# Switching *End-on* into *Side-on* C≡N Coordination:  A Computational Approach

Chun-Fang Huo,[†] Tao Zeng,[†] Yong-Wang Li,[†] Matthias Beller,[‡] and Haijun Jiao*,[†,‡]

*State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, People's Republic of China, and Leibniz-Institut für Organische Katalyse an der Universität Rostock e.V., Albert-Einstein-Strasse 29a, 18059 Rostock, Germany*

The stability of the *end-on* and *side-on* complexes of acetonitrile with $HCo(L)_3$ [L = CO, $PH_3$, $PPh_3$, $PMe_3$, 1,2-bis(dimethyl)phosphinoethane (dmpe), *N*-heterocyclic carbene (NHC)] has been computed at the B3LYP density functional level of theory. It is found that the most common *end-on* coordination mode of nitriles to transition metals can be changed into the *side-on* coordination via reasonable ligand tailoring. The dmpe- and NHC-modified catalyst, HCo(dmpe)(NHC), prefers the *side-on* complex over the *end-on* complex of acetonitrile by 1.1 kcal/mol in free energy. The driving force for this conversion is addressed.

## Introduction

Primary amines, amides, and *N*-acyl amino acids are of major importance in human life and chemical industry,[1] and especially useful as pharmaceutically active substances, dyes, agrochemicals, vulcanization accelerators, and fine chemicals. Their syntheses include alkylation of organic halides with ammonia, hydration or hydrogenation of nitriles, reductive amination of carbonyl compounds, hydroamination of olefins, and amidocarbonylation.[2,3] Utilizing easily available nitriles as feedstocks to produce amines, amides, and *N*-acyl amino acids is an interesting and challenging project, of which C≡N activation is the key step. Although hydrogenation of nitriles with heterogeneous catalysts is an established technology,[4] e.g., for the transformation of adiponitrile to hexamethylenediamine over a million-ton scale, similar reactions with defined homogeneous catalysts are basically unknown.

Transition metal complexes play a crucial role in homogeneous catalysis. High catalytic activity and selectivity are generally achieved through metal choice, ligand design, and fine-tuning. For homogeneous transition metal catalysis, the first step is the substrate coordination and activation. As shown below, nitrile coordination to metal can occur in two possible ways. One is the *end-on* mode via the nitrogen lone pair ($\eta^1$-nitrile, notated as *E*), and the other is the *side-on* mode through the C≡N $\pi$-orbital ($\eta^2$-nitrile, notated as *S*). However, both experimental and theoretical studies[5] have revealed that the *end-on* coordination (*E*) is by far the most common bonding mode, in which the C≡N bond is less activated. Therefore, the C≡N functionalization is difficult to accomplish in homogeneous catalysis. In this paper, we present a density functional study on catalyst design for switching the *end-on* (*E*) to the *side-on* (*S*) coordination of acetonitrile.
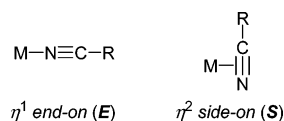


## Computational Details

All calculations were carried out at the B3LYP[6] density functional level of theory with the Gaussian 03 program.[7] The 6-311+G(d) basis set was used for cobalt, while the 6-31+G-(d) basis set was employed for carbon, oxygen, hydrogen, nitrogen, and phosphorus. The structures of all species were fully optimized without symmetry constraints. The frequency analyses were also performed at the same level to confirm the optimized structures to be local minima without imaginary

* To whom correspondence should be addressed. E-mail: haijun.jiao@ifok-rostock.de.
† Chinese Academy of Sciences.
‡ Leibniz-Institut für Organische Katalyse an der Universität Rostock e.V.
(1) Müller, T. E.; Beller, M. *Chem. Rev.* **1998**, *98*, 675.
(2) Ricci, A. *Modern Amination Methods*; Wiley-VCH: Weinheim, 2000.
(3) (a) Seayad, A.; Ahmed, M.; Klein, H.; Jackstell, R.; Gross, T.; Beller, M. *Science* **2002**, *297*, 1676. (b) Utsunomiya, M.; Kuwano, R.; Kawatsura, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2003**, *125*, 5608. (c) Utsunomiya, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2004**, *126*, 2702. (d) Ackermann, L.; Bergman, R. G.; Loy, R. N. *J. Am. Chem. Soc.* **2003**, *125*, 11956. (e) Huang, X. H.; Anderson, K. W.; Zim, D.; Jiang, L.; Klapars, A.; Buchwald, S. L. *J. Am. Chem. Soc.* **2003**, *125*, 6653.
(4) Weissermel, K.; Arpe, H.-J. *Industrielle Organische Chemie*; Wiley-VCH: Weinheim, 1998.

