

## ARTICLE

# Density Functional Theory Calculations on Ni–Ligand Bond Dissociation Enthalpies

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The formation and breaking of Ni–L (L=*N*-heterocyclic carbene, tertiary phosphine *etc.*) bond is involved in many Ni-catalyzed/mediated reactions. The accurate prediction of Ni–L bond dissociation enthalpies (BDEs) is potentially important to understand these Ni-complex involving reactions. We assess the accuracy of different DFT functionals (such as B3LYP, M06, MPWB1K, *etc.*) and different basis sets, including both effective core potentials for Ni and the all electron basis sets for all other atoms in predicting the Ni–L BDE values reported recently by Nolan *et al.* [J. Am. Chem. Soc. 125, 10490 (2003) and Organometallics 27, 3181 (2008)]. It is found that the MPWB1K/LanL2DZ:6-31+G(d,p)//MPWB1K/LanL2DZ:6-31G(d) method gives the best correlations with the experimental results. Meanwhile, the solvent effect calculations (with CPCM, PCM, and SMD models) indicate that both CPCM and PCM perform well.

**Key words:** Density functional theory, Ni complex, Bond dissociation enthalpy

## I. INTRODUCTION

In the past decades, nickel complexes have attracted much attention as efficient catalysts, which have been applied to organic reactions such as cross-coupling [1], cycloaddition [2], reduction [3], and polymerization reactions [4]. They can also work as electrocatalyst [5]. In most of these reactions, ancillary ligands play key roles in providing appropriate stereochemical and electronic environments around metal centers and hence controlling the catalytic efficiencies [1(d)]. Experimental and theoretical studies show that the ligand dissociation and exchange are involved in many of these reactions [6]. For example, Jamison *et al.* recently reported the Mizoroki-Heck-type reaction [6(a)], and found that the dissociation of one PCy<sub>2</sub>Ph took place to allow the coupling to occur. Therefore, the accurate prediction of Ni–L (L=*N*-heterocyclic carbene, tertiary phosphine *etc.*) bond dissociation enthalpies (Ni–L BDEs) is potentially important.

However, experimental Ni–L BDEs are comparatively few [7] due to the limitations such as instabilities of many nickel complexes and high cost. In 2003, Nolan *et al.* carried out a substitution reaction, using FTIR (Fourier transform infrared spectroscopy) to measure BDE values of two types of (CO)<sub>2</sub>Ni–L complexes [8].

Then in 2008, they determined the enthalpy changes of ligand substitution reactions by anaerobic solution calorimetry and got the BDE values of six (CO)<sub>2</sub>Ni–L<sub>2</sub> complexes [9].

In recent years, DFT methods have developed rapidly and performed well in studies on transition metal compound participated reactions [10], and theoretical predictions of bond strengths of organic [11]/organometallic [12, 13] compounds. In 2005, Nolan *et al.* investigated BDEs of a series of (CO)<sub>n</sub>Ni–L (*n*=2, 3; L=NHC, PR<sub>3</sub>) by DFT calculations [14]. Energies and geometries were evaluated using the local exchange-correlation potential by Vosko *et al.* [15], augmented in a self-consistent manner with Becke's [16] exchange gradient correction and Perdew's [17] correlation gradient correction. In their study, efforts were mainly put on the comparison of different ligands, while a systematic assessment and verification of the calculation method was not carried out. As different calculation methods may give distinct results [18], it is valuable to find out a reliable method to calculate the Ni–L BDEs accurately. The clarified method can be significantly helpful in case experimental data is lacking.

To achieve this goal, we use the BDE values reported by Nolan *et al.* to establish an optimal method. After examining the calculation results with different DFT functionals (such as B3LYP [16, 19], M06 [20], MPWB1K [21] *etc.*) on different basis sets (including both effective core potentials for Ni and the all electron basis sets for all other atoms), we find that the MPWB1K/LanL2DZ:6-

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TABLE I The BDE values calculated with different DFT functionals<sup>a</sup> and the experimental data are also shown for comparison.

