Theoretical study of formation of pyridines by interaction of a cobaltacyclopentadiene with model nitriles (hydrogen cyanide or trifluoroacetonitrile): Electronic effects of nitriles on the reaction mechanism

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ABSTRACT

Theoretical calculations on the reaction of HCN with (η^5-cyclopentadienyl)cobaltacyclopentadiene (**1**) were made by using B3LYP and CCSD(T) methods. Since it is coordinatively unsaturated, **1** is more stable in the triplet state than in the singlet state. However, when HCN interacts with **1**, the singlet state becomes more stable, and the C≡N bond inserts into the Co–C bond in the singlet state to form an azacobaltacycloheptatriene intermediate (**4aS**). The reaction can follow two courses from **4aS**. One is reductive elimination to give an η^4-pyridine complex (**5aS**) that retains a singlet spin state. The other involves a change in spin state to the triplet state to form the more stable triplet state azacobaltacycloheptatriene (**4T**), from which reductive elimination takes place to give a triplet η^2-pyridine complex (**5bT**). The η^4-pyridine complex in the singlet state (**5bS**) is the most stable pyridine complex and contains four carbon atoms of the pyridine ring coordinated to the Co atom. The rearrangement reactions of **5aS** or **5bT** to give **5bS** involve a change in the spin state. The mechanism therefore shows two-state reactivity. This mechanism is different from the reaction of acetonitrile, in which [4 + 2] cycloaddition of MeCN to cobaltacyclopentadiene **1** takes place in the singlet state instead of insertion into the Co–C bond and reductive elimination. This difference can be rationalized in terms of the difference in the energies of the frontier orbitals, so that an electron-donating group favors [4 + 2] cycloaddition and an electron-withdrawing group favors insertion of the C≡N bond into the Co–C bond. This was confirmed by calculations on the reactions of CF₃CN.

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1. Introduction

Compounds containing pyridine rings are of medical, synthetic, and biological importance [1]. In this regard, interest in the preparation of pyridine compounds has a long history [2–5]. Following the pioneering work of Wakatsuki et al. [6,7], in which pyridine compounds were prepared from (η^5-cyclopentadienyl)cobaltacyclopentadiene (**1**) and acetonitrile, a range of compounds containing a pyridine nucleus have been prepared in the presence of a number of different transition metal catalysts [8–55].

We have previously made a theoretical study on the formation of 2-methylpyridine (2-picoline) from (η^5-cyclopentadienyl) cobaltacyclopentadiene (**1**) and acetonitrile [56], and we found that the most favorable mechanism is the two-state reactivity

mechanism shown in Fig. 1. The ground electronic state of (η^5-cyclopentadienyl)cobaltacyclopentadiene (**1**) is a triplet state [56–59]; however, in the most favorable pathway, the formation of the C–C and C–N bonds takes place in the singlet state. Therefore, the electron spin has to change during the course of the reaction. This can be assumed to take place through the minimum-energy crossing point (MECP) between the energy surfaces of two electronic states [60,61]. In the triplet state, we identified the weak reactant complex **2TA** shown in Fig. 1. Starting from this complex, rearrangement to the end-on acetonitrile complex **2SA** in the singlet state takes place through the crossing point **CP2A**. **2SA** is the reactant for the [4 + 2] cycloaddition in the singlet state, which takes place through the four-centered transition state (TS) to give the η^4-2-methylpyridine complex **5aSA**, which has a small activation energy. **5aSA** rearranges through the triplet state to the more stable isomer **5bSA**.

Several groups have made theoretical studies on the formation of pyridine from acetylene and nitriles in the presence of cobalt,
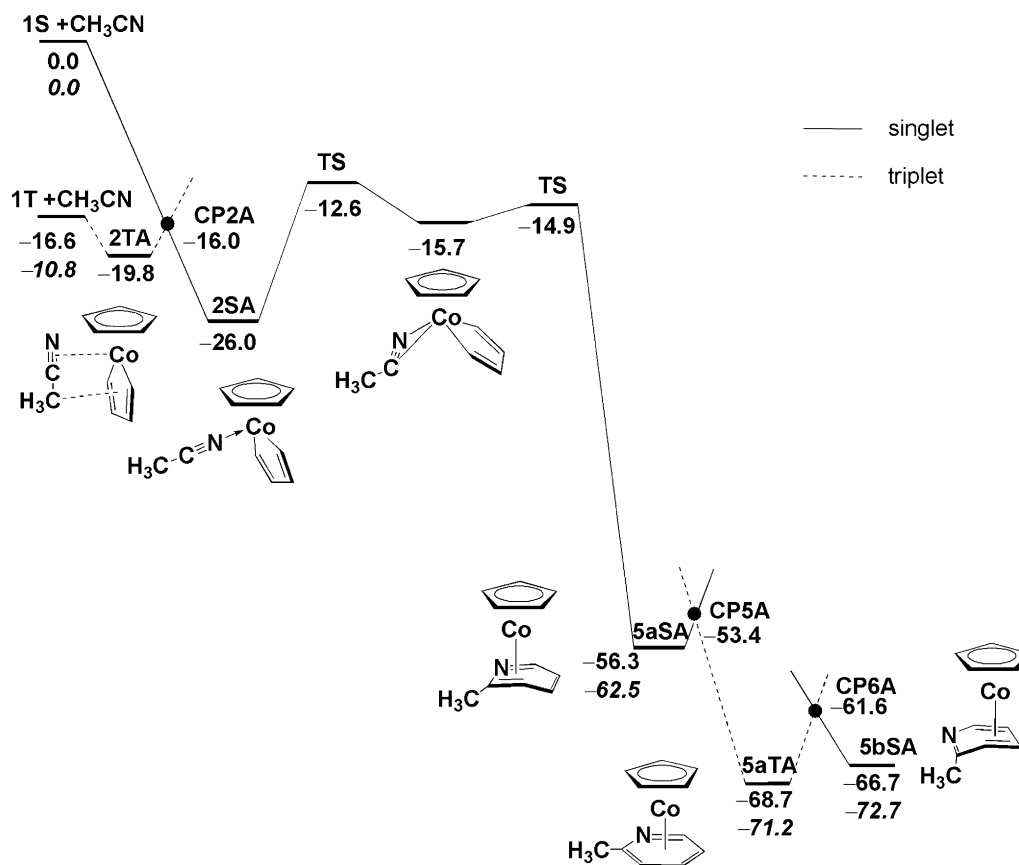
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Fig. 1. Profile for the reaction of CH_3CN with singlet (η^5-cyclopentadienyl)cobaltacyclopentadiene (**1S**) or the corresponding triplet **1T** [56]. All energies are at the B3LYP level with ZPE correction and relative to **1S** + CH_3CN. The numbers in italics are at the CCSD(T)//B3LYP level with B3LYP ZPE-correction.

rhodium, or ruthenium catalysts [62–64]. Dazinger et al. have studied the formation of pyridine from acetylenes and nitriles catalyzed by RuCpCl, CoCp, and RhCp complexes to clarify the favored reaction path and discuss about the chemoselectivity between the formation of pyridine and benzene derivatives [62]. Orian et al. found in their theoretical study for the case of the rhodium catalyst that acetonitrile and acetylene compete with each other in the coordination to rhodacyclopentadiene [63]. In their combined experimental and theoretical study on the preparation of pyridine by the reaction of ruthenacyclopentatriene with nitriles having electron-withdrawing and electron-donating groups, Yamamoto et al. found that the reaction occurs readily in the presence of nitriles including electron-withdrawing groups such as a trifluoromethyl group for which the activation energy is lower compared to the reactions with nitriles including electron-donating groups such as a methyl group [64].

