นิพนธ์ต้นฉบับ

การศึกษาเชิงทฤษฎีของฟอสฟีนอสมมาตร สำหรับเมทานอลคาร์บอนิลเลชัน (ตอน 1)

A Theoretical Study of Asymmetric Phosphine for Methanol Carbonylation (PART I)

Keywords : Theoretical study, Asymmetric Phosphine, Methanol Carbonylation, Quantum Mechanics, Hartree Fock, Density Functional Theory.

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Abstract

Quantum Mechanics (QM) calculations based on Hartree-Fock (HF) and the Density Functional Theory (DFT) have been carried out for an asymmetric phosphine ligand $PF_2PCH_2CH_2PMe_2$ 1.1. This ligand was employed as a promoter of the rhodium catalyzed methanol carbonylation. A rhodium cation 1.2 are calculated. Complexes 1.3 and 1.4 are also investigated on electronic properties to specify the most stable structure. A comparison between the various methods indicated that DFT with LANL2DZ basis set is the appropriate method for such structures.

By the consideration of the B3LYP/LANL2DZ calculated energies, complex 1.3 is more stable than complex 1.4. It can notices that the stereochemistry at rhodium in which the $P(Me)_2$ *trans* to the CO and the PF_2 *trans* to the Me group are preferred. The results indicate that the presence of strong electronegativity fluorine atoms in PF_2 makes them weak σ-donors but much stronger π- acceptors and the presence of Me groups in $P(Me)_2$ makes them stronger σ-donors but much weaker π- acceptors, with confirming by 2.356 and 2.456 Å of a $Rh-P(F_2)$ and the $Rh-P(Me_2)$ bond lengths in complex 1.3.

The molecular orbital confirmed that the d_{z^2} orbital is lower energy than the $d_{x^2-y^2}$ orbital as expected for a low-spin d^8 orbital Rh (I) configuration. The differences of energy (ΔE) values were used to calculate the equilibrium constant and confirmed the possibility to make this model 1.3.

บทคัดย่อ

การคำนวณด้วยวิธีฮาร์ทรี-ฟอกซ์ (HF) และทฤษฎีความหนาแน่นเชิงฟังก์ชัน (DFT) ของกลศาสตร์ควอนตัม (QM) ถูกนำมาใช้เพื่อคำนวณคุณสมบัติทางอิเล็กทรอนิกส์ของลิแกนด์ฟอสฟีน หรือ 1.1 ลิแกนด์อสมมาตรชนิดนี้ถ้ารวมกับสารประกอบโรเดียมเกิดเป็นแคตไอออน 1.2 สารเชิงซ้อน 1.3 และ 1.4 แล้ว ก็สามารถที่จะเป็นตัวเร่งในปฏิกิริยาเมทานอลคาร์บอนิลเลชันได้ในการคำนวณทั้งสองวิธีนี้ได้ใช้เซตมูลฐานที่แตกต่างกัน ผลการคำนวณบ่งชี้ว่าการใช้ DFT และมี LANL2DZ เป็นเซตมูลฐาน (DFT/LANL2DZ) จะให้ผลที่น่าเชื่อถือและเหมาะสมมากที่สุด

