition states, for the migratory insertion steps of the pathways with hydride initially transferred to the double-linked carbon atom on the five-membered ring, were calculated to be more than 6 kcal mol^{-1} higher than those in the other four pathways. From a chemical point of view, this means an easier hydride transfer to the protonated carbon atom of the double bond. Therefore we further analyzed the pathways *S*1, *S*2, *R*1, and *R*2 (Figure 3). The migratory insertion step of the pathway 1 was calculated to be *S* stereoselective (the difference in stabilities of the migratory insertion transition states of *S*1 and *R*1 pathways is 2.1 kcal mol^{-1}). In contrast, the transition states of the *S*2 and *R*2 pathways were found to be almost equally stable. Hence, the experimentally observed *S*-enantioselective reaction means that the migratory insertion by the *R*2 pathway does not actually take place.

In search of a possible reason for this, we have simulated the approach of the substrate to the catalyst, thus resulting in the coordination of the substrate appropriate for the occur-

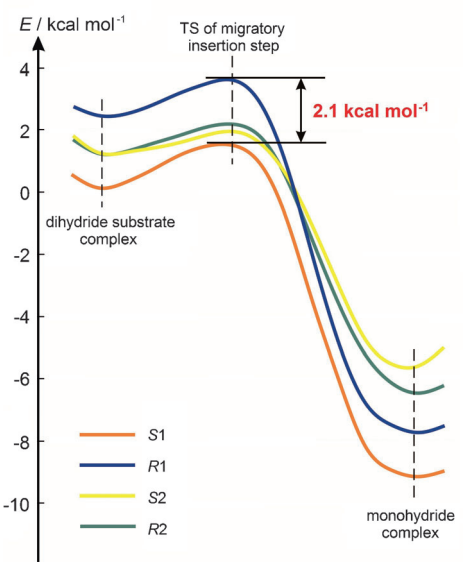

Figure 3. Reaction pathways *S*1, *S*2, *R*1, and *R*2 for the migratory insertion step in the hydrogenation of **5** catalyzed by **1**.

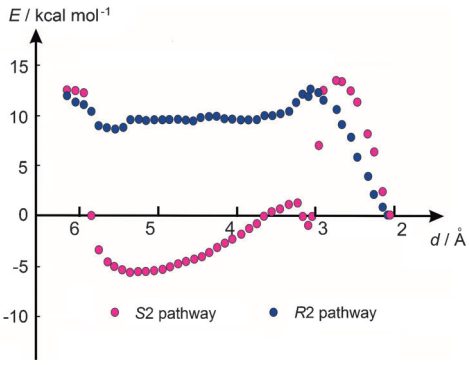

Figure 4. Energy scans simulating the approach of **5** to the catalytic hydride. The final minima correspond to the completely optimized structures of the adducts.

rence of the migratory insertion by *S*2 and *R*2 pathways. The corresponding energy scans are shown in the Figure 4.

When approaching the catalyst by the *S*2 pathway, the substrate rapidly finds a minimum through hydrogen-bond formation with the axial hydride. In contrast, for the case of the *R*2 pathway such an interaction is reliably switched off by one of the phenyl substituents of the catalyst.[11] As a result, only the pathway *R*1 (Figure 5) must be considered as a competing pathway to the formation of the *S* product by either of the *S*1 or *S*2 pathways.

The optimized structures of catalyst/hydride/substrate complexes for the *R*1, *S*1, and *S*2 pathways are shown in Figure 5. The *S* pathways have hydrogen-bonding effects between the carbonyl group of the substrate and the hydrogen atom on the phenyl ring of the catalyst. In contrast, in the *R* pathway there is steric hindrance between the CH_2 group of the five-membered ring of the substrate and the phenyl ring of the catalyst. The transition state of the pathway *S*1 is slightly more stable than that of *S*2, and may be due to the additional