On this basis and in continuation of our theoretical studies on the formation of the pyridine nucleus in the presence of cobalt catalysts, we report a theoretical study on the formation of pyridine and 2-(trifluoromethyl)pyridine by the interaction of (η^5-cyclopentadienyl)cobaltacyclopentadiene with hydrogen cyanide and trifluoroacetonitrile, respectively, for the purpose of investigating the effects on the reaction pathways of replacing an electron-donating group (CH_3) by a hydrogen atom or an electron-withdrawing group (CF_3). A number of mechanisms for this reaction have been suggested in experimental studies [13,17,18,65]. In our theoretical study, the suggested pathways in Scheme 1 were studied, taking into account the possibility of a change in spin state.

2. Computational methods

All the molecular geometries were optimized at the density functional theory (DFT) level by using the B3LYP hybrid functional with the Gaussian 98 and Gaussian 03 suite of programs [66,67]. The B3LYP method involves Becke's three-parameter hybrid exchange functional and the nonlocal correlation functional of Lee, Yang, and Parr [68,69], and it therefore takes account of electron correlation effects. For all the atoms, the all-electron split valence basis set 6-31G(d,p) was used, and this contains polarization functions for heavy atoms and hydrogen atoms [70–72]. In other words, the B3LYP/6-31G(d,p) level of theory used in this work is a reasonable method for obtaining reliable geometries. Normal coordinate analysis was performed for all stationary points to characterize the transition states (TSs) and equilibrium structures. The minimum-energy structures reported in this paper therefore show positive eigenvalues of the Hessian matrix, whereas TSs have one negative eigenvalue. Intrinsic reaction coordinate (IRC) calculations [73,74] near the TS region, followed by optimization of the geometries of both reactants and products were performed for all the reactions to confirm the connectivity of the TS. Unscaled vibrational frequencies were used to calculate the zero-point energy (ZPE) correction for the total energy. The structures of MECPs between the singlet and triplet potential-energy surfaces were optimized with a constraint [75]. Vibrational analysis at this point was performed within the (3N-7)-dimensional hypersurface of the seam of crossing [75].

Unless otherwise noted, we refer to the B3LYP relative energies with the ZPE correction. In addition, to confirm the B3LYP/6-31G(d,
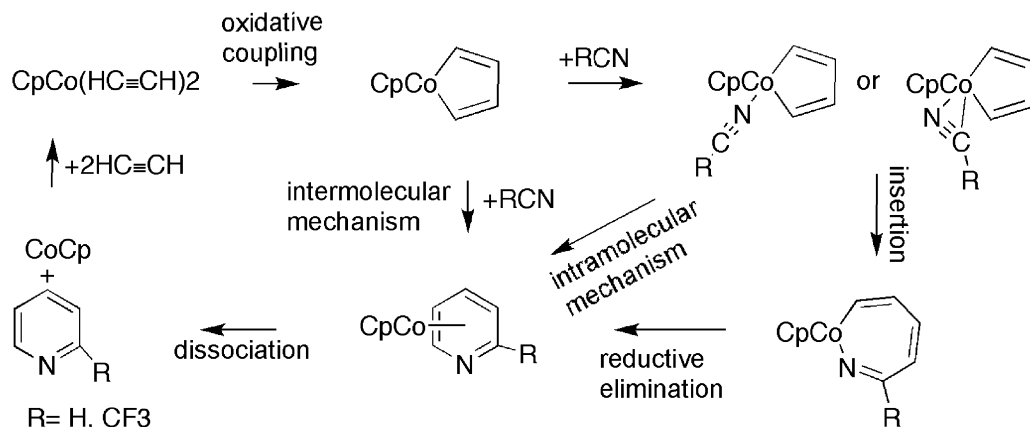
Scheme 1. Suggested mechanisms studied in this work.

p) results for the reaction of HCN, we performed single-point energy calculations for all the intermediates and transition states by means of the coupled cluster theory with single, double, and triple substitutions CCSD(T) [76–81]. It is known that the B3LYP method overstabilizes a high-spin state because of the Hartree–Fock exchange component. Because, as will be discussed later, the change in spin state is important in the present reactions, we also performed the calculations for the reaction of HCN by using the B3LYP* method, in which the weighting of the Hartree–Fock exchange was reduced to 15% [82]. Also, the BP86 method as a pure density functional method was used for comparison [83,84]. The B3LYP* and BP86 results are similar and presented in the Supplementary material. In comparison with the CCSD(T) calculations, the energy difference between the two states seemed to be improved by these methods, but the results were unchanged qualitatively.

3. Results and discussion

3.1. (η^5-Cyclopentadienyl)cobaltacyclopentadiene and its complex with hydrogen cyanide

(η^5-Cyclopentadienyl)cobaltacyclopentadiene with a singlet closed-shell electronic structure is referred to as **1S** (Fig. 2); it has a lowest unoccupied orbital (LUMO) that consists mainly of the Co d orbital and which extends over the vacant coordination site (called 'the front side') [57,58]. This LUMO, shown in Fig. 3, has a sufficiently low energy to introduce a pseudo Jahn–Teller distortion, so that the two Co–C bond distances in the cobaltacyclopentadiene differ from one another [56–59,85]. On the other hand, the ground electronic state of cobaltacyclopentadiene **1** is the triplet state, in which the LUMO of **1S** is singly occupied. According to the B3LYP method, the optimized structure for the triplet state **1T** in Fig. 2 is more stable by 16.5 kcal/mol than **1S** [56–59].

The reaction in the triplet state passes through a weak **1T**···HCN complex (**2T** in Fig. 2) in which the binding energy is only 3.7 kcal/mol, and there is a large distance between the H atom of HCN and the C4 atom of the cobaltacyclopentadiene (2.447 Å). On the singlet potential-energy surface (PES), there is an end-on complex of HCN (**2S**) in which HCN coordinates to the Co atom through the lone pair of electrons on the N atom and is oriented almost perpendicular to the cobaltacyclopentadiene ring. The end-on coordination with the vacant orbital of **1S** is so strong that **2S** is more stable than **2T** by 5.0 kcal/mol. Whereas **1S** is an unsaturated 16-electron species with a central Co(III) atom, **2S** is a saturated 18-electron species. It is apparent therefore that **2S** has a C_s symmetry, so that the pseudo Jahn–Teller deformation present in **1S** has disappeared.

Although the singlet state of cobaltacyclopentadiene **1** is an excited state, we will first discuss the favorable reactions in the singlet electronic state; we will then examine the two-state reactivity mechanism and show that this is plausible.

3.2. Reactions in the singlet state

The optimized structures in this reaction are shown in Figs. 2 and 4, and the energy profile is presented in Fig. 5. The singlet electronic structure of **1S**, which has a low-lying LUMO, leads to a high reactivity. For instance, the [4 + 2] cycloaddition of **1S** and an acetylene molecule is downhill on the PES [58], indicating that the reaction does not require an activation energy. This occurs because this reaction is symmetry-allowed and because the acetylene molecule maintains coordination with the Co atom by using the
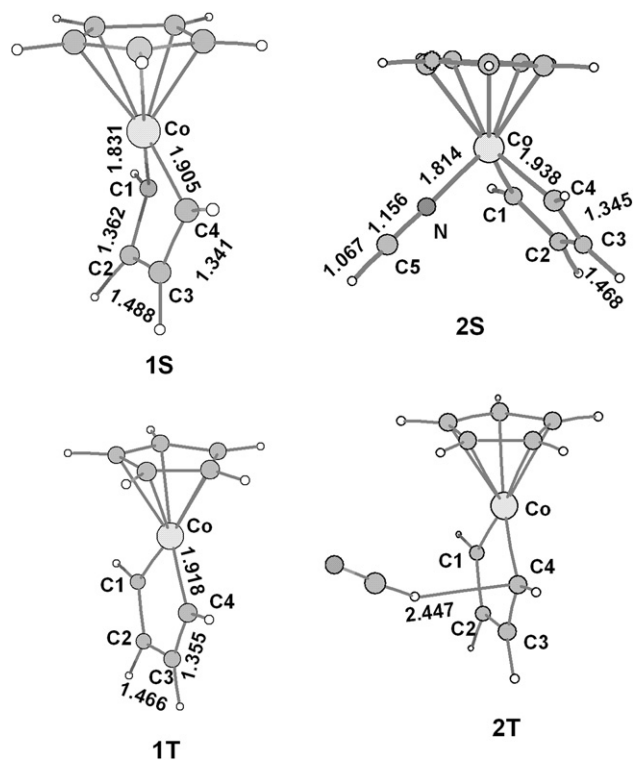

