

Quantum Mechanics Calculations: Asymmetric Phosphines for Methanol Carbonylation (Part I)

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ABSTRACT This work presents quantum mechanics calculations based on density functional theory (DFT) for the newly designed asymmetric diphosphine ligand **1.1** that can be a promoter for methanol carbonylation. Because of its chiral centers with electron withdrawing and electron donating groups, this is the reason why the different trans-influence and trans effect of complex type “Rh(L)L'(1.1)” would favor the formation of different isomers. Rhodium complexes **1.3**, **1.4**, **1.5** and **1.6** can be expected to combine high catalytic activity with thermal stability under the mild conditions of the methanol carbonylation process. The difference in energy (ΔE) values and the calculated equilibrium constant clearly indicate that the most stable isomer **1.5** is the initial catalytically active species and should be possible to prepare.

(Asymmetric phosphine, methanol carbonylation, quantum mechanics, density functional theory, catalyst)

INTRODUCTION

The carbonylation of methanol to acetic acid is one of the most important and successful industrial applications of homogeneous transition metal catalysis [1, 2]. Since its original development by Monsanto about forty years ago, a rhodium/iodide catalyzed process, so-called the Monsanto catalyst $[\text{RhI}_2(\text{CO})_2]^-$, has predominated [3, 4, 5].

Attempts 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 conditions 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) [6]. 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 report has stated that the use of the diphosphinesulfide $\text{Ph}_2\text{PCH}_2\text{P(S)Ph}_2$ (dppms) as a promoter for rhodium catalyzed methanol carbonylation allows a surprisingly substantial rate increase under industrially

feasible conditions [10, 11, 12]. At 185 °C, 30 atm, the rate increased eight times higher than $[\text{RhI}_2(\text{CO})_2]^-$ (for commercial viability, the conditions under which the catalyst operates are crucial). Rhodium(I) carbonyl complexes containing phosphino-thiolate and -thioether ligands are almost four times as active in catalyzing the carbonylation of methanol, and the crystal structure of one precatalyst, $[\text{Rh}(\text{SC}_6\text{H}_4\text{PPh}_2)(\text{CO})_2]_2$, has been reported [7, 8]. 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 $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ (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. Rhodium complexes of unsymmetrical diphosphines of the type $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PAR}_2$ are catalysts for the carbonylation of methanol. The diphosphines, some of which are known, [10, 11, 12, 13, 14, 15] were made and fully characterized (see Figure 1.).

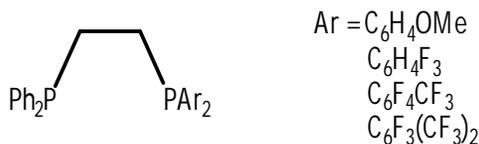


Figure 1. Some diphosphines ligands used as promoters in methanol carbonylation.

Several important homogeneous catalysts now utilize bidentate ligands for which the stereoproperties are less well understood [16]. Although the bidentate ligand “bite angle” has been shown to be important, the understanding of the observed behavior at the molecular level is incomplete and the quantification of ligand effects on individual steps from catalytic quite rare [16, 17, 18].

In addition to the high electron density at rhodium [19], ligand steric and electronic effects play a key role in determining organometallic reactivity trends and catalytic behavior [20]. Recently, the observation of [Rh(Cp⁺(CH₂)₂PEt₂)(C(O)Me)I] under methanol carbonylation conditions suggests that the rhodium centre has become so electron rich that the reductive elimination process has become rate determining for methanol carbonylation.

Methanol carbonylation has been studied in detail not only experimentally but also from a

theoretical point of view. Computational chemistry especially quantum mechanics calculations is used as a tool to understand the mechanism and reaction [21, 22, 23]. A theoretical study of steric and electronic effects in the rhodium-catalyzed carbonylation reaction using DFT have been carried out on the catalytic cycle and found that the migratory insertion process presents an important step in methanol carbonylation [24].

