

Cobalt-Mediated [2 + 2 + 2] Cycloaddition versus C–H and N–H Activation of 2-Pyridones and Pyrazinones with Alkynes: A Theoretical Study

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Abstract: DFT computations have been executed aimed at illuminating the variety of pathways by which pyridones react with alkynes in the presence of [CpCoL₂]: NH-2-pyridones furnish *N*-dienylated ligands (N–H activation pathway), *N*-methyl-2-pyridones are converted into ligated cyclohexadienes ([2 + 2 + 2] cocycloaddition path-

way), and *N*-alkynyl-2-pyridones may undergo either [2 + 2 + 2] cocycloaddition or *C*-dienylation (C–H activation), depending on the length of the tether.

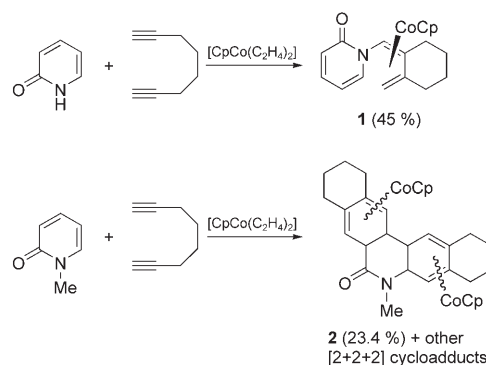
Keywords: C–H activation • cobalt • cycloaddition • density functional calculations • N–H activation

The calculations predict the formation of the experimentally observed products, including their regio- and stereochemical make up. In addition, the unusual regiochemical outcome of the all-intramolecular [2 + 2 + 2] cycloaddition of *N,N*-dipentynylpyrazinedione was rationalized by computation, which led to the discovery of a new mechanism.

Introduction

The [2 + 2 + 2] cocycloaddition of C–C double and triple bonds is one of the most elegant methods for forming six-membered rings in a single operational step. For instance, the cocyclization of three alkynes gives benzene derivatives, whereas that of two alkynes to one alkene allows the construction of 1,3-cyclohexadienes. Transition metals, as catalysts or reagents, are often used to effect such transformations. Cobalt complexes of type [CpCoL₂] (L = CO, PR₃, alkenes) have proven to be particularly versatile, in as much as they do so in a highly chemo-, regio-, and stereoselective way, and with a broad substrate scope.^[1] In an exploration of the cobalt-mediated activation of C–C bonds in heteroaromatic systems toward the [2 + 2 + 2] cycloaddition with alkynes, we have shown that furans,^[2] benzofurans,^[3] thio-

phenes,^[2] indoles,^[4] pyrroles,^[5] imidazoles,^[6] and pyrimidines^[7] produce novel fused dihydroheteroaromatics that are inaccessible by conventional methods. As a continuation of this work, we targeted pyridones and pyrazinones as new cyclization partners^[8] and observed a puzzling divergence in reactivity from the expected [2 + 2 + 2] cycloaddition mode to one in which C–H or N–H bond activation with simultaneous double alkyne insertion took place, depending on the nature of the substrates. For instance, in the presence of [CpCo(C₂H₄)₂], the parent 2-pyridone and 1,7-octadiyne led to *N*-dienylated heterocycle **1** with the *Z*-configuration, via N–H activation (Scheme 1). On the other hand, *N*-methyl-2-pyridone gave rise to double [2 + 2 + 2] cycloadducts such as



Scheme 1. Cobalt-mediated cycloadditions of 1,7-octadiyne to 2-pyridones.

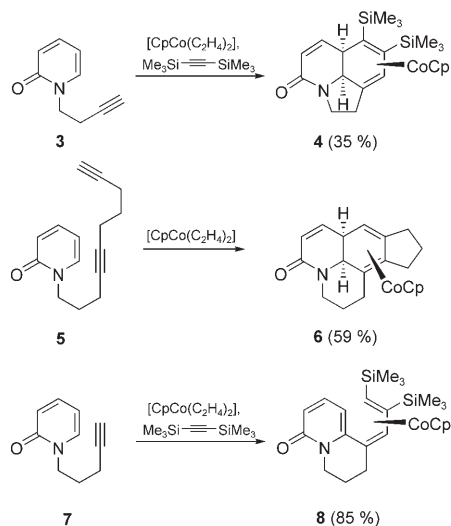
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2, seemingly without discrimination between the two types of double bonds in the heterocycle and with only moderate stereoselectivity.

Tethering one or both of the alkyne cocyclization units to the pyridone nucleus, as in **3** and **5**, permitted regioselective enamine double bond activation, as in **4** and **6** (Scheme 2).



