

# Ligand effects on the stability of the insertion products: A DFT study of oxidative addition of NH<sub>3</sub> to iridium(I) complex

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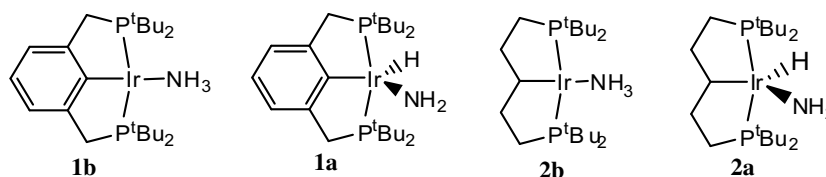
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Dedicated to Professor F. A. Cotton, in Memorial.

## Abstract

The density functional theory (DFT) calculations were used to study the effects of PCP ancillary ligands on the relative stabilities of hydrido amido complexes and ammonia coordination complexes. Calculations on the four compounds **1a**, **1b**, **2a** and **2b** containing PCP ligands with *t*-butyl groups on P atoms showed that **1b** is more stable than **1a** and **2a** is more stable than **2b**. Calculations also showed that the relative energies of hydrido amido complexes with respect to the isomeric ammonia coordinated complexes vary with the different substituent groups (R = H, Me and *t*Bu) on the P atoms of the PCP ligands. An alternative method to study the ligand effects introduced by different substituents on the P atoms is to vary the nuclear charge on the P atoms of PCP ligand. The relative energies were predicted to decrease with the nuclear charge of the P atoms on the PCP ligands, which indicates that increasing the electron donating ability tend to favor the hydrido amido complexes over the ammonia coordination complexes:



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**Keywords:** Density functional theory; Iridium

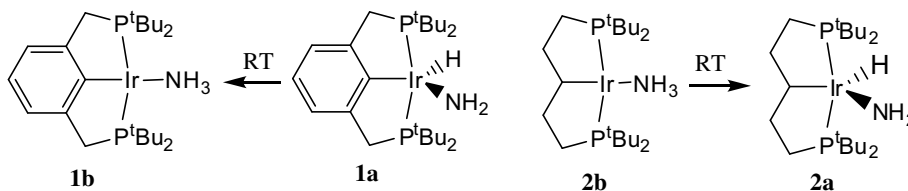
## 1. Introduction

Activation and cleavage of element–hydrogen bonds, E–H, where E = H, C, N, and O via oxidative addition to a transition metal complex is an important step of many catalytic cycles. Hence, an understanding of the factors that influence the oxidative addition and reductive elimination of H–E bonds is necessary to develop efficient catalysts, and has attracted a lot of attention, especially for activa-

tion of dihydrogen and alkanes [1–7]. However, transition metal catalyzed reactions of ammonia by oxidative addition or reductive elimination of H–N bonds are rare [8–10]. The difficulties in activation of the H–N bond of ammonia might be partially due to its strong Lewis base character [5], together with strong  $\pi$ -donating properties of the amide ligand.

The first example of the oxidative addition of ammonia to a mononuclear transition metal complex was reported by Casalnuovo and coworkers in 1987 [8]. The iridium complex containing labile ethylene ligands, Ir(PEt<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)Cl, was reported to insert the N–H bond of ammonia to form

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Scheme 1.

a very stable amide bridged dinuclear iridium complex. The high stability of the amido bridge prohibits further reaction of the dimer. Therefore, formation of the amido bridge should be avoided for a system to be suitable for a catalytic cycle. The first terminal amido complex prepared by oxidative addition of ammonia was not reported until 2005 [11]. Elegant work by Hartwig and coworkers reported that an Ir(I) complex containing a PCP tridentate-pincer ligand cleaved the N–H bond of ammonia readily at room temperature to form a hydrido amido Ir(III) complex. They found that oxidative addition of ammonia can be achieved by switching from an aromatic backbone to an aliphatic backbone of PCP ligand (Scheme 1) and this was attributed to the stronger electron donating ability of PCP ligand with aliphatic backbone than that of the PCP ligand with aromatic backbone.