	BDE/(kcal/mol)							ME	RMSE	<i>R</i>
	I <sup>t</sup> Bu	IAd	IMes	ICy	PCy <sub>3</sub>	P( <i>p</i> -Tol) <sub>3</sub>	PPh <sub>3</sub>			
B3LYP	36.8	37.4	24.6	30.3	17.6	19.3	19.2	-4.7	5.6	0.9316
BB1K	38.7	39.2	28.0	31.6	23.9	24.9	23.2	-1.2	2.1	0.9622
M05	34.5	35.2	27.3	30.4	20.3	21.7	20.9	-4.0	4.9	0.9029
M052X	38.0	38.8	31.1	33.3	24.8	24.5	24.5	-0.5	2.7	0.9125
M06	44.4	45.8	39.3	40.4	30.9	30.3	29.8	6.1	6.9	0.8726
M062X	33.4	34.2	30.4	30.8	22.3	22.0	21.0	-3.5	5.0	0.8217
M06L	49.7	51.5	43.6	45.1	35.7	33.7	33.8	10.7	11.2	0.8866
MPW1K	39.1	39.5	26.7	32.2	22.3	23.0	23.7	-1.7	2.7	0.9514
MPW3LYP	38.9	39.7	28.2	33.1	20.6	22.2	21.7	-2.0	3.6	0.9197
MPWB1K	40.1	40.7	30.6	33.8	26.1	27.0	25.2	0.7	2.1	0.9536
PBE	47.1	48.5	35.3	40.7	27.8	28.3	28.2	5.4	6.4	0.9298
TPSS	45.3	46.8	31.6	38.1	25.2	26.1	25.7	2.9	4.4	0.9447
TPSSLYP1W	39.2	40.4	28.1	33.4	19.3	20.5	20.3	-2.4	4.4	0.9126
Experiment <sup>b</sup>	39	43	27.5	30.1	26.6	26.4	25.7			

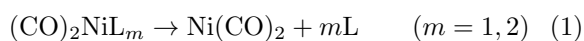
<sup>a</sup> The regression slopes for all correlations of calculation and experimental results are fixed at 1.00.

<sup>b</sup> (CO)<sub>2</sub>Ni-L [8] and (CO)<sub>2</sub>Ni-L<sub>2</sub> [9], and the uncertainty is ±3.0 kcal/mol.

31+G(d,p)//MPWB1K/LanL2DZ:6-31G(d) method gives the best correlations with the available experimental results. Considering reported experiments were carried out in solvent (*i.e.* heptane and toluene), different solution phase calculations (including different solvation models) are tested, which shows that both CPCM and PCM work well.

## II. METHODS

The Ni-ligand BDE in (CO)<sub>2</sub>NiL<sub>*m*</sub> is estimated from the following equation:



$$\text{BDE}(\text{Ni} - \text{L}) = \frac{1}{m} [\text{H}(\text{Ni}(\text{CO})_2) + m\text{H}(\text{L}) - \text{H}((\text{CO})_2\text{NiL}_m)] \quad (2)$$

For I<sup>t</sup>Bu (1,3-bis(tert-butyl)imidazol-2-ylidene) and IAd (1,3-bis(1-adamantly)imidazol-2-ylidene), *m*=1; for IMes (1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene), ICy (1,3-bis(cyclohexyl)imidazol-2-ylidene), PCy<sub>3</sub> (tricyclohexylphosphine), P(*p*-Tol)<sub>3</sub> (tri(*p*-Tolyl)phosphine) and PPh<sub>3</sub> (triphenylphosphine), *m*=2. The enthalpy of each species is calculated by adding the thermal corrections of enthalpies and the total electronic energies.

All calculations in this work are performed with Gaussian 09 suit of program [22]. In assessing different DFT methods, geometry optimizations are performed using different density functionals, including six global hybrid meta-GGAs (BB1K [23], M05 [24], M05-2X [25], M06 [20], M06-2X [20], MPWB1K [21]),

three meta-GGAs (M06-L [26], TPSS [27], TPSSLYP1W [28]), three hybrid GGAs (B3LYP [16, 19], MPW1K [29], MPW3LYP [21]) and one GGA functional (PBE [30]), combined with SDD [31] for Ni and 6-31G(d) for all other atoms. Energies are evaluated at the same level. When assessing different ECPs (LanL2DZ [32], LanL2MB [32], SDD) for Ni, geometry optimizations and energy calculations are conducted by DFT/ECP:6-31G(d). When assessing different all electron basis sets (including 6-31G(d), 6-31+G(d), 6-311++G(2d,2p)) for nonmetal atoms and different solvation model (*i.e.* PCM [33], CPCM [34], SMD [35]), MPWB1K/LanL2DZ:6-31G(d) (M1) optimized geometries are used. Energies include thermal correction to enthalpy calculated at the optimized level. Heptane is used as solvent for I<sup>t</sup>Bu and IAd; Toluene is used as solvent for IMes, ICy, PCy<sub>3</sub>, P(*p*-Tol)<sub>3</sub> and PPh<sub>3</sub>; corresponding to the experimental conditions [8, 9]. Each optimized structure is confirmed by the frequency calculated at the optimized level to rule out any imaginary vibration frequency.