(5) (a) Fung, W. K.; Huang, X.; Man, M. L.; Ng, S. M.; Hung, M. Y.; Lin, Z.; Lau, C. P. *J. Am. Chem. Soc.* **2003**, *125*, 11539. (b) Timoshkin, A. Y.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **2003**, *125*, 9998. (c) Schelter, E. J.; Bera, J. K.; Bacsa, J.; Galán-Mascarós, J. R.; Dunbar, K. R. *Inorg. Chem.* **2003**, *42*, 4256. (d) Culkin, D. A.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 9330. (e) Shearer, J.; Jackson, H. L.; Schweitzer, D.; Rittenberg, D. K.; Leavy, T. M.; Kaminsky, W.; Scarrow, R. C.; Kovacs, J. A. *J. Am. Chem. Soc.* **2002**, *124*, 11417. (f) Breno, K. L.; Pluth, M. D.; Tyler, D. R. *Organometallics* **2003**, *22*, 1203. (g) Voll, M. A. O.; Rominger, F.; Eisenträger, F.; Hofmann, P. *J. Organomet. Chem.* **2002**, *641*, 220.
(6) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Stevens, P. J.; Devlin, F. J.; Chablowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.

**Table 1. Relative Free Energies (ΔG, kcal/mol) and Enthalpies (ΔH, kcal/mol) between the Axial Substitution (*a* or *ea*) and the Equatorial Substitution (*e* or *ee*) of Phosphine or NHC Ligands in Modified Catalysts**

| Cat. | equatorial (*e*) | axial (*a*) | $\Delta G(\mathbf{I})^a$ | $\Delta H(\mathbf{I})^a$ |
|---|---|---|---|---|
| 1I | | | 1.4 | 2.0 |
| 2I | | | 2.4 | 2.7 |
| 3I | | | 1.9 | 1.8 |
| 5I | | | 2.5 | 2.6 |

| Cat. | equatorial (*ee*) | axial (*ea*) | $\Delta G(\mathbf{II})^b$ | $\Delta H(\mathbf{II})^b$ |
|---|---|---|---|---|
| 1II | | | 1.0 | 2.4 |
| 2II | | | 5.5 | 5.6 |
| 4II | | | −14.0 | −13.2 |

[a] $\Delta G(\mathbf{I}) = G(\boldsymbol{a}) - G(\boldsymbol{e})$; $\Delta H(\mathbf{I}) = H(\boldsymbol{a}) - H(\boldsymbol{e})$. [b] $\Delta G(\mathbf{II}) = G(\boldsymbol{ea}) - G(\boldsymbol{ee})$; $\Delta H(\mathbf{II}) = H(\boldsymbol{ea}) - H(\boldsymbol{ee})$. [c] At B3LYP/6-31+G(d) (6-311+G(d) for cobalt).

**Table 2. Relative Free Energies (ΔG, kcal/mol) and Enthalpies (ΔH, kcal/mol) between the Most Stable *Side-on* (S) and *End-on* (E) Acetonitrile Complexes**

| Cat. | *end-on* (E) | *side-on* (S) | $\Delta G^a$ | $\Delta H^a$ |
|---|---|---|---|---|
| 0 | | | 11.1[b] | 10.1[b] |
| | | | 11.1[c] | 10.0[c] |
| 1I | | | 8.7[b] | 7.1[b] |
| | | | 8.8[c] | 7.2[c] |
| 1II | | | 3.5[b] | 2.1[b] |
| 1III | | | 1.9[b] | 0.5[b] |
| 2I | | | 7.8[b] | 5.9[b] |
| | | | 7.8[c] | 6.0[c] |
| 2II | | | 1.2[b] | −0.7[b] |
| 2III | | | 2.2[b] | −3.2[b] |
| 3I | | | 8.6[b] | 7.4[b] |
| 4II | | | 1.9[b] | −0.6[b] |
| 5I | | | 6.3[b] | 4.5[b] |
| | | | 6.5[c] | 4.7[c] |
| 2II/5I | | | 1.8[b] | −2.3[b] |
| 4II/5I | | | −1.1[b] | −3.3[b] |
| 5III | | | −0.2[b] | −3.2[b] |

