

# The Lewis Assisted C—CN Bond Activation of Benzonitrile Using Zerovalent Group 10 Metal Complexes with Dippe Ligand

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## ABSTRACT

The C—C bond activation has captured attention for its role in industrial applications and intricate organic molecule synthesis.

By employing advanced computational tools at TACC, we performed density functional theory (DFT) calculations to study the reaction mechanism of the C—C bond activation.

This study delves into a comparison of the C—CN bond activation of benzonitrile by group 10 metals (Ni, Pd, Pt).

## INTRODUCTION

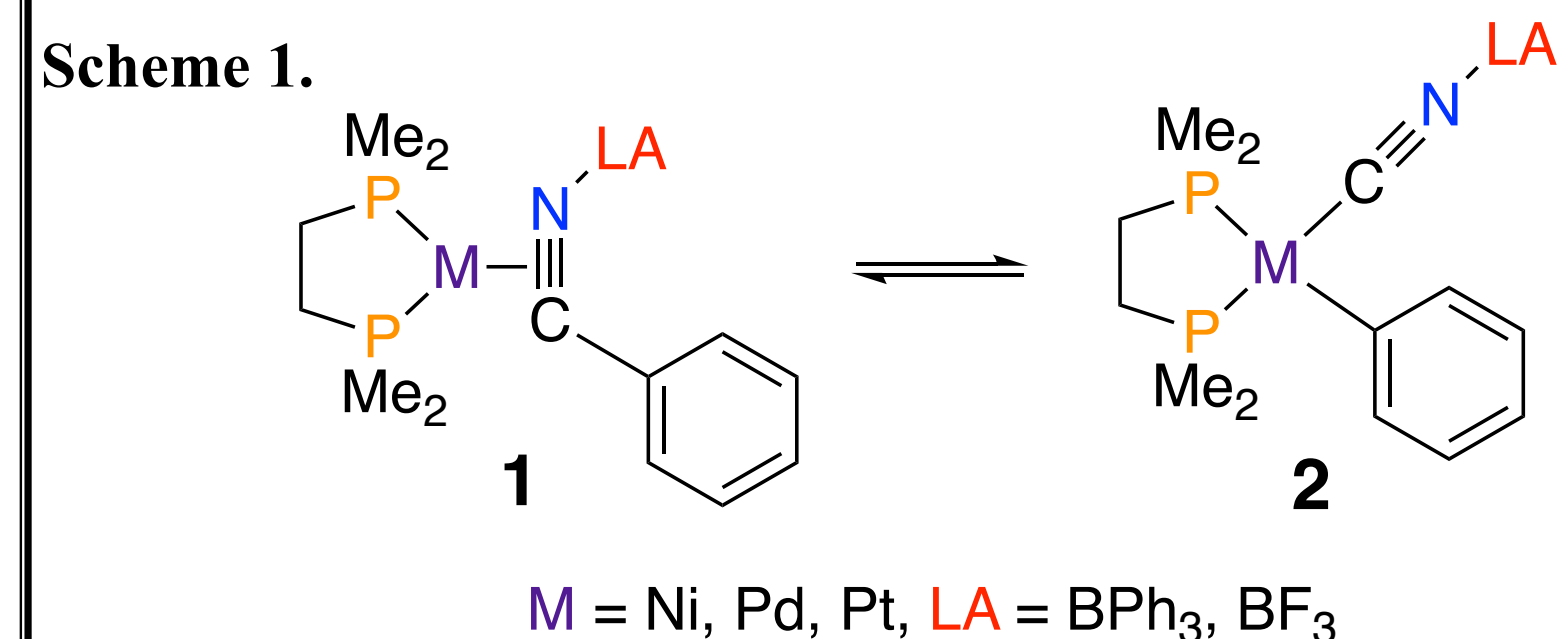
The exploration of C—C bond activation is significantly propelled by homogeneous transition-metal catalysts.

Nonetheless, the formidable challenge of effecting mild and homogeneous activation of thermodynamically stable and kinetically inert C—C  $\sigma$ -bonds persists.

Prevailing activation strategies predominantly entail systems driven by strain relief or aromatization, excepting the activation of unstrained C—CN bonds within nitriles.

Prior investigations leveraging [(dippe)Ni] fragment alongside Lewis acids have unveiled the manipulation of reaction mechanisms of the C—CN bond in benzonitrile.

In this study, we will compare the C—CN bond activation reaction of benzonitrile by Ni with its heavier analogs (Pt, Pd).



## COMPUTATIONAL METHODS

Geometries were optimized with B3LYP with Gaussian 16. 6-31G(d,p) for C, H, N, O, B and F, ECP of the Stuttgart group and associated basis sets were used for Ni, Pd, Pt and P together with *f*-polarization functions for group 10 metals and *d*-polarization functions for P.