## III. RESULTS AND DISCUSSION

### A. The experimental Ni-L BDEs

The experimental Ni-ligand bond dissociation enthalpies (BDEs) of 7 Ni complexes reported by Nolan *et al.* [8, 9] are selected for comparison, shown in Table I.

### B. Gas phase optimizations

Following our previous studies in calculating M-L BDEs [13], we first carry out the gas phase calculations

TABLE II Ni–L bond lengths obtained by calculation and X-ray crystal diffraction<sup>a</sup>.

	Ni–L bond length/Å						RMSE
	I <sup>t</sup> Bu	IAd	IMes	ICy	PCy <sub>3</sub>	PPh <sub>3</sub>	
BB1K	1.9637	1.9726	1.9910	2.2780	2.2207	2.2174	0.0152
MPWB1K	1.9611	1.9707	1.9898	2.2657	2.2260	2.2144	0.0116
X-ray	1.9567 [8]	1.9535 [8]	1.9826 [9]	2.0074 [9]	2.2604 [37]	2.2167 [38]	

<sup>a</sup> For the complex with two ligands, the Ni–L bond length here is the mean value.

TABLE III The BDE values calculated with different ECPs for Ni<sup>a</sup>.

		BDE/(kcal/mol)							ME	RMSE	<i>R</i>
		I <sup>t</sup> Bu	IAd	IMes	ICy	PCy <sub>3</sub>	P( <i>p</i> -Tol) <sub>3</sub>	PPh <sub>3</sub>			
BB1K/ECP:6-31G(d)	SDD	38.7	39.2	28.0	31.6	23.9	24.9	23.2	−1.2	2.1	0.9622
	LanL2DZ	38.4	38.8	26.5	30.4	22.8	23.5	21.9	−2.3	2.8	0.9677
	LanL2MB	38.7	39.3	27.8	31.7	25.4	24.8	24.1	−0.9	1.8	0.9720
MPWB1K/ECP:6-31G(d)	SDD	40.1	40.7	30.6	33.8	26.1	27.0	25.2	0.7	2.1	0.9536
	LanL2DZ	40.0	40.4	29.0	32.7	25.1	25.6	23.9	−0.2	1.8	0.9619
	LanL2MB	40.2	40.9	30.3	34.1	27.7	26.9	24.8	0.9	2.1	0.9555
Experiment <sup>b</sup>		39	43	27.5	30.1	26.6	26.4	25.7			

<sup>a</sup> The regression slopes for all correlations of calculation and experimental results are fixed at 1.00.

<sup>b</sup> (CO)<sub>2</sub>Ni–L [8] and (CO)<sub>2</sub>Ni–L<sub>2</sub> [9], and the uncertainty is ±3.0 kcal/mol.

to simulate the thermodynamics in low-polarity solvents (heptane and toluene).

### 1. Different DFT methods

With the combined SDD (for Ni) and 6-31G(d) (for all other atoms) basis sets, the performance of 13 different DFT functionals (including B3LYP, BB1K, M05, M05-2X, M06, M06-2X, M06-L, MPW1K, MPW3LYP, MPWB1K, PBE, TPSS, and TPSSLYP1W) are examined. The calculated BDEs with different methods and the mean error (ME), the root mean square error (RMSE), and the linear correlation coefficient (*R*) between the calculation and experimental results are given in Table I.

From Table I, it can be seen that the BDEs calculated with BB1K, MPW1K, and MPWB1K functionals show good linear correlations with the experimental ones. The linear fit correlation coefficients (by fixing the slope as 1) for BB1K, MPW1K, and MPWB1K are all above 0.95. In addition, BB1K and MPWB1K give the smallest RMSE as 2.1 kcal/mol, while BB1K is likely to underestimate the BDE by 1.2 kcal/mol and MPWB1K tend to overestimate the BDE by 0.7 kcal/mol systematically. In contrast, the performances of all other methods, especially the M06-class (M06, M06-L, and M06-2X), are unsatisfactory, due to the relatively poor linear fit parameters (*R*) and the large RMSE values. Meanwhile, B3LYP, M05, M06-2X underestimate the Ni–L BDEs as they result in a negative ME more than

3 kcal/mol, while M06, M06L, PBE tend to overestimate the BDE values.