[a] $\Delta G = G(\boldsymbol{S}) - G(\boldsymbol{E})$; $\Delta H = H(\boldsymbol{S}) - H(\boldsymbol{E})$. [b] At B3LYP/6-31+G(d) (6-311+G(d) for cobalt). [c] At B3LYP/6-311+G(d).

frequency (NImag = 0) and provide the thermal corrections to enthalpies and Gibbs free energies (298.15 K and 1 atm). Considering the entropy effects, our discussions are based on the free energies ($\Delta G$). To estimate the basis set effect, B3LYP/6-311+G(d) calculations were carried out on single phosphine or *N*-heterocyclic carbene (NHC) modified systems, since B3LYP/6-311+G(d) has been found to be appropriate for cobalt carbonyl chemistry, as indicated by the excellent agreements in CO vibrational frequencies and dissociation energies between theory and experiment.[8] Two methods give very close results, with the largest discrepancy of 0.2 kcal/mol for the relative energies between the *side-on* (S) and *end-on* (E) complexes (see Table 2). To save computational cost, the first method was chosen for the large systems. In addition, the natural charges of $NCCH_3$ in the *end-on* (E) and *side-on* (S) complexes were calculated with the NBO program.[9] The calculated total electronic energies, ZPE, thermal correction to enthalpies and Gibbs free energies, and bond parameters for the designed catalysts are provided in the Supporting Information.

**Design Principle.** It is well known that the electron donor−acceptor and steric properties of ligands in transition metal complexes impose a strong influence on their catalytic behaviors.[10] Our basic idea is the switch of C≡N coordination

(7) 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*; Gaussian, Inc.: Pittsburgh, PA, 2003.
(8) Huo, C.-F.; Li, Y.-W.; Wu, G.-S.; Beller, M.; Jiao, H. *J. Phys. Chem. A* **2002**, *106*, 12161.

(9) Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. *NBO* Version 5.
(10) (a) Bourissou, D.; Guerret, O.; Gabbaï, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39. (b) Tillack, A.; Jiao, H.; Castro, I. G.; Hartung, C. G.; Beller, M. *Chem. Eur. J.* **2004**, *10*, 2409.
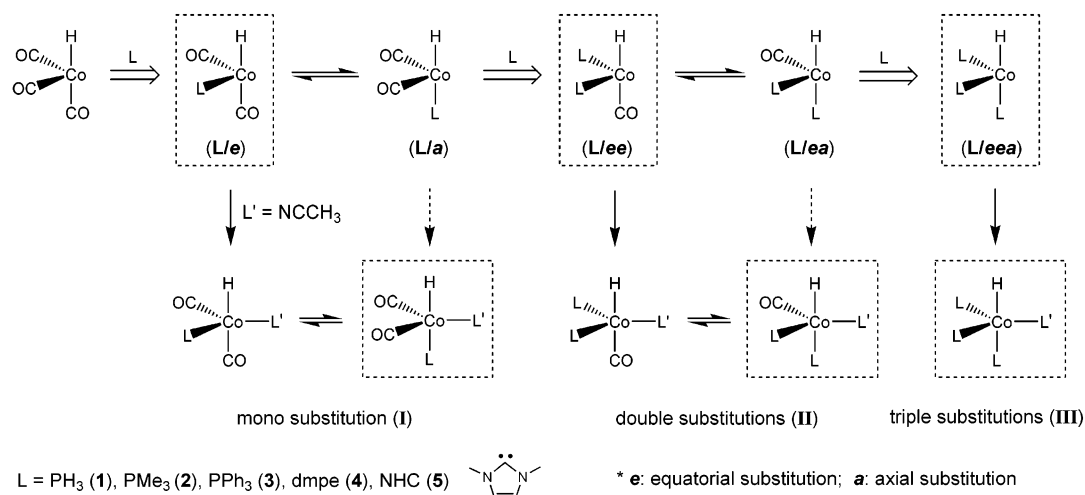
**Figure 1.** Modified catalysts $HCo(CO)_{3-n}(L)_n$ and acetonitrile complexes.

mode by ligand tailoring. Due to having a high catalytic ability, cobalt and rhodium carbonyl derivatives are widely used in many industrially important processes, of which hydroformylation is one of the most representative examples.[11] These catalysts are often modified with typically P-containing ligands[11] (phosphines and phosphites) to improve their stability, catalytic activity, and selectivity. Recently, novel *N*-heterocyclic carbenes (NHC)[12] as ligands have also been explored to complete and extend the capability of the ubiquitous phosphines and play an increasing important role in homogeneous catalysis.[13] Much of the interest in NHC derives from their advantages, e.g., improving stability and activity and preventing deactivation due to their greater electron-donating ability.