นำวิธีการนี้มาคำนวณคุณสมบัติต่าง ๆ ของแคตไอออน 1.2 สารเชิงซ้อน 1.3 และ 1.4 ผลการคำนวณพลังงานพบว่าสารเชิงซ้อน 1.3 จะมีพลังงานต่ำกว่าสารเชิงซ้อน 1.4 สเตอริเคมีของอะตอมโรเดียมในสารเชิงซ้อน 1.3 มีหมู่ $P(Me)_2$ อยู่ในตำแหน่งทรานส์กับหมู่ CO และหมู่ PF_2 ทรานส์กับหมู่ Me จะทำให้สารเสถียรมากกว่า และผลการคำนวณชี้ชัดว่าการที่มีหมู่ PF_2 ที่มีประกอบด้วยอะตอมฟลูออรีนที่มีค่าสภาพไฟฟ้าลบมากกว่าส่งผลให้หมู่ PF_2 เป็นหมู่ที่ให้ซิกมาที่ไม่ดี แต่จะเป็นหมู่รับไพที่ดี และในทำนองเดียวกันการที่สารเชิงซ้อนมีหมู่ PMe_2 ส่งผลให้ซิกมาที่ดี แต่จะเป็นหมู่รับไพที่ไม่ดี ซึ่งยืนยันได้จากความยาวพันธะระหว่างโรเดียมกับฟอสฟอรัส โดยที่ความยาวพันธะ $Rh-PF_2$ เท่ากับ 2.356 อังสตรอม ที่สั้นกว่าความยาวพันธะระหว่าง $Rh-P(Me_2)$ ซึ่งมีค่าเท่ากับ 2.456 อังสตรอม

การศึกษาออร์บิทัลโมเลกุลทำให้ทราบว่าโครงแบบของโรเดียมมีพลังงานของ $d_z{}^2$ ออร์บิทัล ต่ำกว่าพลังงานของ $D_x{}^2{}_{-y}{}^2$ ออร์บิทัล ซึ่งเป็นการยืนยันว่าโรเดียมมีเลขออกซิเดชันเท่ากับ 1 (Rh(I) ที่มี 8 อิเล็กตรอนใน d ออร์บิทัล (d^8) และมีสปินต่ำ ความแตกต่างของค่าพลังงานที่คำนวณได้นำไปคำนวณหาค่าคงที่สมดุลและยืนยันว่ามีความเป็นไปได้ที่จะสังเคราะห์สารประกอบเชิงซ้อน 1.3

Introduction

The carbonylation of methanol to acetic acid (Equation 1.1) is one of the most important and successful industrial applications of homogeneous transition metal catalysis.[1] Since its original development by Monsato some thirty years ago, a rhodium/iodide catalyzed process so called the Monsanto catalyst $[RhI_2(CO)_2]$- has predominated.[2-4]

$$CH_3OH + CO \xrightarrow[\text{[Cat]/H}]{150\text{-}200\,^{\circ}C \;\; 10\text{-}60\text{ bar}} CH_3COOH \qquad 1.1$$

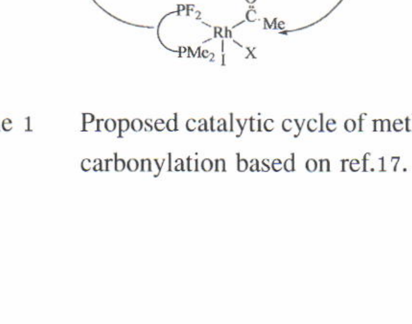
Attempt to modify this catalyst and increase its activity by introducing electron-donating ligands have been hampered by the instability of many complexes of such ligands under the harsh reaction condition required for carbonylation. Recent reports have identified a number of mixed-donor ligands, which promote carbonylation under very mild conditions (typically<130 °C and <20 bar).[5-7] However, these mild conditions are not well suited to commercial operation where high absolute reaction rates are required and engineering constraints favor high temperatures and therefore higher pressures. One recent report has stated that the use of the diphosphinesulfide $Ph_2PCH_2P(S)Ph_2$ (dppms) as a promoter for rhodium catalyzed methanol carbonylation allows a surprisingly substantial rate increase under industrially feasible conditions.[8] At 185 °C, 30 atm, the rate increased eight times higher than $[RhI_2(CO)_2]$- (for commercial viability, the conditions under which the catalyst operates are crucial). The dppms ligand gives the expected fast oxidation and it also promotes the subsequent CO insertion step (by a factor of *ca.* 3000 compared with $Ph_2PCH_2CH_2PPh_2$ (dppe).[9] Strong donor ligands, particularly phosphines, are known to accelerate the rate determining oxidative addition of methyl iodide to Rh (I) and hence promote catalysis. The new *Cativa* process uses an iridium-iodide catalyst and is even more efficient than rhodium system that it has begun to replace.[10]