To achieve the oxidative addition of ammonia, a hydrido amido complex should be favored over the isomeric ammonia coordinated complex. The work herein, density functional theory (DFT) calculations were used to study the effects of PCP ancillary ligands on the relative stabilities of hydrido amido complexes and ammonia coordinated complexes. The geometries and energies of the four compounds **1a**, **1b**, **2a**, and **2b** containing PCP ligands with *t*-butyl groups on P which are the same ligands used in experiments were calculated. To evaluate the electronic and steric effects of the PCP ligand, different substituents have been substituted for the *tert*-butyl group on phosphorous atoms for each of the four compounds. An alternative method using charge variation on P atoms to study the ligand effects is also reported.

## 2. Computational details

All DFT calculations were performed using the Amsterdam Density Functional (ADF) software package, version 2004.01, developed by Baerends et al. [12] and vectorized by Ravenek [13]. The numerical integration scheme used was developed by teVelde et al. [14], and the geometry optimization procedure was based on the method of Versluis and Ziegler [15]. All geometry optimizations were carried out with no symmetry constraints under the  $C_1$  point group by using the local exchange-correlation potential of Vosko et al. [16] and the non-local exchange and correlation corrections of Perdew and Wang (PW91) [17]. All atoms were described using a triple- $\zeta$  Slater type orbital (STO) basis set with one polarization function (TZP); the core was frozen

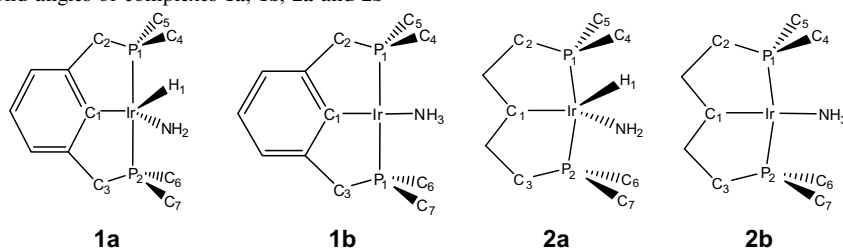
at the 4f level for iridium, 1s for the second row atoms and 2p for the third row atoms. All atoms were corrected for scalar relativistic effects by using the Zeroth Order Regular Approximation (ZORA) method [18]. All calculations utilized an INTEGRATION value of 7, geometries were converged to a gradient of  $10^{-4}$  a.u./Å. The self-consistent field energy was converged to a value of  $10^{-8}$ . Frequencies were calculated by numerical differentiation of energy gradients in slightly displaced geometries using double-sided displacements [19]. Molecular orbitals were visualized using molecular graphics package MOLEKEL [20].

## 3. Results and discussion

The geometries and energies of the four iridium compounds, **1a**, **1b**, **2a** and **2b**, which bear the same ligands used in the experiments, were calculated [11,21]. The purpose was to evaluate the theoretical method chosen. The choice of the level of theory for this work is mainly based on earlier work of this group [22–25]. Where it was found that the PW91/TZP described many transition metal complexes and actinide complexes fairly well. Unfortunately, the iridium compounds were not among those calculated in these studies. Therefore, it was necessary to evaluate the accuracy of this method for iridium complexes. The selected geometrical parameters of these compounds are given in Table 1.

The calculated structures of **1b** and **2a** are close to experimental crystal structures except that the calculated bond angles C(7)–P(2)–C(6) deviate from the experimental values by an average of  $10^\circ$ . This could be attributed to the crystal packing effects in the solid state structures. For compound **2a**, both the calculated and experimental structures show that the H1, Ir, C1 and N atoms are in the same plane (the sum of the angles H(1)–Ir–N, H(1)–Ir–C(1) and N–Ir–C(1) are 360.0 and 360.2°) and the molecule exhibits a distorted trigonal bipyramidal structure. For compounds containing the aromatic backbone PCP ligand, the ammonia coordinated compound (**1b**) is calculated to be 0.60 kcal/mol lower in energy than the hydrido amido compound (**1a**). While for compounds containing the aliphatic backbone PCP ligand, the hydrido amido compound (**2a**) was calculated to be 2.95 kcal/mol lower in energy than the ammonia coordinated compound (**2b**). Corrections for zero-point energies were not included for the above calculations. Although the difference in zero-point energies for the ammonia coordinated compound to hydrido amido

Table 1  
Selected bond lengths and bond angles of complexes **1a**, **1b**, **2a** and **2b**