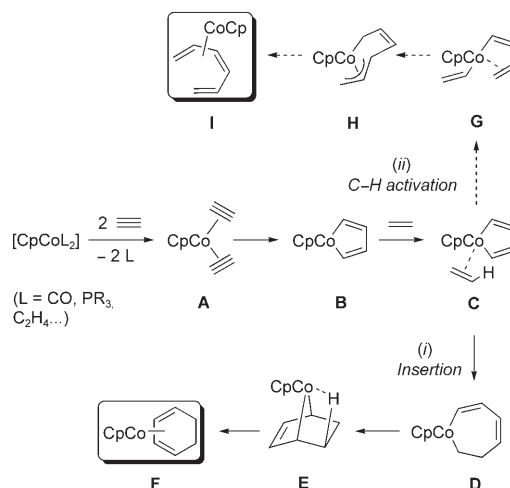
Scheme 2. Cobalt-mediated [2+2+2] cycloadditions versus C–H activation with *N*-alkynyl-2-pyridones.

The products were obtained as single diastereomers, displaying an *anti* relationship of the metal and the hydrogens at the ring junction. Surprisingly, in view of the results obtained with **3** and **5**, analogue **7** transformed by C–H activation to give C-dienylated pyridone **8**.^[8] While we had never encountered previously N–H activations of the type leading to **1** in this chemistry, C-dienylation was noted occasionally with other heterocycles, in the case of some furans and thiophenes even catalytically.^[2,4a,7a] Moreover, recent work in our laboratories has revealed that even simple alkenes, including ethene, undergo this process.^[9] A clue with respect

Abstract in German: *Es wurden DFT Berechnungen angestellt, um Licht in die vielfältigen Reaktionswege zu bringen, durch die Pyridone mit Alkinen in Gegenwart von [CpCoL₂] reagieren: NH-2-Pyridone ergeben N-Dienliganden (N–H Aktivierung), N-Methyl-2-pyridone geben komplexierte Cyclohexadiene ([2+2+2] Cocycloaddition), und N-Alkynyl-2-pyridone unterlaufen in Abhängigkeit von der Kettenlänge entweder eine [2+2+2] Cocycloaddition oder C-Dienylierung (C–H Aktivierung). Die Berechnungen sagen die experimentell beobachteten Produkte voraus, inklusive deren regio- und stereochemischem Aufbau. Darüberhinaus konnte durch Berechnungen der ungewöhnliche regiochemische Verlauf der komplett intramolekularen [2+2+2] Cycloaddition von N,N-Dipentinylylpyrazindion erklärt werden, was zur Entdeckung eines neuen Mechanismus führte.*

to the mechanism of these insertions was provided in early investigations by Yamazaki and Wakatsuki, in which both types were observed during the thermolysis of Cp cobaltacyclopentadienes,^[10] implicating the latter as intermediates. Indeed, DFT calculations addressing this issue with ethene, benzene, furan, and thiophene confirmed this pathway and delineated the details of the more commonly encountered [2+2+2] cycloaddition.^[11]

A summary of the outcome of these estimations, as it pertains to the subject of this paper, is shown in Scheme 3. In



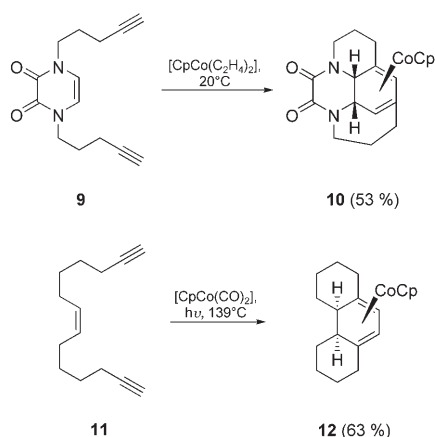
Scheme 3. The two relevant mechanisms on route to [2+2+2] and C–H activation products discussed in this paper.

this proposal, the bisethyne cobalt complex **A** is converted into the cobaltacyclopentadiene **B**,^[12] which then ligates ethene to give the corresponding 18-electron complex **C**. The latter may continue in two ways: In the first (*i* in Scheme 3), insertion into a Co–C σ bond furnishes cobaltacycloheptadiene **D** which rearranges into cobaltanorbornene **E**, and subsequently undergoes reductive elimination to CpCo-complexed cyclohexadiene **F**.^[13,14] In the second (*ii* in Scheme 3), a hydrogen transfers from the coordinated alkene to the α -carbon atom of the metallacyclic moiety, generating the dienylvinyl cobalt complex **G**. This compound isomerizes into the π -allyl system **H**, which reductively eliminates to provide the triene complex **I**.