The basic idea behind this work is that ligands which increase the electron density at the metal should promote an oxidative addition process. To this purpose, a ligand **1.1** was designed as a promoter for catalysis of a methanol carbonylation. Such a ligand can have its electronic properties tuned by a 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.

EXPERIMENTAL SECTION

The designed structures under this study are a ligand PF₂PCH₂CH₂PMe₂ **1.1**, a cation **1.2** and complexes **1.3**, **1.4**, **1.5** and **1.6** as shown in Figure 2.

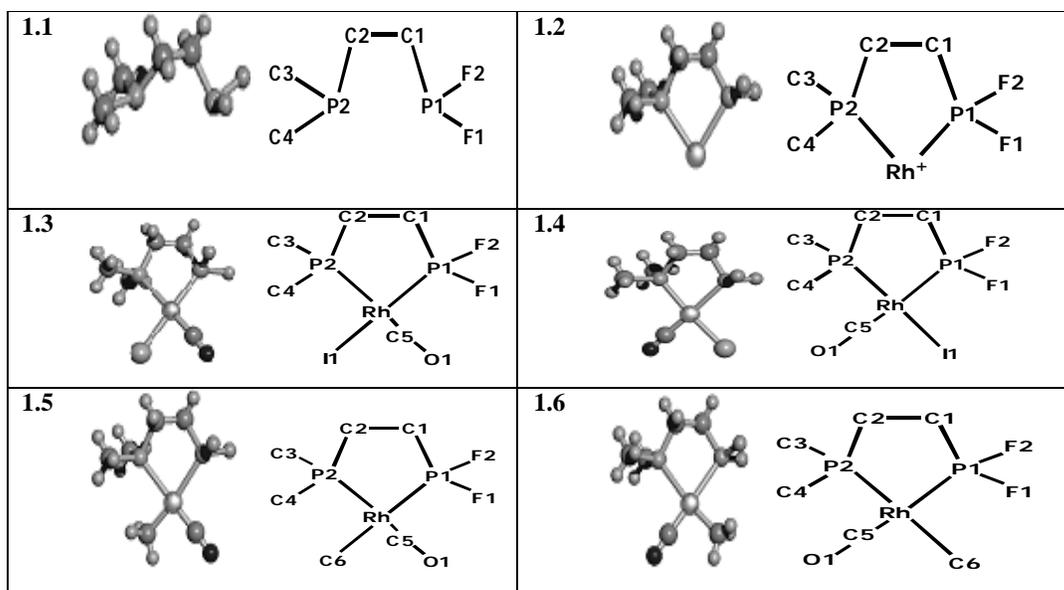


Figure 2. Designed ligand **1.1**, cation **1.2**, and complexes **1.3**, **1.4**, **1.5** and **1.6**. Hydrogen atoms in Chemdraw model are omitted for clarity.

The complexes have square planar geometry at rhodium. Isomeric complexes **1.3** and **1.4** contain CO and I. The isomer **1.3** has CO *trans* to the PMe₂ moiety of the ligand; this arrangement is reversed in **1.4**. Complexes **1.5** and **1.6** differ from complexes **1.3** and **1.4** only in that the Me⁻ group replaces the I ligand of **1.3** and **1.4**. For computational methodology, initial structure geometries were constructed at the UFF level using the Cerius² program [25]. 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) [26]. All quantum mechanics calculations were performed using the Gaussian 98 program [27]. All geometries were first 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 structure, full optimization at density functional theory (DFT) level B3LYP/LANL2DZ was performed. These optimized geometries were compared to those similar structures. The molecular orbitals yielded from these quantum mechanics calculation were generated using the GaussView program [28, 29].