Fig. 2. Optimized structures of (η^5-cyclopentadienyl)cobaltacyclopentadiene in the singlet (**1S**) and triplet (**1T**) states, and of the corresponding HCN complexes **2S** and **2T**. All bond lengths are in Å.
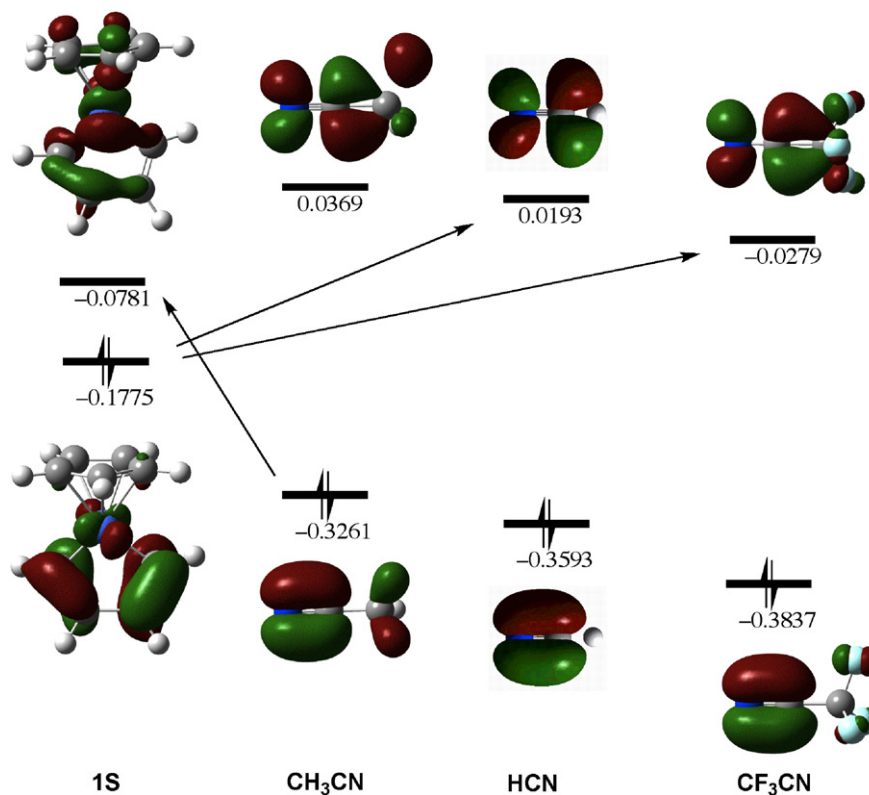
Fig. 3. Highest occupied and lowest unoccupied Kohn−Sham orbitals. The arrows show important electron donation and back-donation.

LUMO of **1S** during the reaction [58]. Similarly, we found that the [4 + 2] cycloaddition of HCN to **1S** is nearly downhill at this level of calculations; as shown in the Supporting material this reaction passes through the side-on HCN complex **2S′** and the transition state **TS$_{2S′-5aS}$** to lead to the η^4-pyridine complex **5aS** (Fig. 4), and the associating activation energy is only 0.02 kcal/mol. Because of this negligible barrier, the reaction mechanism in the singlet state can be regarded as a so-called collapse mechanism. The driving force for this collapse mechanism is the high exothermicity of −61.8 kcal/mol arising from the formation of the new C4−C5 and C1−N σ-bonds, and the aromaticity of the pyridine ring.

Insertion of a hydrogen cyanide molecule into the Co−C4 bond converts **2S** into azacobaltacycloheptatriene **4aS** via transition state **TS$_{2S-4aS}$** with an activation energy of 14.7 kcal/mol. The reaction coordinate at **TS$_{2S-4aS}$** is mainly stretching of the C4···C5 bond. This distance is therefore reduced from 3.547 Å in **2S** to 2.416 Å in **TS$_{2S-4aS}$**, and the formation of the C4−C5 bond is complete in **4aS** with a bond length of 1.496 Å. The C5−N bond formally changes from a triple bond to a double bond, and thus it elongates from 1.156 Å in **2S** to 1.269 Å in **4aS** through **TS$_{2S-4aS}$** (1.173 Å).

Azacobaltacycloheptatriene **4aS** has a puckered structure in which the C3−C4 bond coordinates to the Co atom, with Co−C4 and Co−C3 distances of 2.181 and 2.269 Å, respectively. This coordination makes the interacting C3−C4 bond (1.380 Å) longer than the C1−C2 bond (1.334 Å). As a result of this interaction, **4aS** can be considered as an 18-electron Co(III) species.

Azacobaltacycloheptatriene **4aS** is transformed into the η^4-pyridine complex **5aS** via transition state **TS$_{4aS-5aS}$**. The reaction coordinate at **TS$_{4aS-5aS}$** for this reductive elimination is mainly the stretching of the newly formed C1···N bond, so that the C1···N distance shortens from 2.555 Å in **4aS** to 2.420 Å in **TS$_{4aS-5aS}$**. The C1−N bond is then formed in **5aS** with bond length of 1.408 Å. The activation energy for this step is small (1.3 kcal/mol) because of

the high exothermicity of −34.6 kcal/mol. This high exothermicity is the result of the formation of a new C1−N σ-bond and the coordination of four atoms from the pyridine ring to the Co atom.

It is observed that in **5aS**, the C1−N−C5−C4 fragment coordinates to the Co atom, and coordination of the C2−C1−N−C5 fragment, which is expected in the least-motion path, does not occur. This has been explained in detail in previous studies on the formation of Co(I) complexes of benzene or 2-methylpyridine, in which the benzene and pyridine rings were found to rotate during the formation of the new C−C or C−N bond because the least-motion path is "symmetry forbidden" [56,58].

There is a more stable η^4-pyridine complex **5bS**, and the rearrangement of **5aS**−**5bS** through **TS$_{5aS-5bS}$** is possible with an activation energy of 14.9 kcal/mol; however, as will be shown later, isomerization through the triplet state is more favorable.