Inspired by these findings, we select a set of typical phosphines and a *N*-heterocyclic carbene as ligands, $PH_3$ (**1**), $PMe_3$ (**2**), $PPh_3$ (**3**), 1,2-bis(dimethyl)phosphinoethane (dmpe, **4**), and *N*-heterocyclic carbene (NHC, **5**), to modify the parent active catalytic $HCo(CO)_3$ species. The catalysts modified by gradual substitution of one (**I**), two (**II**), or three (**III**) CO's from $HCo(CO)_3$ are depicted in Figure 1. By examining the corresponding complexes with acetonitrile in both *end-on* (**E**) and *side-on* (**S**) coordination, the effects of catalyst ligands on the nitrile−cobalt bonding modes are revealed. It is found that stronger electron-donating ligands can considerably reduce the energy gap between the *side-on* (**S**) and *end-on* (**E**) modes and even reverse their stability sequence. Furthermore, the driving force for this conversion is elucidated.

### Results and Discussion

**(1) Structures and Energies of Designed Catalysts.** As shown in Figure 1, phosphine or NHC ligands can substitute equatorial or axial CO of $HCo(CO)_3$, forming two isomers in mono (*e* and *a*) and double (*ee*

(11) (a) Cornils, B.; Herrmann, W. A. *Applied Homogeneous Catalysis with Organometallic Compounds*; Wiley-VCH: Weinheim, 2002; Vol. 1. (b) Herrmann, W. A.; Cornils, B. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1047. (c) Agbossou, F.; Carpentier, J.-F.; Mortreux, A. *Chem. Rev.* **1995**, *95*, 2485. (d) Beller, M.; Cornils, B.; Frohning, C. D.; Kohlpaintner, C. W. *J. Mol. Chem. A* **1995**, *104*, 17.
(12) For a review, see: Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290, and references therein.
(13) For some recent applications: (a) Kaur, H.; Zinn, F. K.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2004**, *23*, 1157. (b) Viciu, M. S.; Kelly, R. A., III; Stevens, E. D.; Naud, F.; Studer, M.; Nolan, S. P. *Org. Lett.* **2003**, *5*, 1479. (c) Herrmann, W. A.; Ofele, K.; von Preysing, D.; Schneider, S. K. *J. Organomet. Chem.* **2003**, *687*, 229. (d) Jackstell, R.; Andreu, M. G.; Frisch, A. C.; Klein, H.; Selvakumar, K.; Zapf, A.; Spannenberg, A.; Röttger, D.; Briel, O.; Karch, R.; Beller, M. *Angew. Chem. Int. Ed.* **2002**, *41*, 986. (e) Tafipolsky, M.; Scherer, W.; Ofele, K.; Artus, G.; Pedersen, B.; Herrmann, W. A.; McGrady, G. S. *J. Am. Chem. Soc.* **2002**, *124*, 5865.
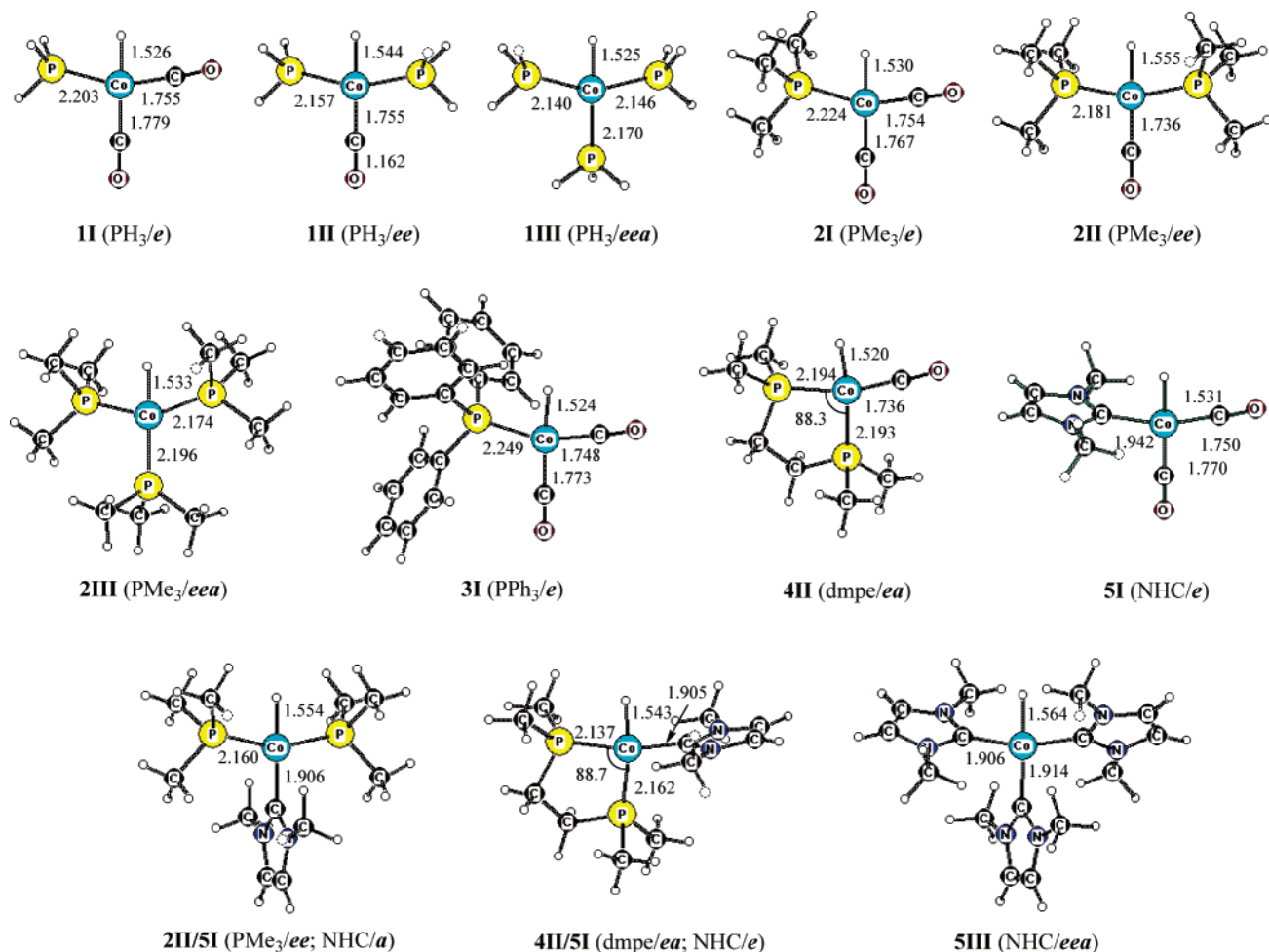