RESULTS AND DISCUSSION

The Optimization of Ligand **1.1** and Cation **1.2**

Based on the DFT calculation, the average P-F bond length of the asymmetric phosphine ligand **1.1** is about 0.149 Å shorter than the average P-Me bond length, indicative of the strong electron withdrawing effect of the F atoms (Table 1). F atoms are highly electronegative (*ca.* -0.4735 au) and wish to obtain additional electron density. As electron-withdrawing (electronegative) groups are placed on the phosphorous atoms, 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 [24]. The highest occupied molecular orbital (HOMO) has stronger lone pairs on PMe₂ than that on PF₂. The stronger electronic property on PF₂ is favored for a lowest unoccupied molecular orbital (LUMO) as shown in Figure 3. Thus one can conclude that PF₂ is poorer σ -donor, but a better π -acceptor. The HOMO–LUMO gap energy is large (+0.2153 au) confirming that the ligand is not planar [30, 31].

Table 1. : The optimized parameters of **1.1** and **1.2**

PARAMETER ^a	1.1	1.2	1.3	1.4	1.5	1.6
P1-C1	1.894	1.874	-	-	-	-
P1-F1	1.745	1.724	-	-	-	-
P2-C2	1.923	-	-	-	-	-
Rh-P1	-	2.232	2.286	2.380	2.357	2.507
Rh-P2	-	2.237	2.442	2.405	2.456	2.348
P2-Rh-P1	-	106.10	83.42	82.76	86.20	86.20
C2-C1-P1	112.60	-	-	-	-	-
C1-C2-P1	113.27	-	-	-	-	-
Energy (au)	-371.1502	-480.5835	-605.4811	-605.4695	-633.9392	-633.9336

^a bond distances are in Å and bond angles are in °

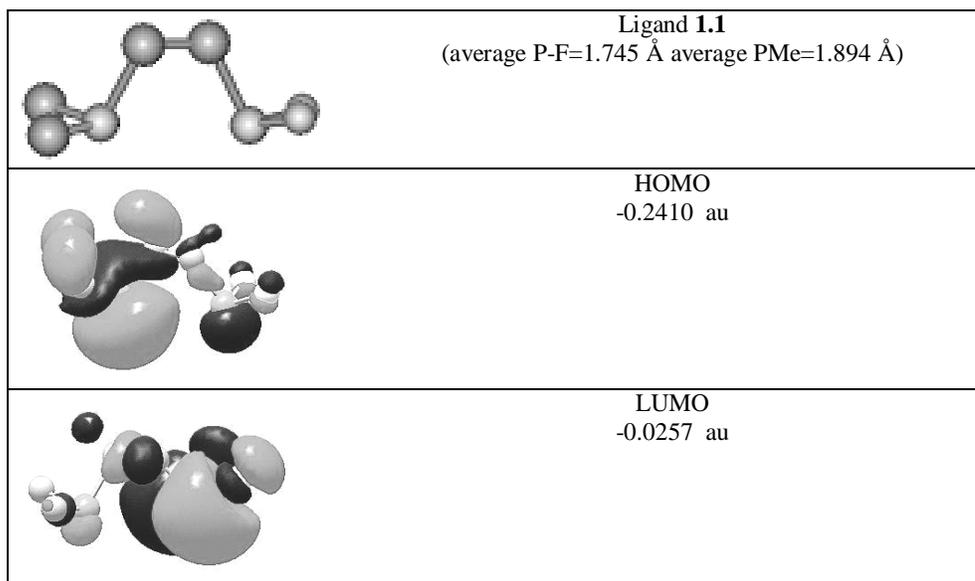


Figure 3. The asymmetric ligand **1.1** and its two molecular orbitals. Hydrogen atoms are omitted for clarity.

The calculated number of IR and Raman bands show the stretching frequency of the PMe_2 moiety is higher than that of PF_2 moiety. As already known, the higher the frequency is the greater the σ -donation [31].