For further comparisons between BB1K and MPWB1K functionals, we examine the correlations between optimized structures of (CO)<sub>2</sub>NiL<sub>*m*</sub> (*m*=1,2) complexes and the reported X-ray crystal structures (Table II).

According to Table II, the calculation results with BB1K and MPWB1K agree well with the reported bond lengths. Considering that BB1K performs slightly better on the calculation of BDE values while MPWB1K gives best structure parameters, we take both of them for further examinations on basis sets.

### 2. Different basis sets

With the BB1K and MPWB1K functionals in hand, we then study the basis set effect. To achieve this goal, we fix the all electron basis set (6-31G(d)) for nonmetal atoms and change the ECPs (including SDD, LanL2DZ, and LanL2MB) for Ni (Table III).

The calculation results in Table III seem to suggest that BB1K/(LanL2MB:6-31G(d)) is a good choice due to the smallest RMSE and the largest *R* values. However, the structure of Ni(CO)<sub>2</sub> is linear with LanL2MB ECP, which significantly deviates the previously reported bent structure of Ni(CO)<sub>2</sub> (∠C–Ni–C=145°) [39]. Note that the bent structure has been successfully reproduced by the calculations with other ECPs (Fig.1). Therefore, LanL2MB is excluded

TABLE IV The BDE values calculated with different all electron basis sets for nonmetal atoms<sup>a</sup>.

	BDE/(kcal/mol)							ME	RMSE	<i>R</i>
	I <sup>t</sup> Bu	IAd	IMes	ICy	PCy <sub>3</sub>	P( <i>p</i> -Tol) <sub>3</sub>	PPh <sub>3</sub>			
6-31G(d)	40.0	40.4	29.0	32.7	25.1	25.6	23.9	-0.2	1.8	0.9619
6-31+G(d)	37.9	38.7	26.6	29.0	24.9	24.9	23.3	-1.8	2.1	0.9878
6-311++G(2d,2p)	38.0	38.8	25.7	28.5	25.2	24.6	23.1	-2.1	2.3	0.9892
Experiment <sup>b</sup>	39	43	27.5	30.1	26.6	26.4	25.7			

<sup>a</sup> The regression slopes for all correlations of calculation and experimental results are fixed at 1.00.

<sup>b</sup> (CO)<sub>2</sub>Ni-L [8] and (CO)<sub>2</sub>Ni-L<sub>2</sub> [9], and the uncertainty is ±3.0 kcal/mol.

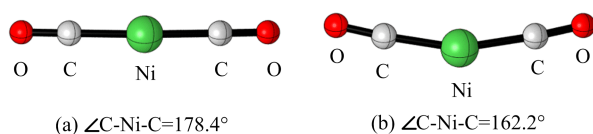


FIG. 1 The structure of Ni(CO)<sub>2</sub> optimized by (a) BB1K/LanL2MB:6-31G(d) and (b) BB1K/LanL2DZ:6-31G(d) methods. This figure is prepared by CYLView [36].

and MPWB1K/LanL2DZ:6-31G(d) (M1) is finally concluded to be the best method in dealing with the Ni-L systems.

Now that the DFT functional and ECP for Ni are determined, we next examine the effects of all different electron basis sets (including 6-31G(d), 6-31+G(d), 6-311++G(2d,2p)) for nonmetal atoms. We carry out single point calculations with those all electron basis sets on the geometry optimized by M1. The related calculation results are given in Table IV.

According to Table IV, the additional diffuse functions to 6-31G(d) makes improvement on the linear correlation coefficient (0.98 *vs.* 0.96), although a slightly larger underestimation of BDEs has been observed. Compared with 6-31+G(d), 6-311++G(2d,2p) gives similar results, while both RMSE and *R* become slightly larger. Therefore, the results of 6-31+G(d) and 6-311++G(2d,2p) basis sets are comparable. Considering that 6-31+G(d) costs less time, we recommend MPWB1K/LanL2DZ:6-31+G(d,p)//MPWB1K/LanL2DZ:6-31G(d) (M2//M1) method to calculate the Ni-L BDEs. The linear correlation between theoretical and experimental BDE values calculated with M2//M1 is shown in Fig.2.