	<b>1a</b>		<b>1b</b>		<b>2a</b>		<b>2b</b>
	Cal.	Cal.	Exp. [21]	Cal.	Exp. [11]	Cal.	
Ir–H(1)	1.511			1.513	1.51(3)		
Ir–N	1.980	2.209	2.215(5)	1.973	1.999(4)		2.202
Ir–C(1)	2.041	2.000	2.013(4)	2.108	2.128(4)		20.72
Ir–P(1)	2.325	2.269	2.2610(13)	2.332	2.2978(11)		2.284
Ir–P(2)	2.325	2.272	2.2737(14)	2.335	2.2995(11)		2.284
H(1)–Ir–N	141.9			142.4	139.4(13)		
H(1)–Ir–C(1)	62.5			65.8	66.8(13)		
N–Ir–C(1)	155.6	178.1	175.87(19)	151.8	153.69(17)		176.2
P(1)–Ir–P(2)	157.9	164.7	164.52(5)	165.0	165.97(4)		161.4
C(2)–P(1)–C(4)	106.5	103.7	104.4(2)	107.0	105.37(19)		104.9
C(4)–P(1)–C(5)	116.4	122.6	110.2(2)	117.1	109.65(18)		122.4
C(5)–P(1)–C(2)	103.6	102.4	102.5(2)	102.4	101.91(18)		102.7
C(3)–P(2)–C(7)	106.5	102.9	102.7(2)	106.4	105.85(19)		104.9
C(7)–P(2)–C(6)	116.4	123.0	110.5(2)	116.5	109.75(18)		122.4
C(6)–P(2)–C(3)	103.6	102.7	102.6(2)	103.2	101.54(19)		102.7

compound could have significant impacts on the absolute numbers of the relative energies, it would not affect the trend that the aliphatic backbone PCP ligand stabilizes the hydrido amido compound more than the aromatic PCP ligand does. This may be due to the stronger electron-donating ability of the aliphatic backbone than that of the aromatic backbone. As shown in Fig. 1, in compound **1b** there are molecular orbitals showing interaction between the ring  $\pi$ -orbitals and d-orbitals on the iridium thus reducing the electron density on the iridium. While

in compound **2b**, there is no such  $\pi$  system on the aliphatic backbone available to interact with the d-orbitals on iridium. The calculated Mulliken charges on iridium are  $-0.0031$  and  $-0.5015$  for **1b** and **2b**, respectively, which indicates that part of the electron density on iridium is delocalized to the  $\pi$  system of the aromatic backbone PCP ligand. These results are consistent with the experimental results [11,21]. Therefore, the level of theory chosen seems able to describe the system appropriately and was used in our further studies of the systems.

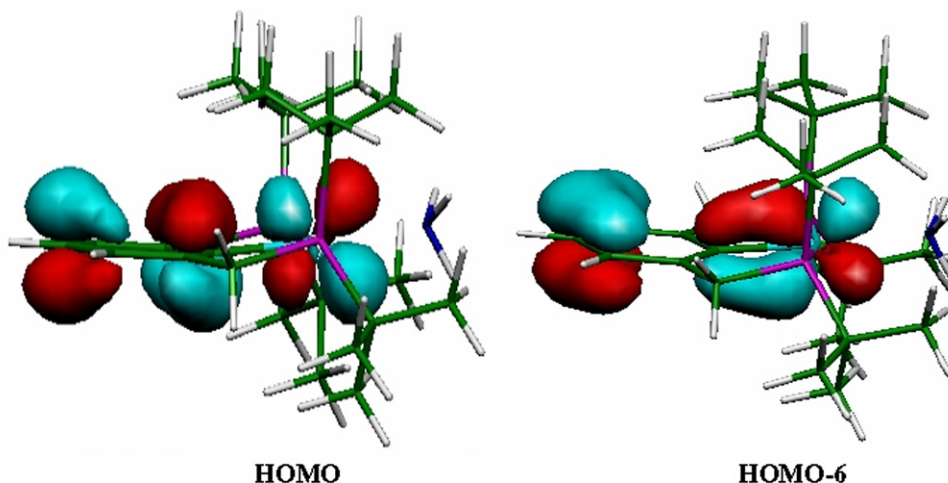


Fig. 1. Molecular orbitals showing interactions between the ring  $\pi$ -orbitals and d-orbitals on the iridium in compound **1b**.