Selected molecular orbitals and molecular orbital energies for the cation **1.2** are shown in Figure 4. The HOMO-1 shows the d_{xz} orbital and has no contribution from the asymmetric ligand **1.1**. Whereas the HOMO shows the d_{xy} orbital. It also has a contribution from the PF_2 moiety of the ligand **1.1**. In other words, the π -orbital from the LUMO of ligand **1.1** contributes to the HOMO of the cation **1.2**. The LUMO illustrates a $d_{x^2-y^2}$ orbital and clearly shows the relation between metal and asymmetric ligand **1.1**. The other two LUMOs illustrate lone pair electrons and the π -electron of metal center. This confirms that there is less electron density on the metal center with a greater π -acidity on PF_2 and a greater σ -donation on PMe_2 .

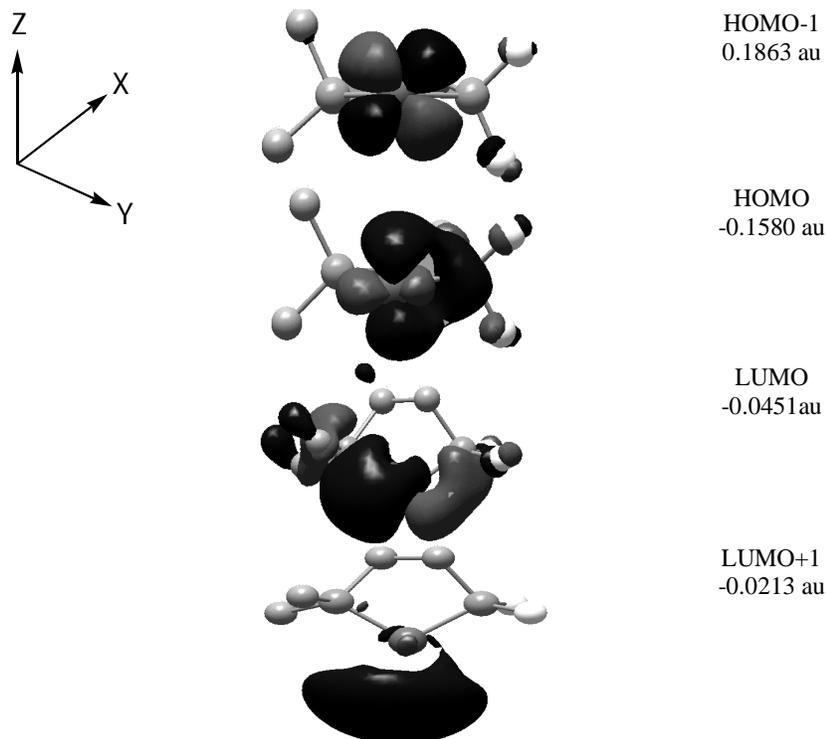


Figure 4: A rhodium cation **1.2** shows the molecular orbitals. Hydrogen atoms are omitted for clarity.

The molecular orbitals of cation **1.2** illustrate clearly how this ligand is bonded to the metal center. It may be expected that ligand **1.1** can generate more than one isomer, reasoning from the different groups (PMe_2 and PF_2). This would favor the formation of different isomers when it promotes the organometallic catalyst complex, namely complexes **1.3**, **1.4**, **1.5** and **1.6**.

The Optimization of Isomers **1.3** and **1.4**

As regards optimized structures **1.3** and **1.4**, the Rh- PMe_2 bond length in **1.3** is 0.037 \AA longer than that in **1.4**, indicating the stronger trans-effect of CO over I. The Rh-PF bond length is 0.094 \AA shorter than that in **1.4**. The Rh-I bond lengths in both structures are not significantly different and are in a good agreement with typical Rh-I distances [31]. As one can see, in **1.3** the CO ligand weakens the bond in the trans position more than I. This is not different to the Rh-CO distance of $[\text{Rh}(\text{CO})\text{I}(\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2)\text{PPh}_2)]$.¹⁵ The Rh-I distance of **1.4** is slightly shorter than that in **1.3** but significantly longer than those in similar structures $[\text{Rh}(\text{CO})\text{I}(\text{Ph}_2\text{PCH}_2\text{PPh}_2\text{S})]$, and its isomer $[\text{Rh}(\text{CO})\text{I}(\text{Ph}_2\text{PCH}_2\text{PPh}_2\text{S})]$ [24]. This is a consequence of the poorer π -donating ability of

PF_2 . The bite angle of **1.3** is 0.64° smaller than that in **1.4** and is about 2.27° smaller than those in ref. 22 indicating less steric effects and lower energy.