Dazinger et al. [62] reported in their theoretical study that the reaction of **1S** with HCN passes through a metallabicycle. Searching for this intermediate leads to **3aS**, as shown in Fig. 4. In the pentagonal ring in **3aS**, the shorter Co−C1 and C2−C3 bonds, which have bond lengths of 1.806 Å and 1.382 Å, respectively, have a double-bond character, whereas the C1−C2, C3−C4, and C4−Co bonds are longer (1.406 Å, 1.451 Å, and 1.988 Å, respectively), showing that they are all single bonds. This bicycle **3aS** transforms into azacobaltacycloheptatriene **4aS** via the transitions state **TS$_{3aS-4aS}$**. The strain imposed in this bicycle makes the activation energy required for the Co−C4 bond cleavage very small (0.05 kcal/mol, without a zero-point-energy correction). With the correction, **TS$_{3aS-4aS}$** becomes more stable than **3aS** by 0.3 kcal/mol, which means that the zero-point-energy-corrected potential-energy surface is downhill. Also, all trials to find a path from **1S** and HCN to bicycle **3aS** failed. These results suggest that the bicycle **3aS** does not play a role in the present reaction. The small activation barrier from **3aS** (0.05 kcal/mol) indicates that the well of **3aS** on the PES is
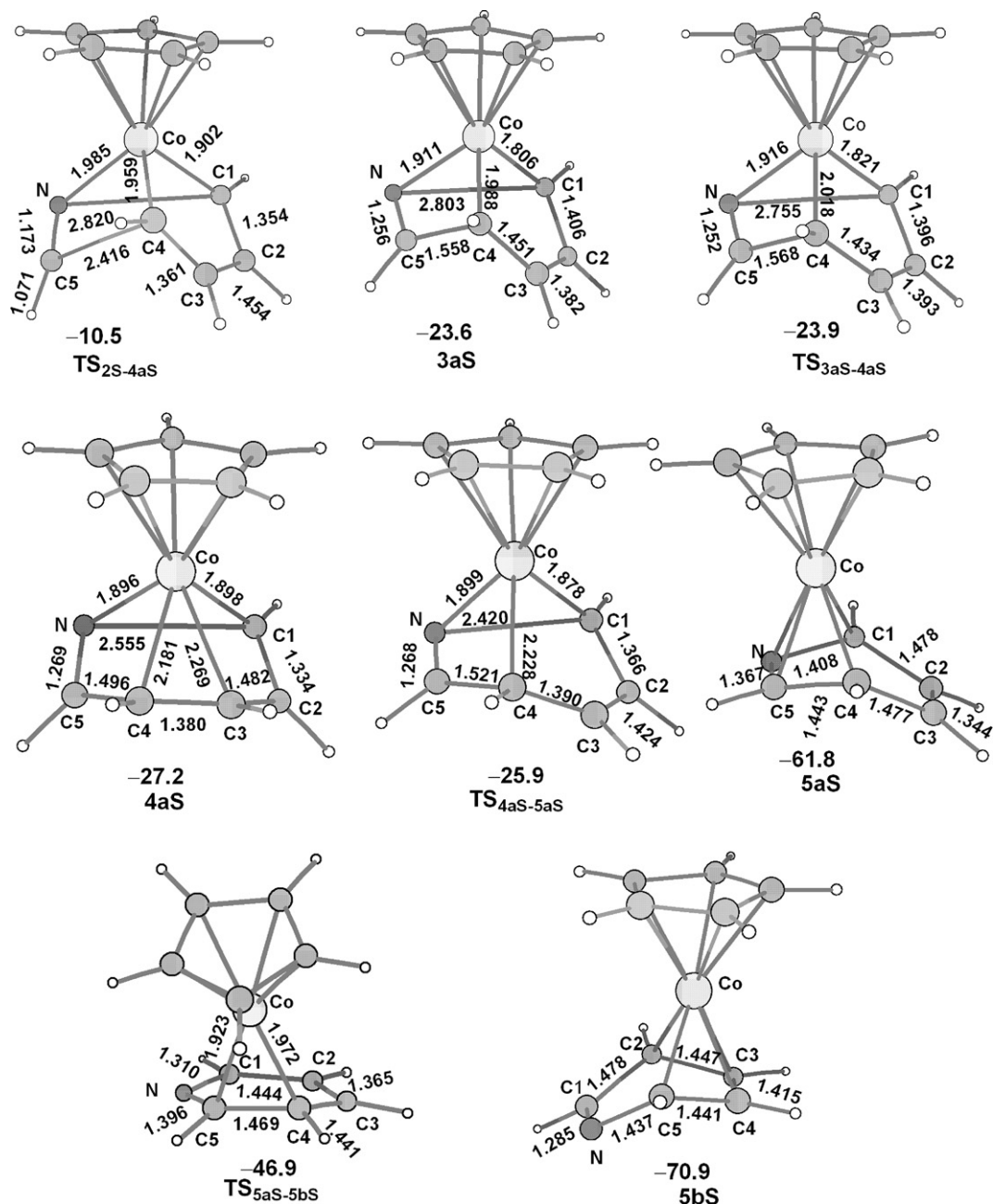
Fig. 4. Optimized structures of azacobaltabicycloheptatriene **3aS**, azacobaltacycloheptatriene **4aS**, η^4-pyridine complexes **5aS** and **5bS**, and the transition states between them in the singlet state. All bond lengths are in Å. The numbers are the B3LYP energies ZPE-corrected and relative to **1S** + HCN in kcal/mol.

very small and shallow, suggesting that, with other computational methods, this minimum may not exist.

The structure of bicycle reported by Dazinger et al. has a long Co–C4 bond distance, and it appears that the structure which we identified as an azacobaltacycloheptatriene was identified as the bicycle with a long Co-C4 bond [62]. With this consideration, the pathway in the singlet state found here is similar to that reported by Dazinger et al. [62] with the sole exception that, while the reactant complex reported in their study is the HCN side-on complex, that in the present study is the HCN end-on complex. At the present level of calculation, although the side-on complex (**2S′**) exists as shown in the supporting material, it is not the intermediate for the reaction of HCN with the Co–C bond but for the [4 + 2] cycloaddition.

3.3. Two-state reactivity

Although **1T** is more stable than **1S**, the coordination of HCN reverses the order of the stability of the states so that **2T** is less stable than **2S**, suggesting that a change in spin state occurs during the reaction. This should take place through an MECP. In other words, the MECP plays the role of a TS in the change of spin state [60,61]. We located the MECPs for the present reaction, and their structures are shown in Fig. 6; the optimized structures in the triplet state, other than **1T** and **2T**, are shown in Fig. 7. The rearrangement of **2T** to **2S** takes place through **CP2**. We also determined the structure of **CP3**, another crossing point from **2T**. As we have discussed above, the reaction of **1S** with HCN to form **5aS** is downhill on the PES. **CP3** is the MECP between this singlet PES and
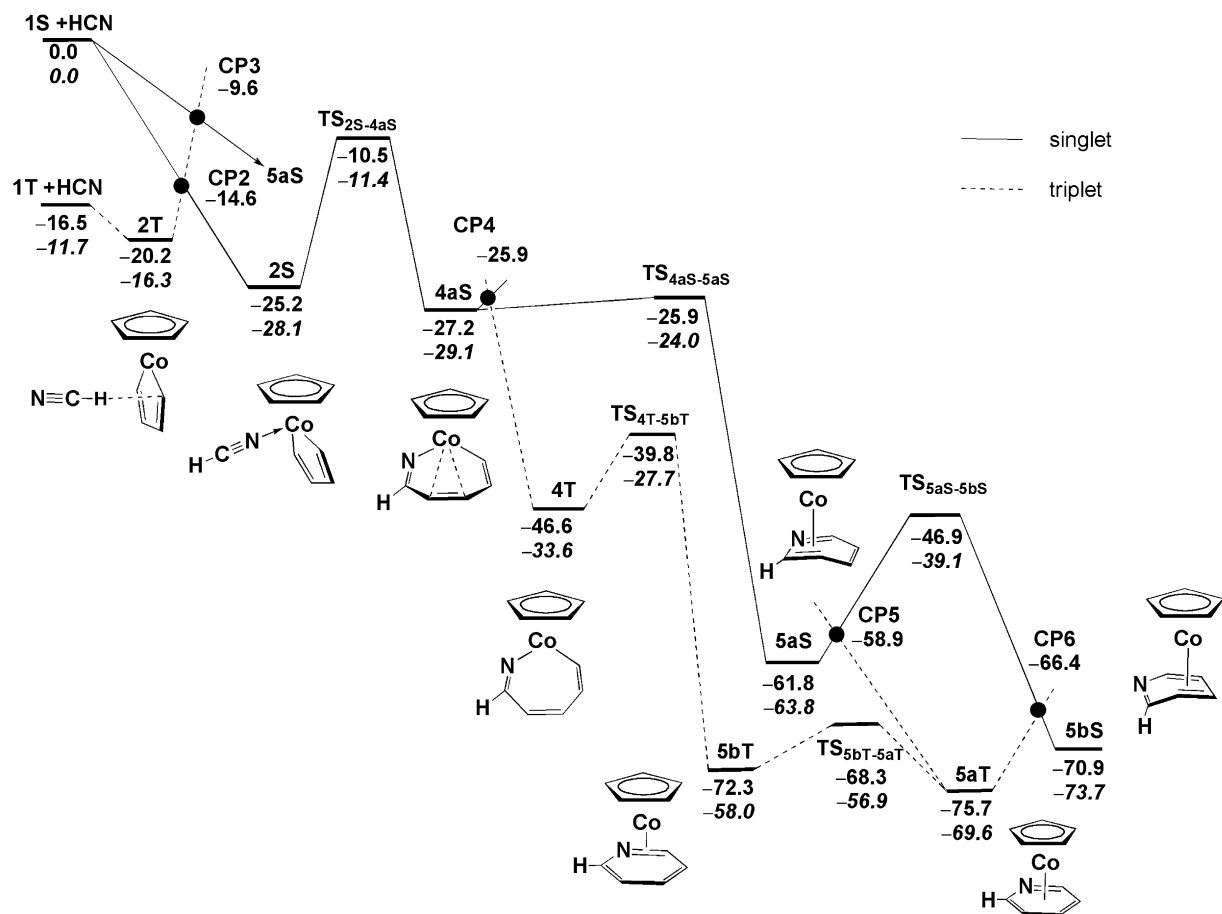
Fig. 5. Profile for the favorable reaction of HCN with (η^5-cyclopentadienyl)cobaltacyclopentadiene in the singlet (**1S**) and triplet (**1T**) states. All energies are at the B3LYP level with ZPE-correction and relative to **1S** + HCN. The numbers in italics are at the CCSD(T)//B3LYP level with B3LYP ZPE-correction.