and *ea*) substitutions. The monosubstituted catalysts with phosphine or NHC at the axial site (*a*) have a butterfly geometry, while the others have a planar geometry with two equatorial ligands tilted to the axial H ligand. To get further insight into the preference of the two isomers, the relative free energies between the axial and equatorial substitution are summarized in Table 1. It clearly shows that the monodentate phosphine or NHC ligands favor the equatorial substitution. With an increase of the electron-donating ability of the phosphine ligands, $PH_3$ (**1**) < $PPh_3$ (**3**) < $PMe_3$ (**2**), the corresponding free energy gap between the axial and equatorial substituted catalysts increases from 1.4 to 1.9 and then to 2.4 kcal/mol for the monosubstitution (**1I** → **3I** → **2I**). A similar tendency from 1.0 to 5.5 kcal/mol is also observed for the double substitutions (**1II** → **2II**). These results indicate that the mono- and bis-equatorial-substituted catalysts (*e* and *ee*) are more favored than the corresponding axial isomers (*a* and *ea*). However, the case for the chelating dmpe is completely different. The bis-equatorial-substituted catalyst (**4II/ee**) is much higher in free energy than the equatorial-axial-substituted isomer (**4II/ea**) by 14.0 kcal/mol, and therefore the *ea* substitution is the exclusive form for the dmpe-modified catalyst. The optimized structures of the most stable catalysts are shown in Figure 2, while those of the less stable isomers are given in the Supporting Information.

**(2) Structures and Energies of Acetonitrile Complexes.** According to the planar geometry of the designed catalysts, acetonitrile can attack the equatorial formal vacancy either in the *end-on* (**E**) or in the *side-on* (**S**) modes, forming the bipyramidal complexes. Interestingly, acetonitrile complexes exhibit an opposite tendency for the substitution-site preference with respect to the corresponding catalysts. In most cases, the phosphine and NHC ligands prefer the axial sites in the acetonitrile complexes (Table S1 in the Supporting Information). Furthermore, for the monosubstitution (**I**), the free energy gaps between the *a* and *e* substitution in the *end-on* complexes (**E**) are in the range of −1.3 to −2.4 kcal/mol, while the corresponding *side-on* complexes (**S**) give smaller values of −0.1 to −0.8 kcal/mol. However, for the double substitutions (**II**), the free energy gaps between the *ea* and *ee* substitution in the