The optimized free CO frequency is 2313 cm^{-1} with 1.143 \AA of bond distance (see Table 2). This number is higher than the experimental value which a free CO is 2143 cm^{-1} with a bond distance of 1.128 \AA from IR spectroscopy [32]. Because of the nature of the computation involved, frequencies are valid only stationary points on the PES. Raw frequency values computed at the DFT level contain systematic errors due to the neglect of electron correlation, resulting in overestimates of about 0-10%. Therefore, it is usual to scale frequencies predicted at DFT level by an empirical factor of 0.9623. Use of this factor has been demonstrated to produce very good agreement with experiment. For this calculation, it is about 200 cm^{-1} higher which is the typical from such a calculation [28, 29].

Table 2: Number of IR and Raman CO stretching frequencies of series 1

CO	ν CO	d (Å)	STRUCTURES	ν CO	d (Å)
Free CO	2143	1.128	1.3	2000.4	1.173
Terminal CO	1850-2120	1.12-1.18	1.4	1973.4	1.177
Doubly bridging CO	1700-1860	-	1.5	1965.1	1.179
This work	2313.0	1.143	1.6	1934.8	1.174

The IR and Raman CO stretching frequencies of isomers **1.3** at 2000.4 cm^{-1} can be observed. This number is higher than that of **1.4** at 1973.4 cm^{-1} . It is a typical number for a terminal CO group [28, 29]. The calculated free CO distance is about 1.143 Å while those of structures **1.3** and **1.4** are 1.173 Å and 1.177 Å respectively. The lower 1.143 Å distance is due to back donation. This occupation of the π^* on CO does lead to a decreased bond order in the carbon monoxide molecule itself. As we might expect, as the π -backdonation becomes stronger, the CO bond order should decrease from that of the free ligand. Two consequences that might be expected if the CO bond order was reduced would be a lengthening of the C-O bond and a decrease in the carbonyl stretching frequency in the IR. Again, the higher the ν CO stretching frequency the weaker the σ -donation.

The DFT/LANL2DZ calculated energies of complex **1.3** are lower than that in complex **1.4**, indicating the more stable complex **1.3** than complex **1.4** (see Table 1). The different energy (ΔE) values were used to calculate the equilibrium constant. By using the equation of $\Delta G = -RT \ln K$, where ΔG is free energy change (kcal/mol), R is the gas constant (1.987 cal/mol/K), T is room temperature (298 K) and K is equilibrium constant. Assuming that $\Delta G \sim \Delta H = -7.28\text{ kcal/mol}$ the ratio of **1.3:1.4** is *ca.* 218530:1.

The Optimization of Isomers **1.5** and **1.6**

As regards optimized structures **1.5** and **1.6**, the Rh-PMe and the Rh-PF bond length in **1.5** are 0.01 Å longer than that in **1.6**. The Rh-CO distances in both structures are essentially the same. This is a consequence of poorer π -donating property of PF_2 . Surprisingly, the bite angle of **1.5** is 1.07° bigger than that in **1.5** and is in a good agreement with work done by Casey *et al.* [10].