the triplet PES from **2T** and is similar in structure to **2S'**. Because **CP2** is more stable than **CP3** by 5.6 kcal/mol, the formation of intermediate **2S** is more favorable than that of **5aS**. After the formation of **2S**, azacobaltacycloheptatriene **4aS** is formed through transition state **TS$_{2S-4aS}$**, which is 1.5 kcal/mol more stable than **CP3**. As mentioned above, whereas the reductive elimination from **4aS** to **5aS** is possible with a small activation energy, the rearrangement of **5aS** to **5bS** requires a substantial activation energy of 14.9 kcal/mol. Thus, as we did for the reaction of MeCN, we determined the two MECPs of the pyridine complexes **CP5** and **CP6**. The reaction of **5aS** to give the η^6-pyridine complex **5aT** passes through **CP5** and that of **5aT** to give **5bS** passes through **CP6**. The structures of **CP5** and **CP6** are not very different from the equilibrium structures of the pyridine complexes. Accordingly, **CP5** is only 2.9 kcal/mol less stable than **5aS**, and **CP6** is 9.3 kcal/mol less stable than **5aT**, suggesting that the rearrangement through the triplet state is easier than that through **TS$_{5aS-5bS}$**.

Although the rearrangement of **4aS** to **5aS** is possible with a small activation energy, there exists a triplet azacobatacycloheptatriene **4T** that is more stable than **4aS**. In **4T**, as seen in the reaction of acetonitrile [56], the wide Co–N–C5 angle of 149.6° and the short Co–N bond distance of 1.732 Å suggest that an interaction occurs between the lone pair on the N atom and the Co atom. Furthermore, the weaker interaction between the Co atom and the C3–C4 bond, as a result of the singly occupied d orbital of the Co atom, results in a greater distance between them. Accordingly, we optimized the structure of MECP (**CP4**) connecting **4aS** and **4T**. **CP4** was calculated to have the same energy as **TS$_{4aS-5aS}$**, and therefore

the spin change may occur. The reductive elimination from **4T** to form a pyridine complex passes through **TS$_{4T-5bT}$**, giving the η^2-pyridine complex **5bT**, which could rearrange to the more stable pyridine complex **5aT** through **TS$_{5bT-5aT}$**.

16-electron **4T** and **5bT** are more stable than 18-electron **4aS** and **5aS**, respectively. This can be ascribed to the fact that triplet CpCo is 35.6 kcal/mol more stable than singlet CpCo [56–58]. This large difference in stability between the singlet and triplet Co complexes makes unsaturated **4T** and **5bT** more stable than saturated **4aS** and **5aS**. While **5bT** is a 16-electron complex with an η^2-pyridine ligand, **5aT** is an η^6-pyridine complex with a sandwich structure and can be considered as a 20-electron species. The electronic structure and binding energy for the 2-methylpyridine analog, CpCo(η^6-2-methylpyridine), was discussed in detail [56]. Jonas et al. have reported that trimerization of 2-butyne catalyzed by a Co complex affords paramagnetic 20-electron CpCo(η^6-C$_6$Me$_6$), that is electronically similar to **5aT** [86].

It is known that hybrid density functional theories such as B3LYP, which is used here, overstabilize high-spin states. Therefore, to confirm the reliability of our B3LYP results, we performed CCSD (T) calculations for the intermediates and transition states. The results are shown in italics in Fig. 5. It is clear that the energies of the triplet state structures are, indeed, overstabilized by the B3LYP method and that the most stable pyridine complex is **5bS** in the singlet state. Also, although **4T** and **TS$_{4T-5bT}$** are more stable than **4aS** and **TS$_{4aS-5aS}$**, respectively, **5bT** is less stable than **5aS** at the CCSD(T) level. This suggests that there is another MECP near the pyridine complex. However, because the structures of **5bT** and
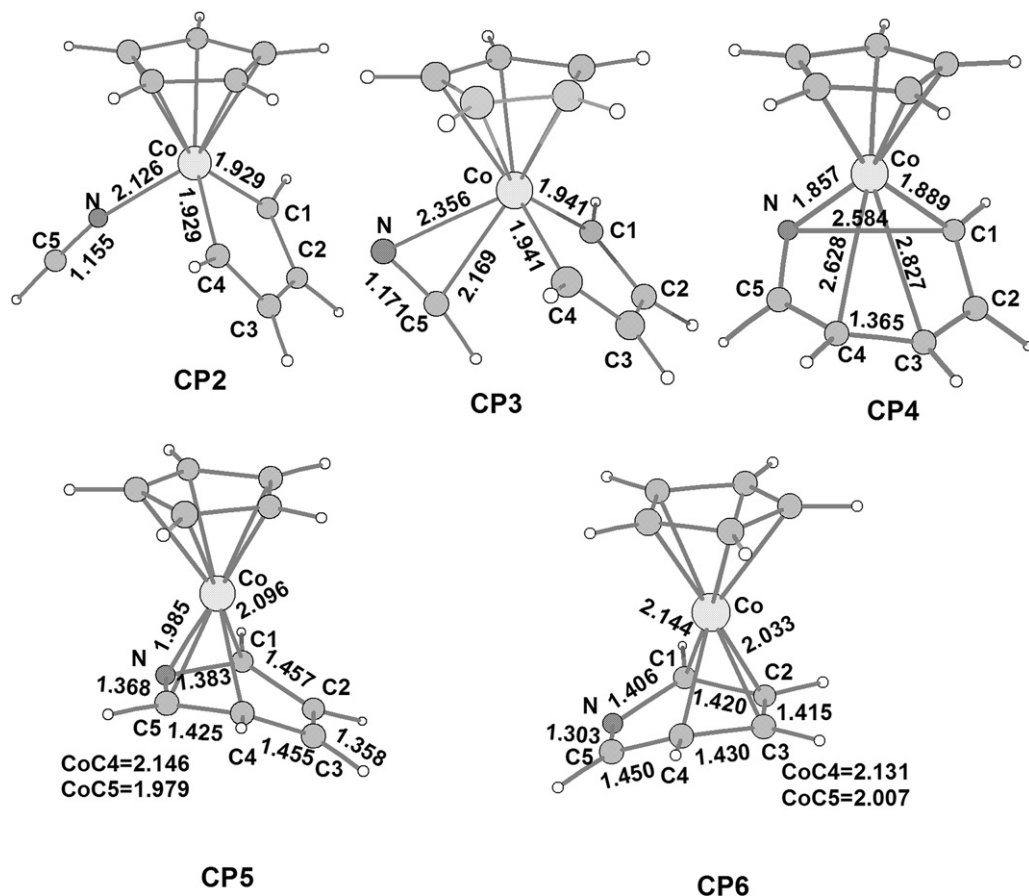
Fig. 6. Optimized structures for the crossing points **CP2** to **CP6**. All bond lengths are in Å.

