**Supporting Information**

# Mechanism for Activation of C-CN Bond of Nitriles by a Cationic CpRh(III)-Silyl Complex: A Systematic DFT Study

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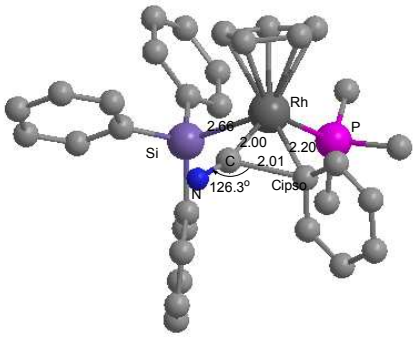
## 1. Additional Computational Results

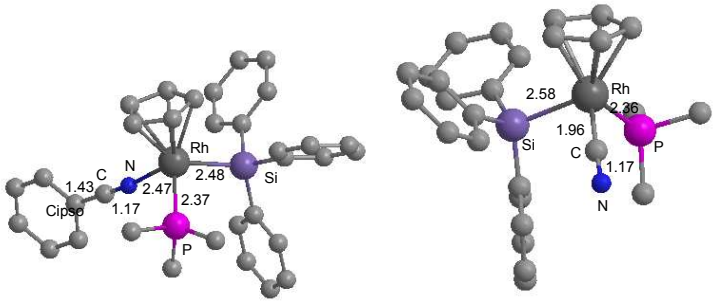
a. Optimized structures for oxidative addition mechanism




**TSoxd**

*Figure S1*. Optimized transition state structure **TSoxd** for oxidative addition mechanism.

b. Relevant intermediates involved in radical mechanisms



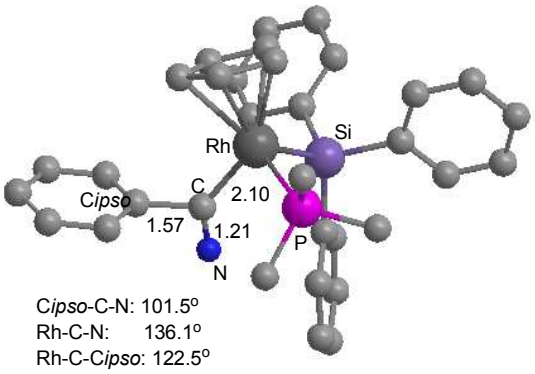

**CP5** **CP6**

*Figure S2*. Relevant intermediates in radical mechanisms.

**CP5** is the critical intermediate involved in SET mechanism which commences with single electron transfer from Rh(III) center to the aryl cyanide ligand. Therefore, **CP5** should be in a triplet state with a Rh(IV) center. Optimization with triplet electron configuration was performed for the location of **CP5**. Intermediate **CP6** with formula **[CpRh(PMe$_3$)(SiPh$_3$)(CN)]$^{+\bullet}$** is the radical cation involved in cyanide

transfer from the PhCN to the Rh center, resulting in the formation of a Rh(IV) intermediate.

c. Y-shape transition state for the isomerization between Ph-CN and Ph-NC at Rh




**TS$_{isomerization}$**

*Figure S3*. Optimized transition state structure **TS$_{isomerization}$** connecting cyanide and isocyanide.

d. Reaction coordinates and selected optimized structures for the favored cyano insertion/deisocyanide mechanism in solvent phase (optimizations were done in solvent)

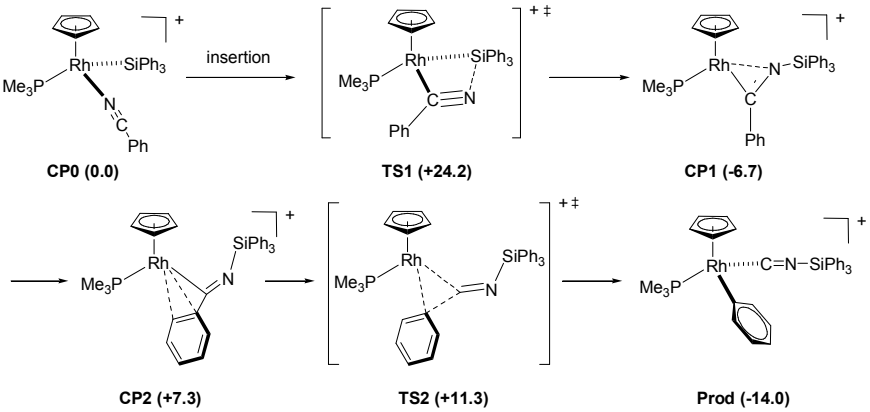



*Figure S4*. Reaction pathway with optimization in dichloromethane phase.