However isomer **1.5** with methyl group *trans* to a good electron withdrawing group is preferred. Isomer **1.5** is about 29 kcal/mol lower in energy

than isomer **1.3**. This confirms that the presence of strongly electronegative 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 - acceptors. This is also indicated by the IR and Raman CO frequencies which are in the range of the terminal carbonyl group. However, the stretching frequency of **1.5** is at 1965.1 cm^{-1} and is higher than that of **1.6** at 1934.8 cm^{-1} . It corresponds with a slightly longer CO bond distance. The slightly longer C-O bond distance in **1.5** (1.179 Å) and the lower C-O frequency (1916.1 cm^{-1}) indicate more $\text{Rh}=\text{C}=\text{O}$ character [12].

The energy value of complex **1.5** is lower than **1.6** by $\sim 3.51\text{ kcal/mol}$, implying $\Delta G \sim \Delta H = -3.51\text{ kcal/mol}$ and therefore a ratio of **1.5:1.6** is *ca.* 380:1. This is to confirm that complex **1.5** is slightly more stable than complex **1.6**.

The Comparison Energies of Isomers **1.3** and **1.5**

The P-Me₂ bond distances of the two isomers **1.3** and **1.5** are about the same. That is because they are *trans* to the strong electron withdrawing CO group. The difference is in the Rh-PF₂ bond distances. The Rh-PF₂ bond lengths in **1.5** are about 0.07 Å higher than that in **1.3**, indicating the stronger *trans*-effect of the CH_3 group over F.

The IR and Raman CO stretching frequencies are in the range for a terminal carbonyl group. However, the frequency for **1.3** is about 88 cm^{-1} higher than that of **1.5**. This corresponds well with the slightly shorter of CO bond distance, indicating more $\text{Rh}=\text{C}=\text{O}$ character. In other words, the slightly longer C-O bond distance in **1.5** (1.179 Å) is related to the lower C-O frequency (1916.1 cm^{-1})

The calculated optimization energy values of complex **1.5** is lower than **1.3** by $\sim 1785.7\text{ kcal/mol}$. This implies that **1.5** is more stable than **1.3**.

To confirm the electronic effects at work, analysis of the molecular orbital is needed (see Figure 5.). The HOMO-1 shows the d_{yz} -orbital with π -bond on the CH_3 . The HOMO is a d_z^2 orbital and has the contribution from the CH_3 group (σ -donation). LUMO+1 is a $d_{x^2-y^2}$ orbital and shows not only the $\text{Rh}=\text{C}=\text{O}$ character, confirmed by the shorter $\text{Rh}-\text{C}(\text{O})$ bond distance. The LUMO+1 also shows a π -bond on the PF_2

moiety. The LUMO+2 shows the d_{xy} on metal with the $\text{Rh}=\text{C}=\text{O}$ character or π - backbonding. The results from DFT/LANL2DZ are in a good agreement. The molecular orbital analysis confirms that an d_z^2 orbital is lower in energy than the $d_{x^2-y^2}$ orbital as expected for a low-spin d^8 orbital $\text{Rh}(\text{I})$ configuration [10].