For ethene, pathway (*ii*) was found to be disfavored over pathway (*i*),^[15] but for C–C bonds of aromatic systems the two options became competitive. Indeed, the reaction of benzene with complex **B** followed preferably the C–H activation route (by 7.5 kcal mol^{−1}) (*ii*), while for (either position in) thiophene this preference was attenuated (<1.5 kcal mol^{−1}), for furan reversed slightly (2–3 kcal mol^{−1}).^[16] These trends indicate that aromaticity (or the loss thereof) is a strong determinant in the relative viability of the insertion step. One notes that various estimates of aromaticity rank, in decreasing order, benzene, thiophene, furan, and pyridone \approx pyrazinone.^[17] Turning to N–H activation, as in the formation of **1**, this process had not been considered by

us computationally prior to its observation in our methodology.^[18]

Because, in the 2-pyridone series, all three modes of reactivity were encountered in a selective manner, the main focus of the present effort was to scrutinize the behaviour of this system in the presence of cyclopentadienylcobaltcyclopentadiene theoretically, to gain some insight into the energies and structures of the intermediate species involved. Since the nitrogen substitution in the corresponding pyrazinones did not alter their reactivity pattern, calculations on this system were not carried out, with the exception of the unique cyclization of *N,N'*-dipentynylpyrazinedione **9**, which leads unexpectedly to the unsymmetrically fused system **10** (Scheme 4).^[8] This behaviour is in stark contrast to other all-



Scheme 4. The differing outcome of the intramolecular [2+2+2] cycloadditions of **9** and **11**, respectively.

intramolecular [2+2+2] cycloadditions mediated by CpCo,^[1a,b,g,4b,5,19] specifically the all-carbon analogue **11**, which was found to convert to the expected symmetrical cyclohexadiene cobalt complex **12**.^[20] The ligand in **10** constitutes formally an anti-Bredt molecule^[21] and, indeed, an investigation of the mechanism of its formation allowed us to uncover a new reaction pathway.

Results and Discussion

Computational details: All geometries of intermediates and transition states were optimized fully without symmetry constraints using the Gaussian 03 program.^[22] The DFT computations were carried out using the RB3LYP functional, as implemented in Gaussian and employing the LACVP(d,p) basis set: The cobalt atom was described by a double- ζ basis set with the effective core potential of Hay and Wadt (LANL2DZ),^[23] and the 6-31G(d,p) basis set^[24] was used for the other elements. Frequency calculations were performed to confirm the nature of the stationary points and to obtain zero-point energies (ZPE). The connectivity between stationary points was established by intrinsic reaction coor-

dinate calculations (IRC). Single point estimates were obtained at the B3LYP/6-311+G(2d,2p) level without any significant changes of the relative energies. Since most of the transformations described herein are intramolecular, the energy values refer to enthalpies (ΔH_{298} and ΔH^\ddagger_{298}), unless stated otherwise. The Chemcraft program was used to draw the calculated structures.^[25]

2-Pyridone cobalt complexes: As depicted in Scheme 3, cobaltcyclopentadiene **B** coordinates π systems to give 18-electron complexes of type **C**. With 2-pyridone, this process^[26] can give rise to a multitude of structures, as the six-membered heterocycle offers various coordination sites. Figure 1 depicts only those complexes relevant to the further

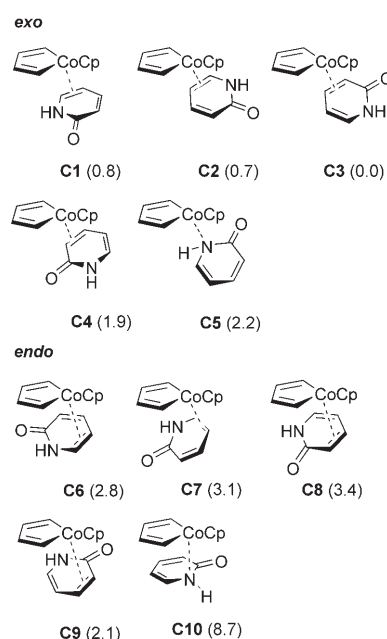
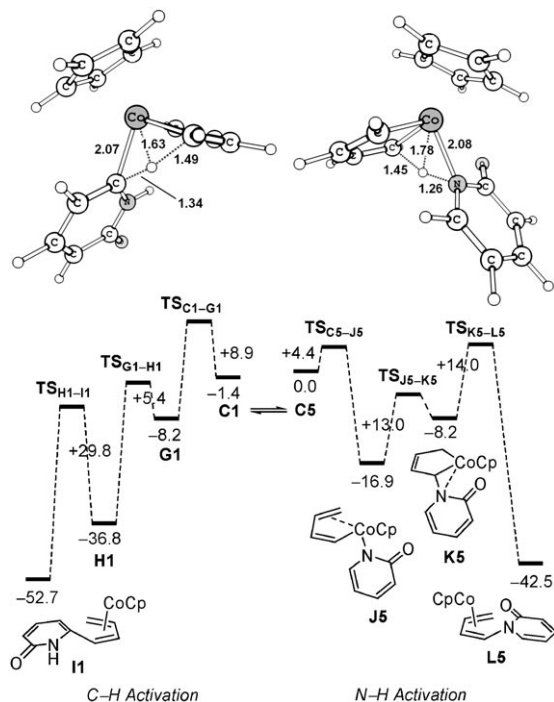