**Figure 2.** The most stable modified catalysts (bond lengths in Å and angles in deg).

*side-on* complexes (−3.7 to −7.2 kcal/mol) are larger than those in the corresponding *end-on* complexes (−0.7 to −5.9 kcal/mol). This can be rationalized by the steric effect. The stronger the steric effect, the less stable the complex.
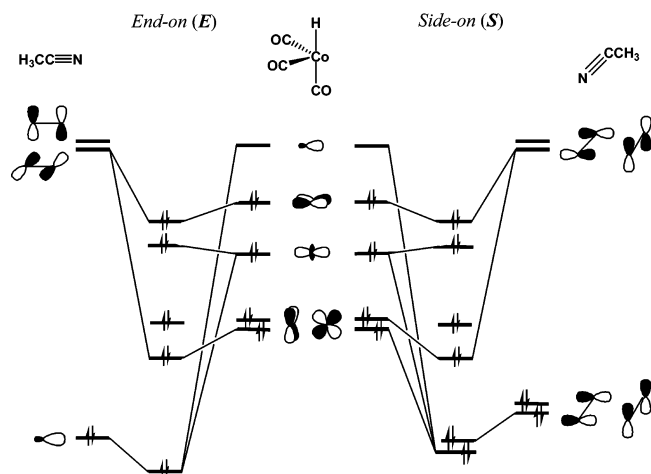
Both experimental and theoretical studies have revealed that stereochemical nonrigidity is a ubiquitous feature of pentacoordinate molecules, and ligand arrangements take place easily.[14] Experimentally, the activation barriers for the rearrangement of $Fe(CO)_5$ and $Fe(CO)_4(olef)$ have been estimated to be 1 and 11−15 kcal/mol,[14e,f] in nice agreement with the ab initio RHF results of 1 and 13 kcal/mol.[14g] Based on the similarity of the acetonitrile complexes $HCo(L)_3(NCCH_3)$ to $Fe(CO)_5$ and $Fe(CO)_4(olef)$, one can expect that the rearrangement of phosphine ligand from the equatorial site (*e*) to the axial site (*a*) in acetonitrile complexes should also occur easily. To verify this deduction, we examined the ligand rearrangement of $HCo(CO)_2(PH_3)$-$(NCCH_3)$ and $HCo(CO)_2(PMe_3)(NCCH_3)$ in both *end-on* (*E*) and *side-on* (*S*) modes. The calculated free energy barriers for the former are 5.1 (*end-on*) and 10.7 kcal/

(14) (a) Ugi, I.; Marquarding, D.; Klusacek, H.; Gillespie, P. *Acc. Chem. Res.* **1971**, *4*, 288. (b) Holmes, R. R. *Acc. Chem. Res.* **1972**, *5*, 296. (c) Meakin, P.; Muetterties, E. L.; Jesson, J. P. *J. Am. Chem. Soc.* **1972**, *94*, 5271. (d) Koga, N.; Jin, S. Q.; Morokuma, K. *J. Am. Chem. Soc.* **1988**, *110*, 3417. (e) Spiess, H. W.; Grosescu, R.; Haeberlen, U. *Chem. Phys.* **1974**, *6*, 226. (f) Wilson, S. T.; Coville, N. J.; Shapley, J. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 4038. (g) Demuynck, J.; Strich, A.; Veillard, A. *Nouv. J. Chim.* **1977**, *1*, 217.

mol (*side-on*), and those for the latter are 6.4 (*end-on*) and 9.7 kcal/mol (*side-on*), respectively. The corresponding structures of the most stable acetonitrile complexes in both *end-on* (*E*) and *side-on* (*S*) modes are illustrated in Table 2, while those of the less stable isomers are given in the Supporting Information.