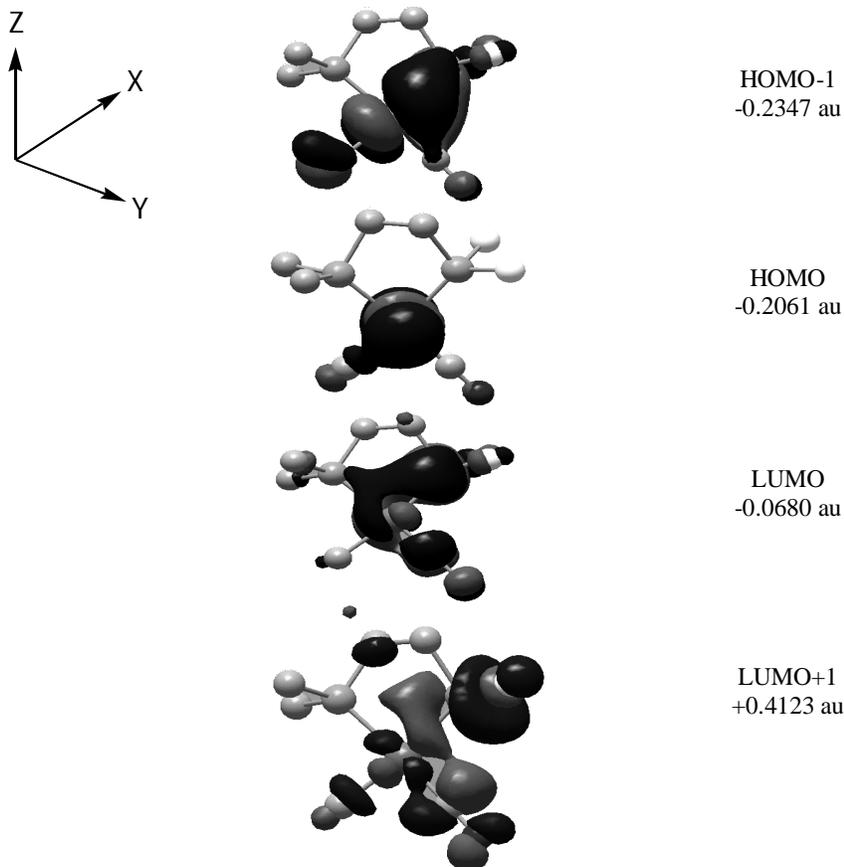


Figure 5: Some molecular orbitals of complex **1.5**. Hydrogen atoms are omitted for clarity.

The rhodium complex **1.5** shows a cis-square-planar geometry with a bite angle of 82.64° . The computed structures all confirm that the preferred stereochemistry at rhodium is that in which the PMe_2 is trans to the carbonyl and the PF_2 lays trans to the methyl group. The presence of the highly electronegative fluorine atoms in PF_2 makes the phosphorus a weak σ -donor but a stronger π - acceptor and the presence of methyl groups in PMe_2 makes it a stronger σ -donor but a weaker π -acceptor, consistent the variation in $\text{Rh}-\text{P}$ bond lengths. This is a consequence of the

electron-donating properties of the PMe_2 moiety, which increases the electron density at the metal center and as a consequence the Rh to CO backbonding (more $\text{Rh}=\text{C}=\text{O}$ character), also indicated by the IR and Raman CO frequencies. It is clearly confirmed that isomer **1.5** is a good structure for such a series and as regards optimized energy, isomer **1.5** has the lowest energy from the all four rhodium complexes.

CONCLUSIONS

Quantum mechanics calculation based on density functional theory (DFT) were carried out for an asymmetric phosphine ligand $\text{PF}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$ **1.1**. This ligand was employed as a promoter of the rhodium catalyzed methanol carbonylation. A rhodium cation **1.2** and complexes **1.3**, **1.4**, **1.5** and **1.6** were investigated in the gas phase based on electronic properties to specify the most stabilization structure.

The B3LYP/LANL2DZ calculated energy of complex **1.5** was lower than those in complexes **1.3**, **1.4** and **1.6**, confirming the most stable structure. The stereochemistry at rhodium in which the PMe_2 *trans* to the CO and the PF_2 lies *trans* to the Me group was preferred. The results indicated that the presence of the strong electronegative fluorine atoms in PF_2 made them weak σ -donors but much stronger π -acceptors and the presence of Me groups in PMe_2 made them stronger σ -donors but much weaker π -acceptors, confirmed by the bond distances of 2.356 and 2.456 Å for Rh- PF_2 and Rh- PMe_2 respectively in complex **1.5**. The electronic property results from B3LYP /LANL2DZ were in a good agreement. All considered complexes adopted a square-planar geometry. The molecular orbital analysis confirmed that the d_z^2 orbital was lower energy than $d_{x^2-y^2}$ orbital as expected for a low-spin d^8 orbital Rh (I) configuration.

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