TS$_{5aT-5bT}$ are very different from that of **5aS**, there should be no MECP. Consequently, the qualitative results are unchanged by the CCSD(T) calculations, except for the point that the most stable pyridine complex is the singlet **5bS**. As shown in the supporting material, the B3LYP* and BP86 calculations gave the qualitatively similar results that **5bS** is the most stable.

We therefore find that the most favorable reaction path passes through singlet azacobaltacycloheptatriene **4aS** following the reaction scheme: **1T** + HCN → **2T** → **CP2** → **2S** → **4aS**. There are therefore two possible reaction pathways. One starts with the reaction in the singlet state and leads to the singlet pyridine complex, and this then rearranges to the most stable pyridine complex **5bS**: **4aS** → **5aS** → **CP5** → **5aT** → **CP6** → **5bS**. The other is a sequence of reactions that includes the formation of the C–N bond in the triplet state: **4aS** → **CP4** → **4T** → **5bT** → **5aT** → **CP6** → **5bS**. We believe that the latter is more favorable, because **4T** and **TS$_{4aT-5bT}$** are more stable than their singlet analogues.

In summary, a path exists via end-on HCN complex and azacobaltacycloheptatriene intermediates, as suggested by Wakatsuki et al. [65] and shown in Scheme 1. This is different from the reaction of acetonitrile, where there is no reaction path via an azacobaltacyclohepatriene intermediate. The ground states for the cobaltacyclopentadiene and azacobaltacycloheptatriene intermediates are the triplet state. Therefore, the two-state reactivity mechanism is adopted. The rearrangement of the pyridine complex that is formed also follows the two-state reactivity mechanism. The rate-determining step is the transformation of **2S** into **4aS** via **TS$_{2S-4aS}$**; this requires an activation energy of 14.7 kcal/mol at the B3LYP/6-31G(d,p) level and 16.7 kcal/mol at the CCSD(T)/6-31G(d,p)//B3LYP/6-

31G(d,p) level. As shown in the supporting material this value is 15.3 and 14.8 kcal/mol at B3LYP*/6-31G(d,p) and BP86/6-31G(d,p) levels, respectively.

3.4. Other reaction pathways studied

We also studied other possible reaction pathways, but these are less favored than the pathways discussed above, or the intermediates do not originate from **1**s and HCN. These alternative pathways are shown in Fig. 8, and detailed results are provided in the Supplementary material.

There exists another singlet azacobaltacycloheptatriene intermediate **4bS**, in which the atom coordinating to the Co atom is the C5 atom of HCN and not the N atom. **4bS** is less stable than **4aS**, and there is no reaction path from **1S** + HCN to **4bS**, unlike the case of **4aS**, suggesting the importance of the interaction of the N lone-pair electrons with the Co atom. Also, though **4bS** can be obtained from azacobaltabicycloheptatriene **3bS**, there is no reaction path from **1S** + HCN to **3bS**. We also studied an intermolecular [4 + 2] cycloaddition path in the singlet state. The calculations showed that this reaction passes through the intermediate **6S** and the transition state **TS$_{6S-5bS}$** to give **5bS**. **TS$_{6S-5bS}$** is much less stable than the other intermediates and transitions states in the singlet state, because HCN attacks the Co atom from the rear side, over which only a small lobe of LUMO extends. This is similar to the reaction of MeCN.

We located the transition states **TS$_{2T-5aT}$(1)** and **TS$_{2T-5aT}$(2)** for the reactions of HCN with the triplet cobaltacyclopentadiene. These reactions start from the weak complex **2T** and end at the
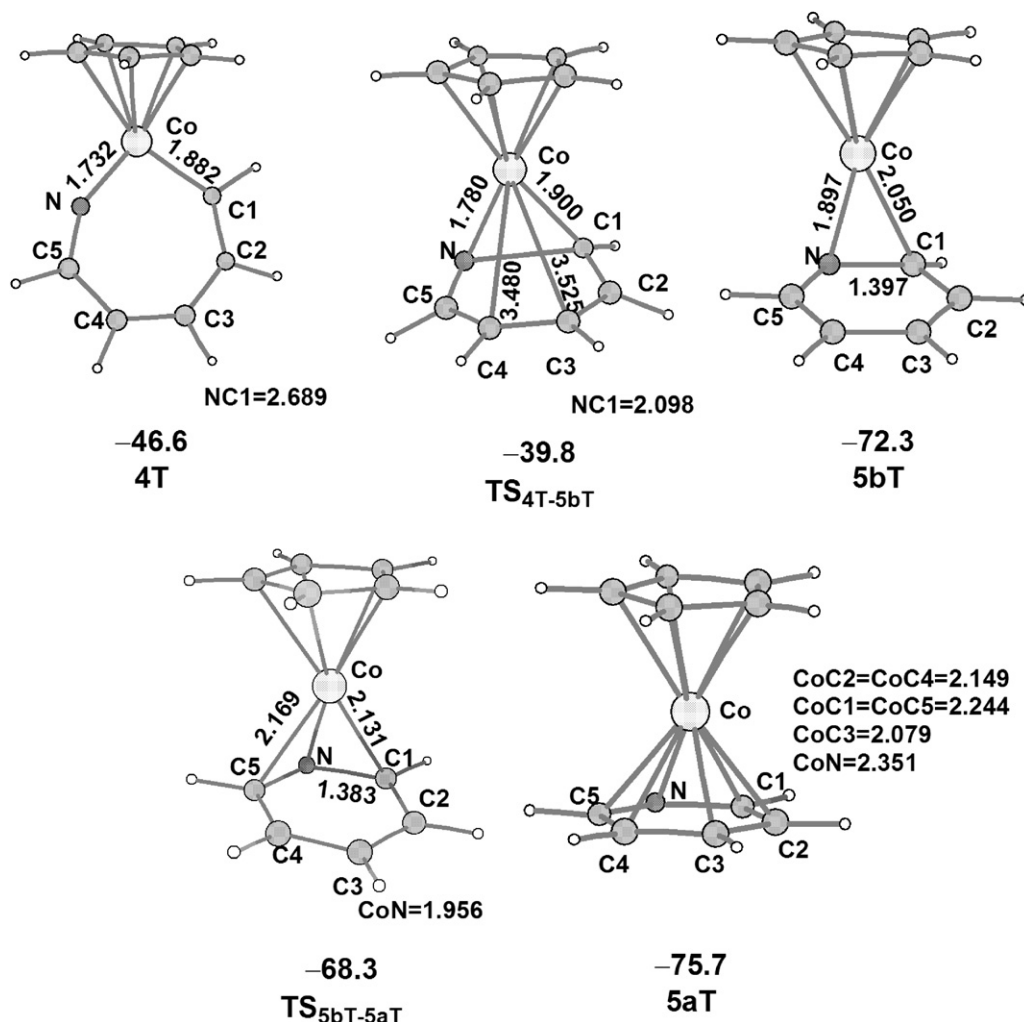
Fig. 7. Optimized structures of azacobaltacycloheptatriene **4T**, η^2-pyridine complex **5bT**, η^6-pyridine complex **5aT**, and the transition states between them in the triplet state. All bond lengths are in Å. The numbers are the B3LYP energies ZPE-corrected and relative to **1S** + HCN in kcal/mol.

