Chinese Chemical Letters Vol. 16, No. 11, pp 1555-1558, 2005
http://www.imm.ac.cn/journal/ccl.html

Spacial Structure of Cationic Phosphorus Ligand –Ru (II) Halide Complexes—by DFT Study

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Abstract: The full-parameter geometry optimization of cationic *(S)* – BINAP – Ru (II) halide complex was performed by DFT method using B3LYP, PW91 and PBE potentials with several basis sets. PW91 with 3-21G / SDD basis sets is found to be the most suitable method with consideration of both precision and efficiency. The dihedral angles (θ) of the binaphthyl or biphenyl with different phosphorus ligand – Ru (II) halide complexes were found changing from 59.9 to 79.3 degree, while the natural bite angle (βn) of those complexes only changes from 87.4 to 90.3 degree. It is different from the common view of asymmetric organic chemists' that θ directly influences βn.

Keywords: Chiral phosphorus ligand, DFT, dihedral angle (θ), natural bite angle (βn).

The increasing demand to produce enantio-pure pharmaceuticals, flavors, and other fine chemicals has advanced the field of asymmetry catalytic technologies. Among all asymmetry catalytic methods, catalytic enantioselective hydrogenation of unsaturated bonds such as olefins, ketones, and imines, which employs dihydrogen and small amounts of transition-metal complexes modified intrinsically by chiral ligands, is now recognized as being the most promising strategy for the synthesis of large amounts of enantiomerically pure products [1], and enormous progress has been achieved in this area. Among these transition metal complex, rhodium (I) and ruthenium (II) complexes and, most often, diphosphine-based chiral ligands have been extensively employed in asymmetric hydrogenation. Experimental results have shown the reaction of ruthenium complexed with diphosphine-based chiral ligands catalyzed asymmetric hydrogenation of β-ketoesters are mild. The reaction proceeded in common conditions of 50-70 ℃ and 1-100 atm H_2 pressure. So it has been used for the synthesis of a large variety of biologically or pharmaceutically important chiral compounds [2].

To explain the different enantioselectivities of chiral phosphorus ligands, asymmetric organic chemists have held the common view that: "one of the predominant factors that can influence the enantio selectivity could be the dihedral angle in the chiral backbone (θ). This correlates to the natural bite angle (βn) in metal complexes. The dihedral angles of the binaphthyl or biphenyl systems are expected to influence the effect

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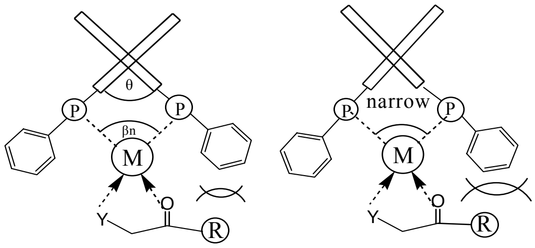
of the steric bulk of the diphenylphosphino group[3]". In studying the θ, some chemists have used MM2 method[4, 5], a molecular mechanism method which eliminates the change of electronic structures with lower precise especially when system containing transition metals. Based on this reason, density functional theory (DFT) method have been performed on the cationic phosphorus ligand - Ru (II) halide.

Figure 1 Steric considerations based on the effect of varying the dihedral angle (θ) in biaryl backbone[1].



θ: Dihedral angle, βn: Natural bite angle

Computational Details and Results

More sophisticated DFT method with different potentials such as B3LYP, PW91 and PBE at different level of basis sets have been applied for the investigation of the cationic (*S*)-BINAP-Ru (II) [BINAP =2, 2'-bis (diphenylphosphino)-1, 1'-binaphthyl] halide complexes (shown in **Figure 2**). The full-parameter optimization results and experimental XRD data[6] are presented in **Table 1**. Among these results, PW91 / basis set IV is found to be the most suitable method with consideration of both precision and efficiency.