### C. Solution phase single point calculations

After confirming the gas phase calculation method (M2//M1), we next carry out solution phase single point calculations to improve the performance of calculation results.

Using the M1 optimized geometries in the gas phase, we test different solvation models (including CPCM,

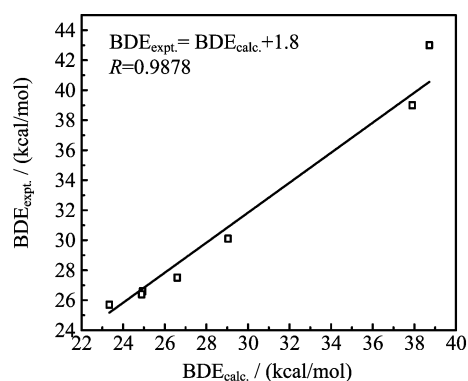


FIG. 2 The linear correlation between BDE values calculated with M2//M1 and experimental ones.

PCM and SMD) combined with the single point calculation method M2 (Table V). It's found that the results of CPCM and PCM are close to each other. The results of CPCM and PCM are also close to the results of the gas phase calculations because of the small solvation effect of low polarity solvent (the linear correlation between the calculation results and experimental ones has been slightly improved when solvent are considered). SMD performs relatively worse as the results show a larger *R* and RMSE values. Similar observation has also been noted in our previous studies of Ir-H BDEs [13(c)]. Meanwhile, with the aid of PCM model, different atomic radii give quite similar results (please see supplementary material for more details). Therefore, CPCM and PCM solvation models with the M2//M1 method are recommended for the calculation of Ni-L BDE in solution phase.

### IV. CONCLUSION

The formation and breaking of Ni-L bond is involved in many Ni-catalyzed reactions, and it is important to get accurate Ni-L bond dissociation enthalpies. In this work, we assess different DFT functionals (including B3LYP, BB1K, M05, M05-2X, M06, M06-2X, M06-L, MPW1K, MPW3LYP, MPWB1K, PBE, TPSS, TPSS-LYP1W) and different basis sets (including LanL2DZ,

TABLE V The BDE values calculated with different solvation models<sup>a</sup>.

	BDE/(kcal/mol)						ME	RMSE	R	
	I <sup>t</sup> Bu <sup>b</sup>	IAd <sup>b</sup>	IMes <sup>c</sup>	ICy <sup>c</sup>	PCy <sub>3</sub> <sup>c</sup>	P( <i>p</i> -Tol) <sub>3</sub> <sup>c</sup>				PPh <sub>3</sub> <sup>c</sup>
CPCM	37.6	38.1	25.4	27.6	24.2	24.2	22.7	-2.6	2.8	0.9880
PCM	38.0	38.5	25.4	27.9	24.5	24.3	22.8	-2.4	2.6	0.9882
SMD	38.4	39.0	22.6	24.3	25.3	24.4	23.6	-3.0	3.5	0.9626
Experiment	39	43	27.5	30.1	26.6	26.4	25.7			

<sup>a</sup> The regression slopes for all correlations of calculation and experimental results are fixed at 1.00. UFF radii are used.

<sup>b</sup> Solvent is heptane.

<sup>c</sup> Solvent is toluene.

LanL2MB, SDD on Ni and 6-31G(d), 6-31+G(d), 6-311++G(2d,2p) on all other atoms) on basis of the recent experimental BDE values reported by Nolan *et al.* and find out that the MPWB1K/LanL2DZ:6-31+G(d,p)//MPWB1K/LanL2DZ:6-31G(d) method gives the best correlations with the available experimental results. Among the assessed 13 computational methods, the M06-class (M06, M06-L and M06-2X) give relatively poor linear correlation between the calculation and experimental results (the Ni–L BDEs have been significantly overestimated with these methods), and B3LYP, M05, PBE result in large systematic deviation. The results suggest that these methods should be used more carefully in dealing with the systems involving the Ni–L bond dissociations. In addition, the solution phase single point calculations (with CPCM, PCM, or SMD model) imply that both the CPCM and PCM perform relatively better than SMD model.

**Supplementary material:** Computed thermodynamic data, Cartesian coordinates of optimized structures and the BDE values calculated with different atomic radii.

## V. ACKNOWLEDGEMENTS

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