η^6-pyridine complex **5aT**. **TS$_{2T–5aT}$(1)** is the transition state for the intermolecular path, judged from the longer distance between HCN and the Co atom, and it corresponds to **TS3T** reported for the reaction of MeCN [56]. On the other hand, at **TS$_{2T–5aT}$(2)** the N and C atoms of HCN attack the C4 and Co atoms, respectively. Like the reactions of MeCN, the former transition state for the intermolecular path is more stable. These transition states are less stable than the intermediates and transition states in the singlet state.

We located another transition state near this region on the PES. This transitions state is more stable than **TS$_{2T–5aT}$(1)** or **TS$_{2T–5aT}$(2)**. Although the C≡N bond interacts with the Co–C4 bond at this TS, both the corresponding reactant and product are cobaltacycloheptatriene **4T**. Therefore, this is not directly related to the present reaction, and we show the results for this transition state (**TS$_{4T–4T}$**) only in the supplementary material.

3.5. Comparison with the reaction of acetonitrile

There is a large difference between the profile of the reaction of HCN and that of MeCN, although both reactions follow a two-state reactivity mechanism. The first difference is that [4 + 2] cycloaddition in the singlet state for the reaction of HCN is downhill whereas a side-on MeCN complex occurs as an intermediate during the reaction of MeCN. The electron-donating methyl group in acetonitrile stabilizes side-on coordination [87,88] (see below).

After the reactions have passed through the end-on complexes of MeCN and HCN in the singlet state, the subsequent pathways are different. The reaction of MeCN follows an intramolecular [4 + 2] cycloaddition, whereas that of HCN passes through azacobaltacycloheptatriene. This difference can be explained in terms of the orbital energies and shapes of HCN, MeCN, and **1S**, as shown in Fig. 3. The LUMO of **1S** consists mainly of the Co d orbital with a small delocalization to the butadienediyl and Cp fragments, and the HOMO is similar to that of butadiene with a small out-of-phase mixing of the occupied d orbital. The former point suggests that π-donation from RCN to **1S** favors the side-on coordination of the CN bond to the Co atom, and thus the approach of RCN for [4 + 2] cycloaddition. π-Back-donation from **1S** to RCN should assist both the addition of RCN to the Co–C4 bond and [4 + 2] cycloaddition. However, the Co–C4 bond distance matches the CN bond distance better than it matches the C1–C4 distance, facilitating overlap between the RCN π^* orbital and the LUMO of **1S**. As can be seen in Fig. 3, the methyl group in MeCN shifts the HOMO and LUMO up in energy, and selectively enhances donation to **1S**, facilitating the intramolecular [4 + 2] cycloaddition. On the other hand, in the reaction of HCN, back-donation from the HOMO of **1S** to the LUMO of HCN, which is more stable than the LUMO of MeCN, is more
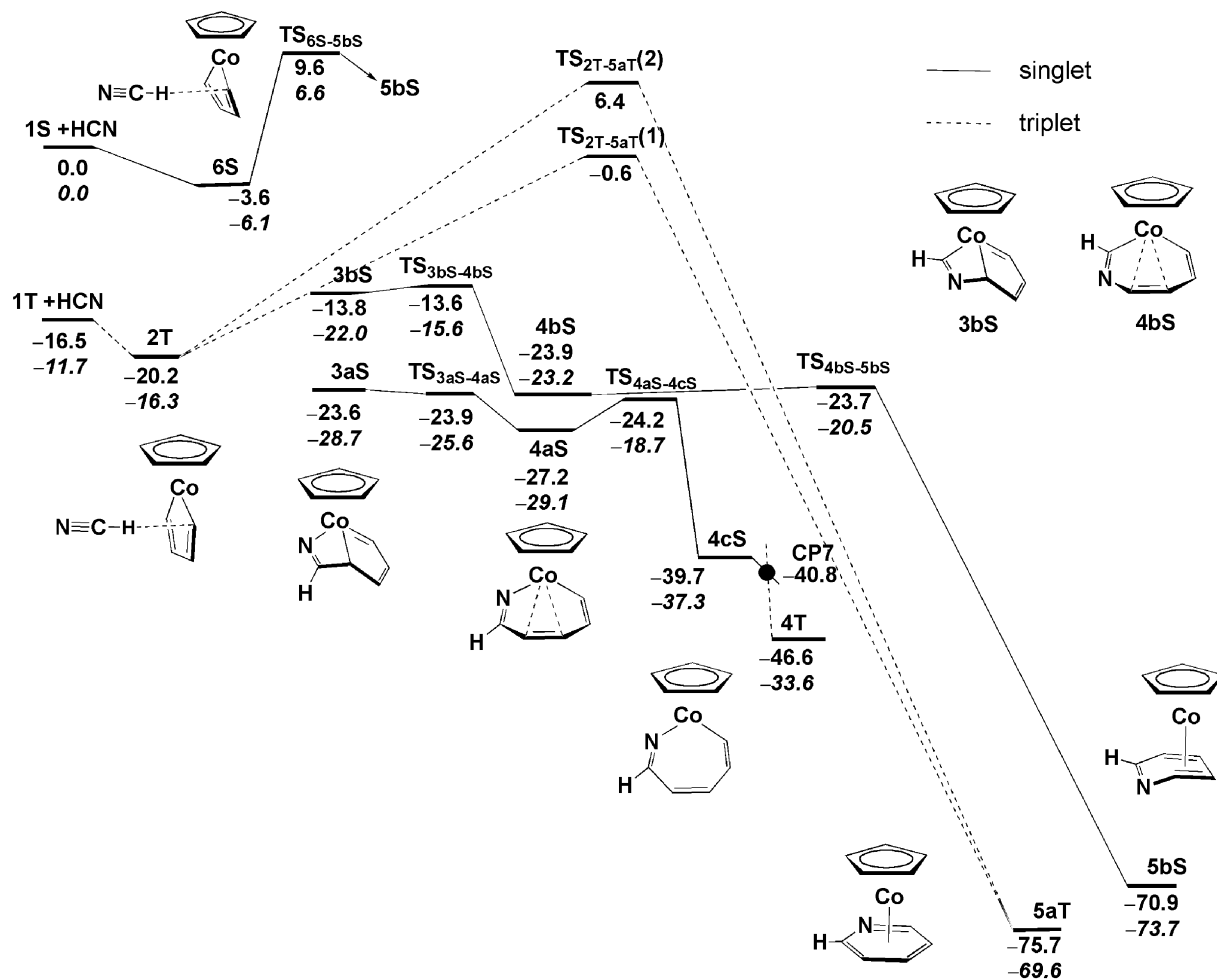
Fig. 8. Profile for the unfavorable reaction of HCN with (η^5-cyclopentadienyl)cobaltacyclopentadiene in the singlet (**1S**) and triplet (**1T**) states, respectively. All energies are at the B3LYP level with ZPE-correction and relative to **1S** + HCN. The numbers in italics are at the CCSD(T)//B3LYP level with B3LYP ZPE-correction.

important. This suggests that the presence of an electron-withdrawing group in RCN should tend to favor the course of the reaction through azacobaltacycloheptatriene. This will be verified in the next section for the case of trifluoroacetonitrile.