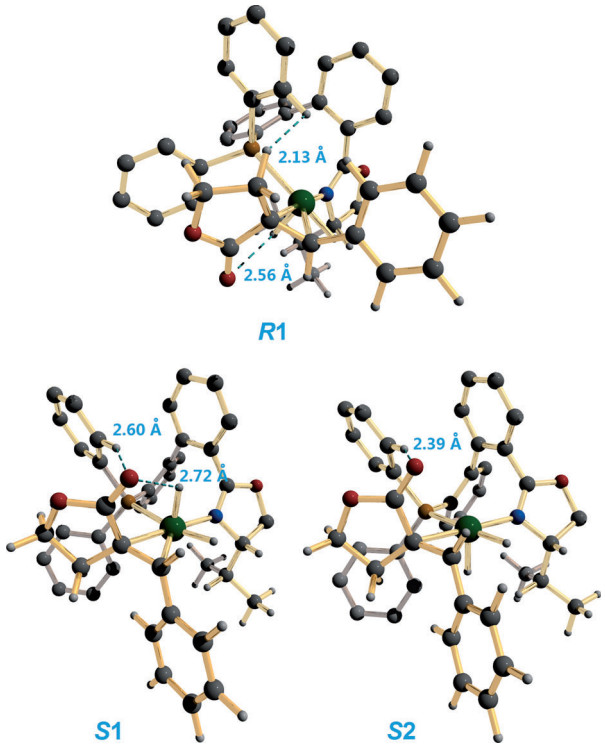

Figure 5. Optimized structures of catalyst/hydride/substrate complexes for the pathways *R*1, *S*1, and *S*2.

hydrogen bonding between the axial hydride and the carbonyl group of the substrate.

Table 1 shows the calculated differences in the free energies of the migratory insertion stage for the *S*1 and *R*1 pathways and the comparison to the experimentally observed *ee* values in the catalytic reactions. One can see that in complete accordance with the experimental data, the computational results reliably predict the *S* stereoselectivity in all cases. Moreover, the substrate dependence of the optical yields is also reasonably reproduced. Analysis of the transition-state structures suggests that the evident decrease of the *ee* values in the case of the substrates containing six-membered rings, is explained by the destabilization of the *S* pathways as a result of the additional CH_2 group of the substrate.

Thus, we conclude that the asymmetric hydrogenation of exocyclic α,β-unsaturated carbonyl compounds catalyzed by a (a*S*)-Ir/*i*Pr-BiphPhox catalyst takes place by initial formation of iridium dihydrides which reversibly form various dimeric species, but can be recovered to effect the catalysis. The enantiodetermining step is the migratory insertion which preferably takes place in the catalyst–substrate adducts with the C=CHPh group oriented coplanar to the *trans*-P-Ir-H fragment. One of the possible *R* pathways is effectively switched off at the stage of the substrate coordination, and the order of enantioselection is regulated by the difference in the stabilities of the transition states of migratory insertion for two *S* pathways and one *R* pathway.

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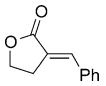
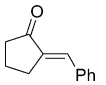
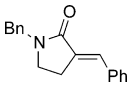
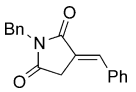
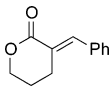
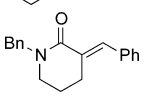
Table 1: Energy differences between corresponding transition states in pathways *S*1 and *R*1 for different kinds of substrates.

Substrates	$\Delta G_{(S1-R1)}$[a] [kcal mol^{-1}]	Experimental *ee* [%][b]	ΔG^{exp}[c] [kcal mol^{-1}]
	2.1	95	2.16
	1.2	92	1.87
	2.9	98	2.71
	3.6	99	3.12
	0.6	71	1.05
	1.1	53	0.70

[a] $\Delta G_{(S1\text{-}R1)}$ = free-energy differences of the transition states for the migratory insertion step in pathways *S*1 and *R*1. Computed under 20 atm at 298.15 K. [b] Enantioselectivities of experimental catalytic hydrogenation reaction. [c] ΔG^{exp} = expected values derived from the experimental *ee* values.[12]

Keywords: density functional calculations · hydrogenation · iridium · NMR spectroscopy · reaction mechanisms

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