To systematically study the ligand effects on the relative stabilities of the ammonia coordinated complexes versus the isomeric hydrido amido complexes, the types of PCP ligands (Fig. 2) due to the rigidity of the PCP ligands were chosen, so that they can be electronically modified for a specific property without changing the steric properties significantly. The obvious way to modify the PCP ligands is to utilize different substituents R on phosphorus atoms and three substituents (R = H, Me and <sup>t</sup>Bu) were used for both Al and Ar PCP ligands. The relative energies and Gibbs free energies (298 K) in Table 2 were defined with respect to ammonia coordinated compound.

Surprisingly, the relative energy is most positive when the substituent on the P atom is a methyl group not an H atom. In general, the methyl group substituted phosphine ligand is considered to be a stronger electron donating ligand than the non-substituted phosphine and thus the methyl substituted phosphorous ligand should stabilize the insertion compound relative to the ammonia complex. However, this is not the case for PCP ligands. It seems that the methyl group acts in an electron withdrawing role. To evaluate the electron-donating ability of the ligands with different substituents, we calculated model compounds with CO coordination to the metal fragments ( $L_n\text{Ir}$ ), where  $L_n$  represents the aliphatic backbone PCP ligands. [Such calculation has not been done for the aromatic backbone PCP ligand]. The stretching frequency of the carbonyl is known to be a sensitive tool for determining the electronic properties of the ligands  $L_n$ . Since frequency calculations are very expensive, we calculated the frequency for complexes with H and methyl substituents only. The computational results show the CO stretching frequency is lower for H ( $1961\text{ cm}^{-1}$ ) than for methyl ( $1978\text{ cm}^{-1}$ ), thus indicating that the ligand with methyl groups is a weaker electron

donor than that with H atoms. Intuitively, this can be attributed to steric effects since the size for different substituents are obviously different. By carefully comparing the geometries of hydrido amido compounds for different substituents on the Al PCP ligands, we found that the Ir–P bond length is the shortest when the substituents are methyl groups (Ir–P bond length: 2.265, 2.255 and 2.332 Å for H, Me and <sup>t</sup>Bu, respectively) but other parameters increase or decrease with the size of substituents. The same phenomena were observed for ammonia coordinated complexes (Ir–P bond length: 2.245, 2.237 and 2.284 Å for H, Me and <sup>t</sup>Bu, respectively). One possible explanation for this is that the ligand with methyl substituents is a better  $\pi$  acceptor than the ligands with H or *t*-butyl substituents. Further studies are necessary to understand this.

An alternative method was used to study the ligand effects introduced by different substituents on the phosphorus atoms [26] through varying the nuclear charge on the phosphorus atoms of PCP ligand. Such variation in nuclear charge on phosphorus atoms is equivalent to modifying the electronegativity of the phosphorus atoms and thus modifying the electronic properties of the ligand. One advantage of this method is that one can choose a small substituent and keep it consistent for all calculations and this significantly reduces the computational cost. In this study, H atoms were used as the substituents for both types of PCP ligands. The nuclear charge of phosphorus atom was varied from 14.6 to 15.4 by 0.2 steps and the electronic energies and Gibbs free energies at 298 K of hydride amido complexes and ammonia coordinated complexes were calculated for each nuclear charge of the phosphorus atoms. Again the relative electronic energies and relative free energies were defined with respect to the ammonia coordinated compound. The relative free energies plotted against the nuclear charge of phosphorus atom are shown in Fig. 3.

As shown in Fig. 3, the relative free energies decrease with the nuclear charge of the phosphorus atoms for both aliphatic and aromatic backbone PCP ligands. Decreasing the nuclear charge of an atom is equivalent to decreasing the electronegativity of the atom thus increasing the electron releasing ability of the atom. Therefore, the PCP ligands with less nuclear charge on the phosphorus atoms are stronger electron donors. The figure shows a straight trend that increasing the electron donating ability favors the hydrido amido complexes over the ammonia coordination complexes. At each nuclear charge, we can also see

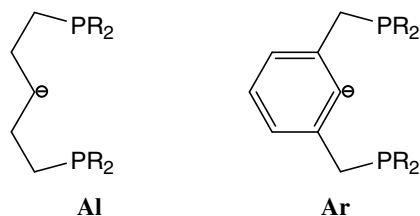


Fig. 2. Types of PCP ligands used for study: Al denotes the type of ligands with an aliphatic backbone and Ar denotes the type of ligands with an aromatic backbone.