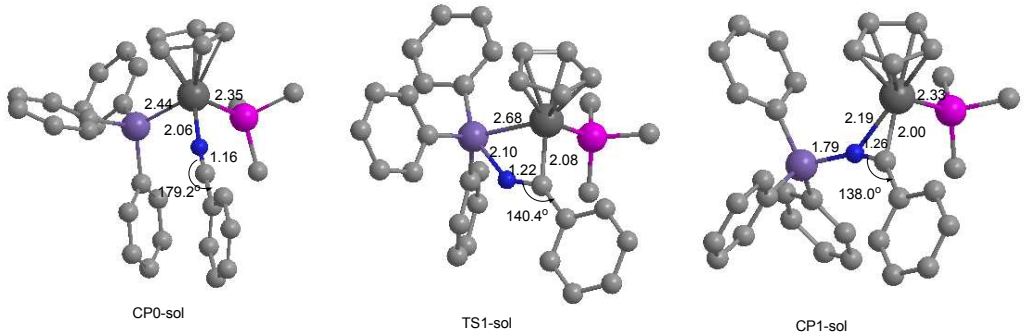



*Figure S5*. Selected intermediates and transition state optimized in dichloromethane.

e. Reaction coordinates for the favored cyano insertion/deisocyanide mechanism using B97D functional taking dispersion effect into account

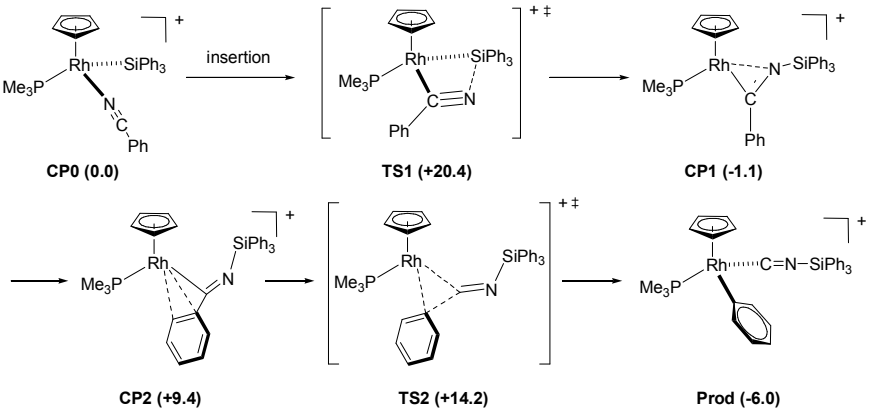



*Figure S6*. B97D-based reaction pathway in dichloromethane phase.

## 2. Optimized Cartesian Coordinates for Stationary Points

This information is summarized in a separate .xyz file called “coordinates.xyz”, which can be visualized by molecular modeling packages, such as Mercury.

## 3. Electronic Energies, Thermal Corrections and Solvation Energies

***Table S1.*** Single Point Electronic Energies, Zero-Point Vibrational Energies, Thermal Corrections to Enthalpies and Gibbs Free Energies, and Solvation Energies in $CH_2Cl_2$.[a]