Methanol carbonylation with original Monsato catalyst has been studied in detail not only experimentally but also from a theoretical point of view.[11-12] Computational chemistry especially theoretical studies such as quantum mechanics calculations are used as a tool to understand mechanism and reaction. The development of computational techniques such as the *ab initio* molecular orbital (MO) theory has made it possible to carry out calculation for organometallic compounds.[13] Asymmetric phosphine catalysis involving organometallic species is undergoing rapid development. Even so, the development of catalysts with higher selectivity is one of the goals of current research with the emphasis on ligands that are electronically asymmetric.[7, 9-10, 14-16]

Ligand steric and electronic effects play a key role in the determining organometallic reactivity trends and catalytic behavior.[17] For monodentate ligands, a number of quantitative parameters such as Tolman's cone angle[18] are known concepts. Several important homogeneous catalysts now utilize bidentate ligands for which the stereoproperties are less well understood.[19] Although the bidentate ligand "bite angle" has been shown to be important understanding[20] of the observed behavior at the molecular level is incomplete[21] and quantification of ligand effects on individual steps from catalytic quite rare. A theoretical study of steric and electronic effects in rhodium-catalyzed carbonylation reaction using DFT have been carried out on the migratory insertion process which presents an important step in methanol carbonylation.[12] However, the rate of determining step of the catalytic is oxidative addition of CH_3I. [22] So that the catalyst design focused on the improvement of this reaction.[11-12,22]

Aim

The basic idea was ligands which increase the electron density at the metal should promote oxidative addition, and by consequence the over rate of production. To this purpose, a ligand $PF_2PCH_2CH_2PMe_2$ 1.1 was designed as a promoter for catalysis of methanol carbonylation (Scheme 1). Such a ligand can be tuned to mimic the electronic properties by varying the constituents on one phosphorus *i.e* make a 'strong-weak' ligand with one strong σ-donor (and poor π-acceptor) and one weaker σ-donor (and stronger π-acceptor). Theoretical methods are employed and investigated. Base on calculation results, this ligand and suitable complexes will finally synthesize.



Scheme 1 Proposed catalytic cycle of methanol carbonylation based on ref.17.

Methodology

(1) Designed Structures.

The designed structures under this study are a ligand $PF_2PCH_2CH_2PMe$, denoted as 1.1, a cation 1.2, complexes 1.3 and 1.4. The complexes have square planar geometry at rhodium. Isomeric complexes 1.3 and 1.4 contain CO and Me. An isomer 1.3 has CO *trans* to PMe_2 moiety of the ligand; this arrangement is reversed in 1.4. The structures are shown in Figure 1.

(2) Computational Methodology

Initial structure geometries for each complex were constructed at the UFF level using the Cerius^2 program.[23] The geometry optimizations were started from an idealized symmetric geometry with chemically equivalent bonds and angles assigned to the corresponding values from International Tables for Crystallography (ITC).[24]

All quantum mechanics calculations were performed using the Gaussian 98 program.[25] All geometrical structures first were performed using a single point energy calculation at HF/3-21G level, as a consistency check on the molecular geometry to be used as the starting point for all subsequent calculations. Then, in order to determine suitable approach, the performing needs the full optimization at Hartree-Fock (HF) level: HF/3-21G and density functional theory (DFT) level B3LYP/LANL2DZ. These optimized geometries are compared to those similar structures and UFF calculation.[26]

Based on the best level, the molecular orbitals yielded from these quantum mechanics calculation were generated using GaussView program.[27]