**(3) Ligand Effect on C≡N Coordination Modes.** The relative free energies between the most stable *side-on* (*S*) and *end-on* (*E*) modes in Table 2 clearly show that all modified catalysts can effectively decrease the free energy difference $\Delta G(S - E)$. With increasing the number of phosphine or NHC ligands, the $\Delta G(S - E)$ decreases considerably. For $PH_3$ substitution (**1I** → **1II** → **1III**), the $\Delta G(S - E)$ decreases from 8.7 to 3.5 and then to 1.9 kcal/mol. A similar case is also found for $PMe_3$ substitution (**2I** → **2II** → **2III**) and NHC substitution (**5I** → **5III**). The $\Delta G(S - E)$ of 1.2 and 2.2 kcal/mol for **2II** and **2III** are smaller than that of **2I** (7.8 kcal/mol). The reverse order for **2II** and **2III** can be attributed to the stronger steric effect in **2III**. Compared to **5I** (6.3 kcal/mol), **5III** gives a very small $\Delta G(S - E)$ of −0.2 kcal/mol, indicating that the *side-on* (*S*) and *end-on* (*E*) modes can coexist equally.

Furthermore, with the increase of the electron-donating ability of the ligands, CO (**0**) < $PH_3$ (**1**) < $PPh_3$ (**3**) < $PMe_3$ (**2**) < NHC (**5**), the $\Delta G(S - E)$ decreases obviously (Table 2). For the monosubstitution (**0** → **1I** → **3I** → **2I** → **5I**), a gradually decreasing tendency of $\Delta G(S - E)$ from 11.1 to 6.3 kcal/mol is observed.

**Figure 3.** Diagram of the orbital interaction between the HCo(CO)$_3$ fragment and NCCH$_3$ in *end-on* mode (*E*) at the left and in *side-on* mode (*S*) at the right.

Similarly, the $\Delta G(\textbf{\textit{S}} - \textbf{\textit{E}})$ for the double substitutions ($\textbf{0} \rightarrow \textbf{1II} \rightarrow \textbf{2II}$) decreases from 11.1 to 1.2 kcal/mol. For the triple substitutions ($\textbf{0} \rightarrow \textbf{1III} \rightarrow \textbf{2III} \rightarrow \textbf{5III}$), the $\Delta G(\textbf{\textit{S}} - \textbf{\textit{E}})$ exhibits a generally decreasing tendency from 11.1 to −0.2 kcal/mol. However, the $\Delta G(\textbf{\textit{S}} - \textbf{\textit{E}})$ for **2III** is slightly larger than that for **1III** (2.2 vs 1.9 kcal/mol), arising from the stronger steric effect in **2III**.

It is noteworthy that the steric effects of PMe$_3$ and NHC play a very important role in the C≡N coordination. For the triple-PMe$_3$-modified catalyst (**2III**), the corresponding *side-on* mode (*S*) is more favored than the *end-on* mode (*E*) in enthalpy by 3.2 kcal/mol, but the large entropy effect reverses the free energy order (Table 2). The same qualitative effect is also found for double-PMe$_3$- and mono-NHC-modified catalyst (**2II/5I**) and triple-NHC-modified catalyst (**5III**).

On the basis of these clear trends, it is therefore expected that stronger electron-donating ligands with smaller steric effects would reverse the stability order from the *end-on* (*E*) to the *side-on* (*S*) coordination. Indeed, this conversion is realized by the dmpe and NHC combination modified catalyst (**4II/5I**). It is found that the corresponding *side-on* complex (*S*) is more stable than the *end-on* isomer (*E*) by 1.1 kcal/mol in free energy. This free energy difference at 298 K gives an estimated equilibrium between the *side-on* (*S*) and *end-on* (*E*) isomers of 6.4 to 1 (or 86%). These results indicate that the normally favored C≡N *end-on* mode (*E*) can be converted to the *side-on* mode (*S*) by reasonable ligand tailoring, and this in turn facilitates the C≡N activation.

**(4) Origin of Ligand Effects.** At this stage, one would ask about the driving force for the conversion of the C≡N *end-on* coordination (*E*) to the *side-on* coordination (*S*). The following discussion focuses on the catalysts HCo(CO)$_3$ (**0**), HCo(PMe$_3$)$_3$ (**2III**), and HCo-(NHC)$_3$ (**5III**) to elucidate this question. The interaction diagram of molecular orbitals between HCo(CO)$_3$[15] and NCCH$_3$ in both *end-on* and *side-on* coordination is displayed in Figure 3.