| Complex | SP (a.u.) | ZPE (a.u.) | ΔH (a.u.) | ΔG (a.u.) | Gsol (kcal/mol) |
|---|---|---|---|---|---|
| **CP0** | -2074.448389 | 0.578168 | 0.616771 | 0.505942 | -12.63 |
| **TS1** | -2074.407937 | 0.577697 | 0.615188 | 0.508039 | -13.54 |
| **CP1** | -2074.457519 | 0.577904 | 0.616366 | 0.503238 | -9.95 |
| **CP2** | -2074.429268 | 0.577363 | 0.615834 | 0.504093 | -13.47 |
| **TS2** | -2074.425065 | 0.57581 | 0.614132 | 0.501119 | -12.48 |
| **Prod** | -2074.46352 | 0.576542 | 0.61556 | 0.500411 | -12.22 |
| **TSoxd** | -2074.33117 | 0.576354 | 0.614608 | 0.507201 | -17.77 |
| **TS1'** | -2074.35812 | 0.576209 | 0.614372 | 0.505079 | -12.33 |
| **CP3** | -2074.394809 | 0.578098 | 0.616045 | 0.507557 | -12.96 |
| **CP4** | -2074.39409 | 0.577131 | 0.615532 | 0.503768 | -13.8 |
| **TS3** | -2074.37148 | 0.575163 | 0.61349 | 0.503062 | -12.45 |
| **Prod'** | -2074.440812 | 0.576185 | 0.615508 | 0.49939 | -11.32 |
| **CP5** | -2074.3898 | 0.574897 | 0.615387 | 0.493621 | -11.17 |
| **phenyl•** | -231.622243 | 0.087653 | 0.092966 | 0.060264 | -1.8 |
| **CP6** | -1842.686054 | 0.484978 | 0.518812 | 0.419258 | -19.53 |
| **$TS_{isomerization}$** | -2074.346706 | 0.574813 | 0.613385 | 0.502733 | -12.84 |
| | ***Substrate effects*** | | | | |
| **$CP0^{MeCN}$** | -1882.662714 | 0.524875 | 0.560557 | 0.457595 | -15.02 |
| **$TS1^{MeCN}$** | -1882.621098 | 0.524248 | 0.558804 | 0.458874 | -17.04 |
| **$CP1^{MeCN}$** | -1882.67134 | 0.524627 | 0.559978 | 0.455836 | -13.79 |
| **$CP2^{MeCN}$** | -1882.643879 | 0.523397 | 0.558665 | 0.454363 | -15.06 |
| **$TS2^{MeCN}$** | -1882.639736 | 0.522359 | 0.557454 | 0.451912 | -15.29 |
| **$Prod^{MeCN}$** | -1882.683739 | 0.523054 | 0.557934 | 0.453933 | -14.55 |
| **$CP0^{iPrCN}$** | -1961.313574 | 0.581794 | 0.620246 | 0.508975 | -13.04 |
| **$TS1^{iPrCN}$** | -1961.270017 | 0.581326 | 0.618548 | 0.512443 | -15.01 |
| **$CP1^{iPrCN}$** | -1961.317186 | 0.581645 | 0.61976 | 0.508792 | -10.83 |
| **$TS2^{iPrCN}$** | -1961.273295 | 0.579442 | 0.61659 | 0.508861 | -12.91 |
| **$CP0^{tBuCN}$** | -2000.638794 | 0.61006 | 0.649754 | 0.537098 | -12.26 |
| **$TS1^{tBuCN}$** | -2000.593376 | 0.60926 | 0.647834 | 0.53993 | -13.35 |
| **$CP1^{tBuCN}$** | -2000.639988 | 0.60979 | 0.649116 | 0.535879 | -10.43 |
| **$TS2^{tBuCN}$** | -2000.594217 | 0.607549 | 0.646753 | 0.533996 | -12.39 |
| **$CP0^{para\text{-}OMe}$** | -2189.00987 | 0.610756 | 0.65208 | 0.53447 | -12.46 |
| **$TS1^{para\text{-}OMe}$** | -2188.969495 | 0.610386 | 0.650547 | 0.53769 | -13.61 |
| **$CP1^{para\text{-}OMe}$** | -2189.01969 | 0.610669 | 0.651797 | 0.532414 | -9.67 |
| **$CP0^{para\text{-}CF3}$** | -2411.589299 | 0.582628 | 0.62406 | 0.506239 | -13.03 |
| **$TS1^{para\text{-}CF3}$** | -2411.549364 | 0.582219 | 0.623491 | 0.505234 | -14.14 |

| | | | | | |
|---|---|---|---|---|---|
| **CP1**$^{para\text{-}CF3}$ | -2411.599816 | 0.582595 | 0.624692 | 0.502863 | -9.72 |

a. note SP: Single point electronic energy; ZPE: Zero-point vibrational energy;
ΔH: Thermal correction to enthalpy; ΔG: Thermal correction to Gibbs free energy;
Gsol: Solvation energy in $CH_2Cl_2$.

## 4. Full Citation of Gaussian03 Program

Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision E.01; Gaussian, Inc.: Wallingford CT, 2004.