Results and Discussion

(1) To Find the Best Tool for Calulation

Because of an asymmetric bidentate rhodium complexes, it must be careful to choose the appropriate and the best tool for these such complexes. To do so, rhodium complexes 1.3 and 1.4 are calculated using the various types of calculations: Hartree-Fock with 3-21G and LANL2DZ level and density functional theory with 3-21G and LANL2DZ. The four different

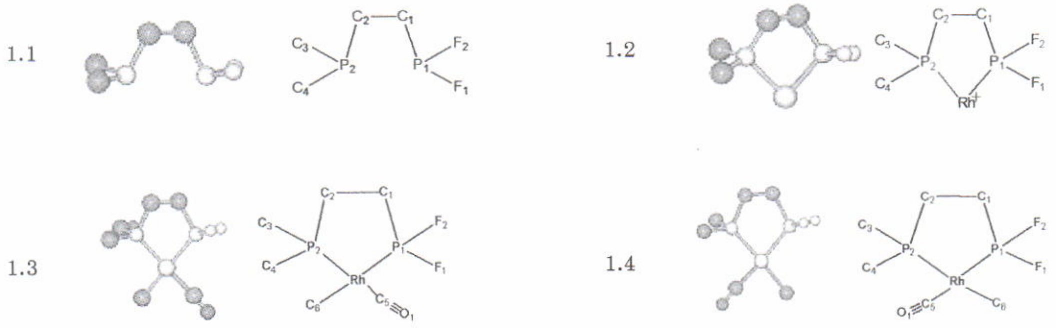


Figure 1 Designed ligand 1.1, a cation 1.2, complexes 1.3 and 1.4. Hydrogen atoms are omitted for clarity.

method optimized parameters of 1.3 and 1.4 are compared with the data from International Table for Crystallography (ITC) is shown in Table 1.

The HF/3-21G and HF/LANL2DZ levels give very poor results (the bond distances are about 0.1 Å and 0.2 Å from data as stated in the international table for X-Ray crystallography). The DFT/3-21G level also gives quite poor results (0.1Å and 0.06Å far from ITC). Although the angles from HF/LANL2DZ level gives fairly agreement, the bond lengths are in poor agreement. The DFT/LANL2DZ results are in the most reasonable.[27]

Table 1 Comparison of computed rhodium complexes 1.3 and 1.4 at different levels of theory: HF/3-21G, HF/LANL2DZ, DFT/3-21G, DFT/LANL2DZ, and typical dimensions.

Parameter	1.3				1.4				ITC
	HF/ 3-21G	**HF/ LANL2DZ**	**DFT/ 3-21G**	**DFT/ LANL2DZ**	**HF/ 3-21G**	**HF/ LANL2DZ**	**DFT/ 3-21G**	**DFT/ LANL2DZ**	
P1-F[a]	1.851	1.684	1.665	1.740	1.622	1.662	1.682	1.732	
P2-Me	1.874	1.868	1.886	1.882	1.880	1.872	1.872	1.887	
Rh-P1	2.425	2.437	2.312	2.357	2.560	2.441	2.566	2.507	2.41[b]
Rh-P2	2.479	2.498	2.412	2.456	2.361	2.286	2.428	2.348	2.33[c]
Rh-C6	2.136	2.119	2.129	2.109	2.134	2.129	2.117	2.101	
Rh-C5	1.993	1.967	1.891	1.880	1.997	1.894	1.962	1.866	
C5-O1	1.131	1.140	1.167	1.179	1.132	1.169	1.141	1.184	
P2-Rh-P1[b]	81.63	81.46	83.05	82.64	81.94	83.10	81.17	81.57	
C6-Rh-C5	84.74	86.50	86.89	88.77	85.39	88.17	86.95	88.62	86.20
C6-Rh-P2	89.06	88.78	87.76	87.55	172.10	170.91	174.28	174.67	
C5-Rh-C2	173.53	175.10	173.95	176.01	102.42	99.73	98.78	96.67	
C5-Rh-P1	104.55	103.24	102.28	100.98	175.13	164.68	176.04	144.85	
C6-Rh-P1	170.67	170.19	170.79	169.98	90.24	88.12	93.06	93.75	

[a] bond distances are in Å and bond angles are in ° [b] data for Rh-PMe_3 [c] data for Rh-PF_3

Table 2 Energies of complexes 1.3 and 1.4.