Several interested chiral complexs were investigated and their diphosphine- based chiral ligands are showed in **Figure 3**. It was thought that increase of the length of the $(CH_2)_n$ chain can influence the θ and change the natural bite angle βn. The selected geometry parameters (from full parameter optimizations by PW91 / IV) are presented in **Table 2**. We may find the θ of those phosphorus ligands complexes which changed from 59.9 to 79.3 degree, while βn only changed from 87.4 to 90.3 degree, respectively.

Table 1 Selected optimized geometries of *(S)*- BINAP-Ru (II). R: bond length in Å, θ: dihedral bond angle, indicated in **Figure 2**, in degree °. Exp: experimental data from Ref 6.

Method.	B3LY	B3LY	B3LY	B3LYP	B3L	PBE	PW91	Exp
Basis Set*	PI	PII	PIII	IV	YPV	IV	IV	
$R_{Ru\text{-}P1}$	2.441	2.416	2.482	2.414	2.415	2.392	2.390	2.379
$R_{Ru\text{-}P2}$	2.407	2.375	2.434	2.389	2.378	2.365	2.365	2.334
$R_{Ru\text{-}Cl}$	2.442	2.429	2.463	2.432	2.425	2.421	2.420	2.393
θ	79.5	79.8	79.9	79.8	80.3	79.3	79.9	80.9

*: Basis sets: I: Lanl2dz for Ru, 3-21g for C, H, P, Cl; II: Lanl2dz for Ru, 6-31g (d) for C, H, P, Cl; III: Lanl2dz; IV: SDD for Ru, 3-21g for C, H, P, Cl ; V: SDD for Ru, 6-31g (d) for C, H, P, Cl.

Figure 2 Optimized geometry of cationic phosphorus ligand - Ru (II) halide (H is omitted).

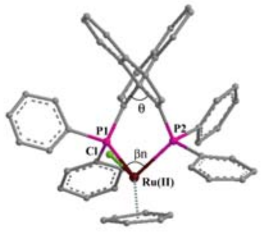


Figure 3 Schematic drawing of *(R)*- (P - P) - Ru (I1) complex, P - P = *(R)* - BINAP, *(R)*-MeO - BIPHEMP and *(R)*-Cn-TunaPhos (n = 1-5)[7].

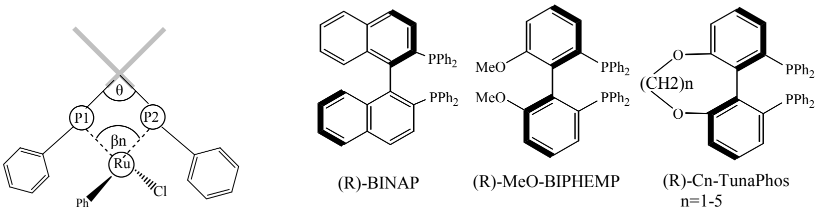


Table 2 Seclected optimized geometry of *(R)* Cn-TunaPhos – Ru (Ⅱ) (C_6H_6) Cl complexes（R: bond length in Å; βn, θ: bond angle in °）

	C1-TunaPhos	C2-TunaPhos	C3-TunaPhos	C4-TunaPhos	C5-TunaPhos	MeO-BIPHEP	BINAP
$R_{Ru\text{-}P1}$	2.382	2.395	2.400	2.388	2.390	2.393	2.392
$R_{Ru\text{-}P2}$	2.357	2.358	2.363	2.361	2.360	2.363	2.363
βn	87.4	89.9	89.4	89.3	89.7	90.3	89.4
θ	59.9	74.7	72.1	74.7	75.2	79.3	78.7

The common view: θ influences the natural bite angle (βn) that is not true. The bond lengths of Ru-P1 and Ru-P2 are -2.39 and -2.36, respectively, regardless of the variety of θ.

Conclusion

Because of the intense complexation between Ru (II) and phosphorus and the two phosphorus atoms hold two sites of octahedral ruthenium having fac-geometry. The natural bite angle (βn) in different complexes is almost fixed, so the dihedral angle in the chiral backbone (θ) could not directly influence it in such complexes.

Acknowledgments

We acknowledge the financial support by the National Natural Science Foundation of China (No.20373014).

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Received 24 January, 2005