Solvent effects in THF and toluene were added using solvation model density. Gibbs free energy calculated at 327.15 K and 1 atm.

ChimeraX and GoodVibes v3.2 used for visualization of the molecules and analyzing the log files, respectively.

## RESULTS

The C—CN bond activation of benzonitrile with Ni gave faster reaction rates with Lewis acid. Nitrogen lone pair coordination that imparts stability through steric bulk or charge redistribution, thereby facilitating C—CN bond cleavage.

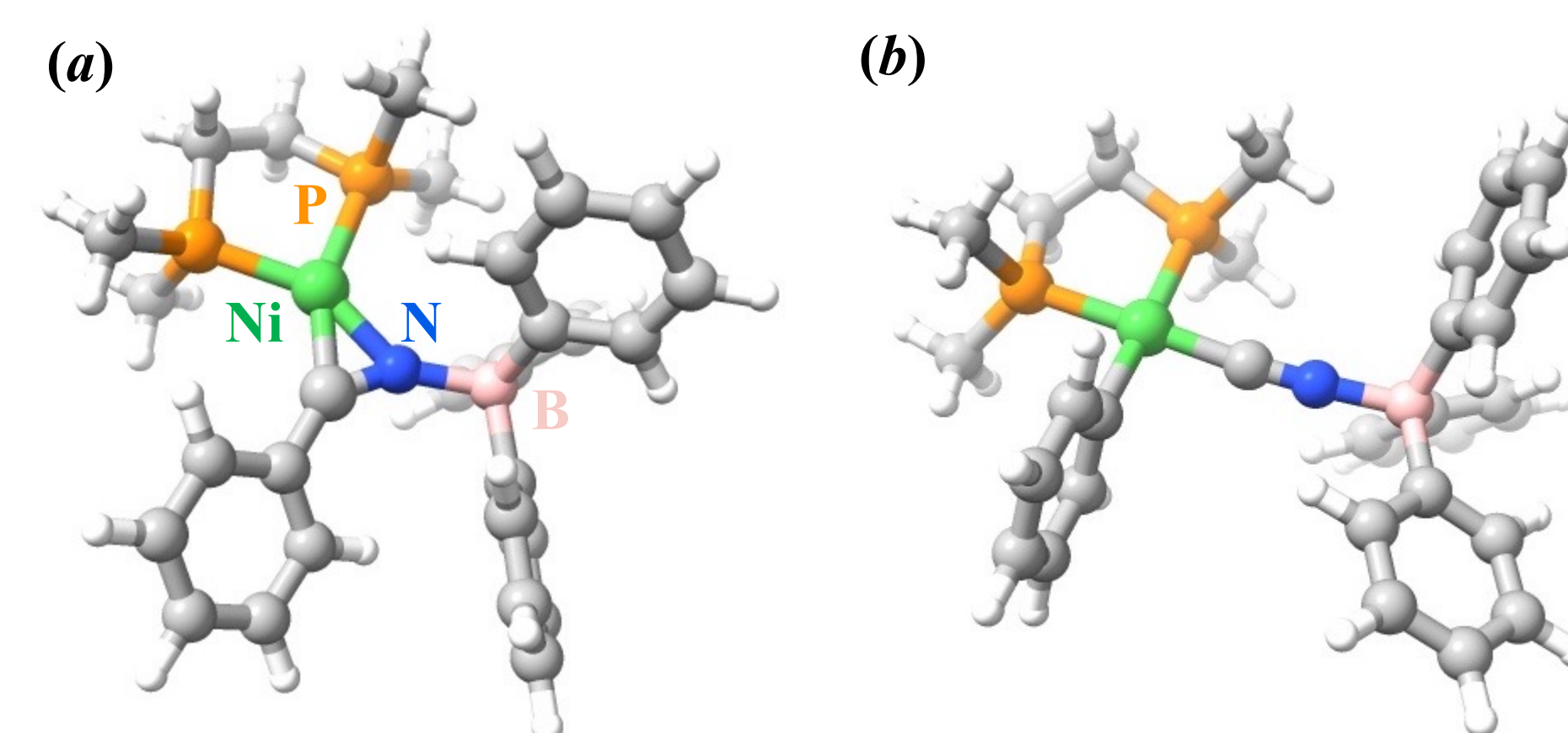
**Table 1.** The relative energy of the C—CN bond activation product with respect to the  $\eta^2$ -nitrile complexes ( $G^{\circ}_2 - G^{\circ}_1$ )

Metal	$\Delta G^{\circ}$ (kcal/mol)		
	Without LA	BF <sub>3</sub>	BPh <sub>3</sub>
Ni	5.41	12.59	0.36
Pd	3.34	6.29	-2.56
Pt	-10.76	-4.31	-14.72

Comparison of the C—CN bond activation of benzonitrile by group 10 metals (Ni, Pd, Pt) shows that C—CN bond activation give relatively more stable products with BPh<sub>3</sub>.