Structure	HF/3-21G	HF/LANL 2DZ	B3LYP/3-21G	B3LYP/ LANL 2DZ	Unit
1.3	-5847.89758	-5854.49991	-629.75300	-633.93920	au
1.4	-5847.89731	-5854.49786	-629.74860	-633.93357	au
ΔE=1.3-1.4	+0.00027	+0.00205	+0.00540	+0.00664	au
	+0.1694	+1.2864	+3.3886	+4.1667	kcal/mol

1 au = 627.5095 kcal/mol

Here are the optimized energy results from calculation using Hartree-Fock method and Density Functional Theory. The energy differences are 0.16, 1.29, 3.39 and 4.17 kcal/mols for HF/3-21G, HF/LANL2DZ, B3LYP/3-21G and B3LYP/ LANL2DZ respectively. As you can see, the Hatree -Fock energy with 3-21G and LANL2DZ basis sets give no significantly different between those two complex. It was only 0.16 and 1.28 kcal/mols. The calculating energy using DFT with 3-21G is about 3.39 kcal/mol. This is quite agreement, but give quite poor angle parameter.[22] Clearly, density function calculating energy with LANL2DZ basis set gives a good agreement, corresponding with the most reasonable data parameters.

In sum, the higher level gives the better results. The presented results indicate that B3LYP calculation with LANL2DZ basis set method was the best tool . Then, it is used to calculate these and similar systems.

(2) A Ligand 1.1 and a Cation 1.2

Ligand 1.1 is the most important in this study. It is used as a promoter for the rhodium catalyst in the methanol carbonylation process. DFT/LANL2DZ are applied to a ligand 1.1 and a cation 1.2. Unfortunately 1.2 is unstable.

Based on the DFT calculation, the average P-F bond length of asymmetric phosphine ligand 1.1 is 0.149 Å shorter than the average P-Me bond length, indicating a strong electron withdrawing group of F. Fluorine is highly electronegative and wishes to obtain additional electron density. As electron-withdrawing (electronegative) groups are placed on the phosphorous atom, the σ-donating capacity of the phosphine ligand tends to decrease. At the same time, the energy of the π-acceptor (σ^*) on phosphorous is lowered in energy, providing an increase in backbonding ability.[22] The results fit well with the electronic property. The fluorine atom from PF_2 moiety is a significant site of negative charge, in contrast to a carbon atom from PMe_2 moiety. This results in an unequal charge distribute among the two phosphorus atoms and the two backbone carbons as shown in Table 3. The larger positive charge located on the phosphorus of PF_2 moiety while the other phosphorus is lower. The one backbone carbon, C1, bonded to PF_2 has more negative charge than C2, corresponding with the shorter P-C1 bonded. It attempts to draw electron from the two carbons which more closer together, in order to share the remaining electron more easily.[22] This can conclude that PF_2 is the lower of σ-donating, but the higher π-acceptor. This results also indicated by the molecular orbitals shown in Figure 2.

Table 3 Some atomic charges of ligand 1.1

Total	Atomic charge*
P1	1.0442
F1	-0.4752
F2	-0.4718
C1	-0.1873

Total	Atomic charge
P2	0.6005
C3	-0.1824
C4	-0.1889
C2	-0.1387

*atomic charge of hydrogen is 0.000 au

A highest occupied molecular orbital (HOMO) has stronger lone pairs on PMe_2 than that on PF_2 . The stronger electronic property on PF_2 is favored for a lowest unoccupied molecular orbital (LUMO) as shown in Figure 2.