For the *end-on* complex (*E*), the electron-donating ligand is the nitrogen lone pair, while the degenerate C≡N antibonding $\pi^*$ orbitals can accept d electron from

**Table 3. Orbital Energies (eV) of the Catalysts HCo(L)$_3$ and Natural Charges ($\delta$) of NCCH$_3$ in the Acetonitrile Complexes**

| FMO | HCo(CO)$_3$ (**0**) | HCo(PMe$_3$)$_3$ (**2III**) | HCo(NHC)$_3$ (**5III**) |
|---|---|---|---|
| LUMO | −3.19 | −0.87 | −0.30 |
| HOMO | −6.80 | −3.24 | −2.01 |
| HOMO−1 | −7.33 | −3.90 | −2.93 |
| HOMO−2 | −7.96 | −4.68 | −3.57 |
| HOMO−3 | −8.49 | −4.89 | −3.83 |
| $\delta$(NCCH$_3$) (*E*) | 0.04[a] | −0.09[a] | −0.13[a] |
| $\delta$(NCCH$_3$) (*S*) | −0.03[b] | −0.41[b] | −0.53[b] |

[a] For the *end-on* (*E*) acetonitrile complex. [b] For the *side-on* (*S*) acetonitrile complex.

Co for the back-donation, similar to the well-known *end-on* CO coordination to transition metals.[16] For the *side-on* complex (*S*), the degenerate C≡N bonding $\pi$ orbitals donate electrons for bonding, while the degenerate C≡N antibonding $\pi^*$ orbitals accept electrons for back-bonding. Qualitatively, the interaction diagrams of HCo-(PMe$_3$)$_3$ and HCo(NHC)$_3$ with NCCH$_3$ should be the same, and similar to the well-studied alkyne coordination to transition metals.[17] According to this diagram, the back-donation in the *end-on* (*E*) form is mainly focused between nitrogen and cobalt center, while the back-donation in the *side-on* (*S*) form has a three-center bonding mode. Therefore, the catalyst with strong back-donating ability favors forming the *side-on* (*S*) complex.

As shown in Figure 3, the four highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbital (LUMO) of the HCo(CO)$_3$ fragment contribute dominantly to the overall interaction with NCCH$_3$. Therefore, it is interesting to compare the energies of these orbitals upon changes of ligands. As shown in Table 3, when the catalyst is modified with three PMe$_3$ or three NHC ligands, the energies of the HOMOs are elevated about 3.5 or 4.5 eV, and the LUMO energies are elevated 2.32 or 2.89 eV. As a result, the energy gaps between the catalyst HOMO and the NCCH$_3$ (LUMOs) are reduced, while the energy gaps between the catalyst LUMO and the NCCH$_3$ HOMO are enlarged. On the basis of the Frontier Molecular Orbital theory, the back-donation interactions are considerably enhanced for HCo(PMe$_3$)$_3$ (**2III**) and HCo(NHC)$_3$ (**5III**), while the donation interactions are reduced to some extent. Indeed, the energy gap between the *side-on* (*S*) and *end-on* (*E*) modes decreases from 11.1 kcal/mol for HCo(CO)$_3$ (**0**) to 2.2 kcal/mol for HCo(PMe$_3$)$_3$ (**2III**) and then to −0.2 kcal/mol for HCo(NHC)$_3$ (**5III**). On the other hand, the NCCH$_3$ fragment in the corresponding complexes becomes more negatively charged, and the most pronounced change of the negative charge is found for the *side-on* (*S*) complex of HCo(NHC)$_3$ (**5III**), followed by HCo(PMe$_3$)$_3$ (**2III**).

## Conclusion

Our study has shown the possibility to switch the normally favored C≡N *end-on* mode (*E*) into the *side-on* mode (*S*) by introducing stronger electron-donating ligands. This change in coordination mode can facilitate the C≡N activation. The driving force of this conversion

(15) Versluis, L.; Ziegler, T.; Fan, L. *Inorg. Chem.* **1990**, *29*, 4530.

(16) Sung, S.-S.; Hoffmann, R. *J. Am. Chem. Soc.* **1985**, *107*, 578.
(17) Toreki, R. *Organometallic Hyper TextBook*; http://www.ilpi.com/organomet/index.html.

is the strong back-donation from cobalt to the C≡N bond. With the increased electron-donating ability of the ligands, the energy gap between the *side-on* (*S*) and end-on (*E*) complexes decreases. The catalyst HCo(dmpe)-(NHC) favors the *side-on* coordination (*S*) of acetonitrile over the *end-on* mode (*E*) by 1.1 kcal/mol in free energy. This presents an exciting example of designing catalysts via ligand tailoring. It is expected that not only NHC and dmpe but also other ligands with stronger electron-donating ability should stabilize the *side-on* coordination (*S*) of the C≡N bond to transition metal centers.

**Supporting Information Available:** Total electronic energies, zero-point energies (ZPE), thermal correction to enthalpies, and Gibbs free energies (298.15 K, 1 atm) for all systems, as well as structures for designed catalysts. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0505054