Table 2  
Relative energies and relative Gibbs free energies (298 K) were given in kcal/mol

	Aliphatic				Aromatic			
	Ir–NH <sub>3</sub>		HIr–NH <sub>2</sub>		Ir–NH <sub>3</sub>		HIr–NH <sub>2</sub>	
	$\Delta E$	$\Delta G_{298\text{ K}}$	$\Delta E$	$\Delta G_{298\text{ K}}$	$\Delta E$	$\Delta G_{298\text{ K}}$	$\Delta E$	$\Delta G_{298\text{ K}}$
H	0	0	3.69	1.95	0	0	8.86	7.10
Me	0	0	30.21	28.78	0	0	23.04	20.95
<sup>t</sup> Bu	0	0	–2.95	–	0	0	0.60	–

Ir–NH<sub>3</sub> refers to ammonia coordinated compound while HIr–NH<sub>2</sub> refers to hydrido amido compound.

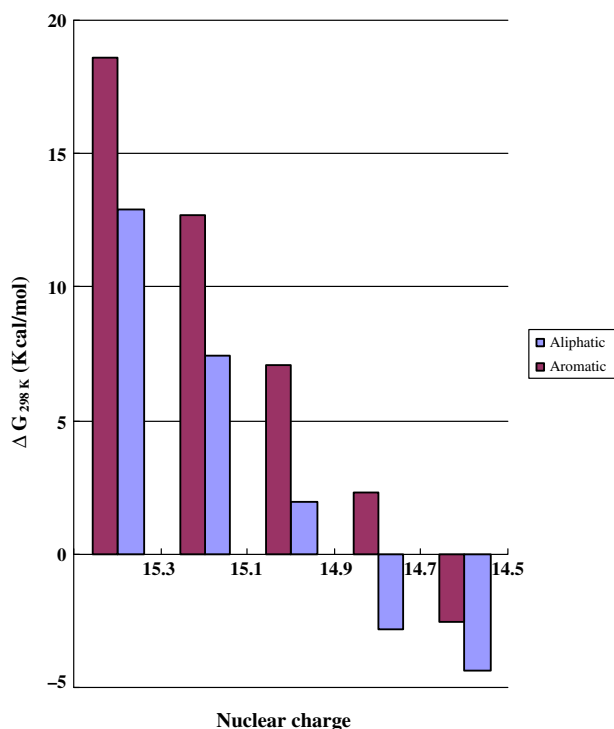


Fig. 3. The relative Gibbs free energies ( $\Delta G_{298 K}$ ) vs nuclear charge of P atom. Red corresponds to aliphatic PCP ligand and blue corresponds to aromatic PCP ligand. (For interpretation of the references to colour in this figure legend, the reader is referred to see the web version of this article.)

that the relative free energy is always higher for aromatic backbone PCP ligands than for aliphatic backbone PCP ligands. Although the negative relative free energy can be approached by decreasing the nuclear charge on the phosphorus atoms for both types of PCP ligand, the aromatic backbone PCP ligand requires a smaller phosphorus nuclear charge than the aliphatic backbone PCP ligand does. In other words, it is harder for an aromatic backbone PCP ligand to favor the insertion over coordination. To achieve such a goal, substituents with better electron donating ability are required for aromatic backbone PCP ligand. This is consistent with the experiment result that the insertion compound is favored by the aliphatic backbone PCP ligand with *t*-butyl substituents and the coordination compound is favored by the aromatic backbone PCP ligand with *t*-butyl substituents.

#### 4. Concluding remarks

The study of the substituent effects has shown that the oxidative addition of ammonia by an iridium complex to form a hydrido amido complex can be achieved by increasing the electron donating ability of the PCP ligand since the ligand with a better electron donating ability stabilizes the insertion compound relative to the coordination compound. Of course, instead of modifying the substituents

on the phosphorous atom of the PCP ligands, we can also modify the backbone of the PCP ligand. One typical example is to use the aliphatic backbone instead of the aromatic backbone. The nuclear charge variation method can also be applied to the backbone modification of PCP ligand. For an earlier theoretical study of the oxidative addition of  $\text{NH}_3$  to late transition metal complexes (see Ref. [27]).

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