3.6. The reaction of (η^5-cyclopentadienyl)cobaltacyclopentadiene with trifluoroacetonitrile

For comparison, we conducted the calculations for the cycloaddition of trifluoroacetonitrile to cobaltacyclopentadiene. While with Co catalysts electron-rich nitriles are more effective [40,89] and the reactions of nitriles having strongly electron-withdrawing substituents have not been reported to the best of our knowledge, the pyridine derivatives are yielded with EtCO$_2$CH$_2$CN [90]. As shown in Fig. 9, the path of this reaction is qualitatively very similar to that of the reaction of HCN. The largest difference is that the bicycle **8aS** is the intermediate in the reaction. As a result, the most favorable reaction starts with **1T** and CF$_3$CN, and the intermediate complex **1T**···CF$_3$CN (**7T**) is formed. On passing through **CP8**, a change in spin occurs to give the CF$_3$CN end-on complex **7S** in the singlet state. As expected, strong coordination of CF$_3$CN occurs in **7S**, and the N−Co bond distance is 1.794 Å. The next step in this mechanism is the addition of the C≡N bond to the Co−C bond, which results in the formation of bicycle **8aS** via **TS$_{7S-8aS}$** with an activation energy of 12.9 kcal/mol. Note that in this step [4 + 2] cycloaddition is not favorable as discussed in the last

subsection. This is followed by rupture of the Co−C4 bond through **TS$_{8aS-9aS}$** to give azacobaltacycloheptatriene **9aS**. The ZPE-correction makes **8aS** less stable than **TS$_{8aS-9aS}$** by 0.01 kcal/mol; so this reaction does not require an activation energy. As in the case of HCN, there are two possible reaction paths from **9aS**. One follows the reaction path in the singlet state, and the other involves a change in the spin state through **CP9** so that the reaction proceeds in the triplet state. In both cases, the subsequent steps involve the formation of a C−N bond to give the corresponding 2-(trifluoromethyl)pyridine complex **10aS** or **10bT** with a small activation energy; the activation energy of the reaction leading to **10aS** is 2.8 kcal/mol, whereas that of **9T** to give **10bT** requires an activation energy of 6.8 kcal/mol. **10aS** rearranges to the more stable 2-(trifluormethyl)pyridine complex **10bS** with an activation energy of 11.7 kcal/mol. However, the reaction through the triplet intermediate **10aT** and two MECPs, **CP10** and **CP11**, is energetically more favorable. Unlike the case of HCN, the η^6-[2-(trifluoromethyl)pyridine] complex **10aT** is less stable than η^2-[2-(trifluoromethyl)pyridine] complex **10cT**, although the energy difference is small. At the B3LYP level, **10cT** and **10bS** are similar in energy. With better methods of calculations, **10bS** would be the most stable 2-(trifluoromethyl)pyridine complex.

CP9, **9T**, and **TS$_{9T-10bT}$** are more stable than **TS$_{9aS-10aS}$**, suggesting that the reaction path in the triplet state is more favorable than that in the singlet state. Consequently, the most favorable reaction path is **1T** + CF$_3$CN → **1T**···CF$_3$CN → **CP8** → **7S** →
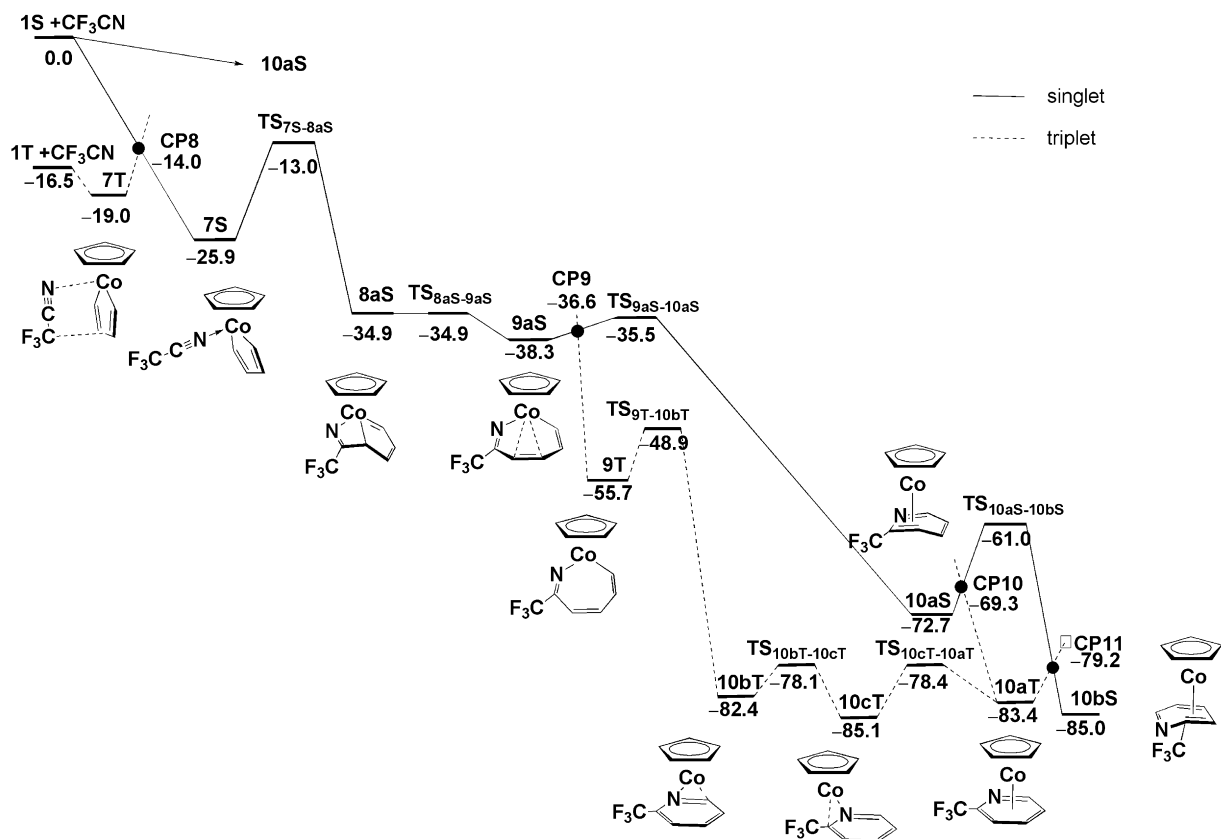
Fig. 9. Profile for the favorable reaction of CF$_3$CN with singlet and triplet (η^5-cyclopentadienyl)cobaltacyclopentadiene in the singlet (**1S**) and triplet (**1T**) states. All energies are at the B3LYP level with ZPE-correction and relative to **1S** + CF$_3$CN.

8aS → 9aS → CP9 → 9T → 10bT → 10cT → 10aT → CP11 → 10bS, in which the addition of the C≡N bond to the Co−C bond is involved and the [4 + 2] cycloaddition is not. The largest activation energy (12.9 kcal/mol) is required in the addition of the C≡N bond to the Co−C4 bond from **7S** to **8aS**.

4. Conclusion

By using the B3LYP theoretical method, we have studied the reaction of HCN with cobaltacyclopentadiene **1** in detail to clarify the favored reaction pathway. Although the reaction begins with **1** in the triplet state, the most stable pyridine complex as a product is the η^4-pyridine complex **5bS**, in which four of the C atoms of the pyridine ring coordinate to the Co atom. We therefore studied the changes in spin state that occur during the course of the reactions by locating energy minimum crossing points between the two spin states. The most favorable pathway that we found passes through azacobaltacycloheptatriene **4aS** (formed by insertion of HCN into the Co−C bond in the singlet state), azacobaltacyclo-heptatriene **4aT**, and the η^2- and η^6-pyridine complexes **5bT** and **5aT** in the triplet state, as follows: **1T** + HCN → **2T → CP2 → 2S → 4aS → CP4 → 4T → 5bT → 5aT → CP6 → 5bS**. This is different from the reaction of acetonitrile, in which [4 + 2] cycloaddition of MeCN to the cobaltacyclopentadiene **1** takes place in the singlet state, instead of insertion into the Co−C bond and reductive elimination. This difference can be rationalized in terms of the difference in the energies of the frontier orbitals, so that the electron-donating group favors [4 + 2] cycloaddition, and the electron-withdrawing group favors insertion of the C≡N bond into the Co−C bond. This was confirmed by calculations for the reactions of CF$_3$CN.

Acknowledgments

Appendix. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jorganchem.2010.06.015.

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