The HOMO-LUMO gap energy is big (+0.2153 au). This is to confirm that this ligand is not a planar.[28-29]

(3) Complexes 1.3 and 1.4

As regards optimized structures 1.3 and 1.4, the Rh-PMe bond length in 1.3 is 0.108 Å longer than that in 1.4, indicating the stronger trans-directing CO over Me, but significant longer than those in similar structures [Rh(CO)Me $(C_5Me_4CH_2PEt_2)$].[30] As one can see, in 1.3 the CO ligand weaken bond in trans position more than Me. The Rh-PF bond length is 0.15 Å shorter than that in 1.4. The Rh-CO distances in both structures are not different. This is a consequence of less π-donating property of PF_2 . Surprisingly, the bite angle of 1.3 is 1.07° bigger than that in 1.6 and is in a good agreement with work done by Casey.[21] However isomer 1.3 with Me trans to a good electron withdrawing group is preferred, confirming by lower energy. These confirm that the presence of strong electronegativity fluorine atoms in PF_2 makes them weak σ-donors but much stronger π- acceptors and the presence of methyl groups in PMe_2 make them stronger σ-donors but much weaker π- acceptor.

To confirm the electronic effects at work, analysis of the molecular orbital is needed. The molecular orbital confirmed that the d_{z^2} orbital is lower energy than $d_{x^2-y^2}$ orbital as expected for a low-spin d^8 orbital Rh(I) configuration.

Ligand 1.1
(average P-F=1.745 Å average PMe=1.894 Å)

HOMO
-0.2410 au

LUMO
-0.0257 au

Figure 2 A symmetric ligand 1.1 and two molecular orbitals. Hydrogen atoms are omitted for clarity.

Figure 3 Some molecular orbitals of complex 1.5. Hydrogen atoms are omitted for clarity.

d_{z^2} (-0.229au) $d_{x^2-y^2}$ (-0.081 au) d_{xy} (-0.085 au)

The B3LYP/LANL2DZ calculated energy of complex 1.3 is lower than that in complex 1.4. This confirmed that complex 1.3 is more stable than complex 1.4. The different energy (ΔE) values were used to calculate equilibrium constant. By using the equation of $\Delta G = -RT \ln k$, where ?G is free energy change (kcal/mol), R is a gas constant (-1.987 cal/mol/k), T is a room temperature (273+25=298K) and k is equilibrium constance. I assumed that $T\Delta S$ from the equation of $\Delta G = \Delta H - T\Delta S$ is same. In this case, the energy value of complex 1.5 is lower than 1.6 by ~4.167 kcal/mol, implying $\Delta G \approx \Delta H$ = ~4.167 kcal/mol and therefore a ratio of 1.5:1.6 of *ca.*1204:1. The calculated isomerization energy is not far away from the experimental estimate at 5.3 ± 0.5 kcal/mol.[12]

Conclusions

The presented results indicate that B3LYP/LANL2DZ method is the best tool for such calculations. As regards electronic property of ligand 1.1, the present of electron-withdrawing groups (F) on the phosphorous atom tends to decrease σ-donating capacity of the phosphine ligand. As electron donation groups (Me), are placed on the phosphorous atom, the σ-donating capacity of the phosphine ligand tends to increase. The results fit well with the molecular orbitals. In sum, PF_2 is a greater π-acidity whereas PMe_2 is a greater σ -donation.

Because asymmetric ligand 1.1 has chiral centers with electron withdrawing group and electron donating group. This would be the reason that the different trans-influence and trans effect of complex type "Rh (L)L'(1.1)" would favor the formation of different isomers 1.3 and 1.4.

The relative model stabilities indicate the more stable isomer,1.3, is the one where the stronger *trans* effect ligand lies in a *trans* position to a worse σ-donor. The differences of energy (ΔE) values were used to calculated equilibrium constant and confirmed the possibility to make this model 1.3.

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