C—CN bond activation products become relatively more unstable with BF<sub>3</sub>.

$\eta^2$ -nitrile complex and C—CN bond activation product of benzonitrile with Ni in the presence of BPh<sub>3</sub> are shown below.



**Figure 1.** Optimized geometries of (a)  $\eta^2$ -nitrile complex (b) C—CN bond activation product of benzonitrile with Ni in the presence of BPh<sub>3</sub>

Comparison of the optimized geometries of the  $\eta^2$ -nitrile complex and the C—CN bond activation of benzonitrile by Ni shows  $\pi$ - $\pi$  interaction in  $\eta^2$ -nitrile complex with BPh<sub>3</sub>.

This interaction is not possible with BF<sub>3</sub>.

The difference between the effects of these two LA could be due to the  $\pi$ - $\pi$  interaction.

Important interatomic distances (Å) of the  $\eta^2$ -nitrile complexes (**Table 2**) and the C—CN bond activation products (**Table 3**) with and without Lewis acid show longer C—N bond for Pt (1.24 Å) and Ni (1.23 Å) than Pd (1.22 Å) in  $\eta^2$ -nitrile complexes, but similar bond lengths in the products.

**Table 2.** Important interatomic distances (Å) of the  $\eta^2$ -nitrile complexes with and without Lewis acid

Metal	Without LA			BF <sub>3</sub>			BPh <sub>3</sub>		
	C—CN	C—N	C—N	C—CN	C—N	N—B	C—CN	C—N	N—B
Ni	1.4656	1.2341	1.4603	1.2446	1.5943	1.4635	1.2419	1.6071	
Pd	1.4625	1.2197	1.4619	1.2294	1.6084	1.4619	1.2294	1.6084	
Pt	1.4657	1.2401	1.4587	1.2512	1.6001	1.4636	1.2489	1.6087	

**Table 3.** Important interatomic distances (Å) of the C—CN bond activation products with and without Lewis acid

Metal	Without LA			BF <sub>3</sub>			BPh <sub>3</sub>		
	C—CN	C—N	C—CN	C—N	N—B	C—CN	C—N	N—B	
Ni	2.7314	1.1714	2.7476	1.1637	1.6286	2.7036	1.1635	1.5804	
Pd	2.906	1.1702	2.9859	1.1628	1.6306	2.9097	1.1624	1.5825	
Pt	2.9144	1.1701	2.9788	1.1631	1.6354	2.9126	1.1623	1.5834	

## CONCLUSION

C—CN bond activation of benzonitrile by group 10 metals (Ni, Pd, Pt) lead to the formation of relatively more stable C—CN bond activation products with BPh<sub>3</sub>.

On the other hand, the C—CN bond activation products become relatively more unstable with BF<sub>3</sub>.

The difference between the effects of these two LA is intriguing.

The optimized geometries of the  $\eta^2$ -nitrile complex and the C—CN bond activation of benzonitrile by Ni reveals  $\pi$ - $\pi$  interaction in  $\eta^2$ -nitrile complex with BPh<sub>3</sub> but not with BF<sub>3</sub>.

## FUTURE WORK

Solvent corrections and empirical dispersion corrections are underway.

Future work will focus on the exploration of the  $\pi$ - $\pi$  interaction with BPh<sub>3</sub>.

Understanding this Lewis acid assisted transition-metal catalyzed reaction is crucial for the design of innovative catalytic systems.

This research has the potential to reshape chemical synthesis methodologies and chart transformative routes toward groundbreaking synthetic pathways.

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## REFERENCES

- Swartz, B. D.; Brennessel, W. W.; Jones, W. D. *Synlett* **2018**, *29*, 747-753.
- Ateşin, T. A.; Li, T.; Lachaize, S.; García, J. J.; Jones, W. D. *Organometallics* **2008**, *27*, 3811-3817.
- Munjanja, L.; Torres-López, C.; Brennessel, W. W.; Jones, W. D. *Organometallics* **2016**, *35* (11), 2010-2013.
- Swartz, B. D.; Brennessel, W. W.; Jones, W. D. *Organometallics* **2011**, *30* (6), 1523-1529.
- Lachaize, S.; Gallegos, D. C.; Antonio, J. J.; Atesin, A. C.; Ateşin, T. A.; Jones, W. D. *Organometallics* **2023**, *42*(15), 2134-2147.