Figure 1. Isomers of CpCo(2-pyridone) **C1–10**. ΔH_{298} values (kcal mol^{-1}) relative to **C3** are given in parentheses.

chemistry under discussion, with ligation to either of the two different C–C double bonds or to the nitrogen lone pair. Each of these sites can give rise to *exo* (**C1–5**) or *endo* (**C6–10**) complexes, presumably equilibrating in solution (Figure 1). Because of the unsymmetrical disposition of the π -ligating pyridone with respect to the remaining molecular frame, the cobalt center is stereogenic, and the pairs **C1/C2**, **C3/C4**, **C6/C7**, and **C8/C9** are diastereomers (see, for example, **C1/C2** and **C3/C4** in Figure 2). These ten isomers were fully optimized and found to lie within an energy range of $8.7 \text{ kcal mol}^{-1}$ (order of stability: **C3** > **C2** > **C1** > **C4** > **C9** > **C5** > **C6** > **C7** > **C8** > **C10**).^[27]

C–H versus N–H activation: Unlike their *endo* counterparts (vide infra), all of the *exo* complexes can undergo migration of hydrogen from carbon or nitrogen, respectively, of 2-pyridone to the α -carbon atom of the metallacycle, as exempli-

fied for **C1** and **C5** in Scheme 5. The N-coordinated isomer **C5** converts most easily, by N–H activation ($\Delta H_{298}^{\ddagger} = 4.4 \text{ kcal mol}^{-1}$, $\Delta H_{298} = -16.9 \text{ kcal mol}^{-1}$). On the other hand,



Scheme 5. Energy profile for C–H and N–H activation pathways of 2-pyridone [ΔH_{298} (kcal mol⁻¹) relative to **C5**; the $\Delta H_{298}^{\ddagger}$ values are absolute for the step depicted].

the most favored C–H activation is that of **C1** at the carbon adjacent to the nitrogen ($\Delta H_{298}^{\ddagger} = 8.9 \text{ kcal mol}^{-1}$, $\Delta H_{298} = -6.8 \text{ kcal mol}^{-1}$). Complexes **C1** and **C5** were connected to the dienylobalt species **G1** and **J5** via transition states that show imaginary frequencies of 897 cm⁻¹ and 1171 cm⁻¹ associated with the movement of the transferred hydrogen atoms (Figure 2). Interestingly, the respective transition states for C–H and N–H activation are very much alike. The transfers take place within the C–Co–C and C–Co–N planes, respectively (C–Co–C–H: 0.5°; N–Co–C–H: -3.4°). The total distance travelled by the hydrogen atom is 2.83 Å for the C···H···C transfer and 2.71 Å for the N···H···C transfer. The Co···H distance is shorter in the C–H activation transition structure (1.63 vs. 1.84 Å). Consequently, the C–H–C angle is slightly more acute than that for the N–H–C frame (160.4° vs. 167.7°). During both types of transfer, the cobalt atom remains in a tetrahedral environment defined by the Cp centroid and the three carbon atoms (or, respectively, the nitrogen and the two carbons atoms) bound to the metal. This detail points to the protonic nature of these H-migrations, during which the Co^{III} center keeps its oxidation state, rather than to oxidative hydrogen migrations, which would involve a Co^V transition structure.^[28] Goddard and co-workers have described a related direct H-transfer for Ir via Ir^V transition structures with a full bond formed

between the migrating hydrogen and iridium.^[29] Although Co^V species are known (but rare),^[30] we could not reproduce a similar mechanism in our systems.^[31]

As previously described for ethene,^[12] complexes **G1** and **J5** display a short distance between the terminal σ -dienyl carbon atom and the cobalt atom (2.30 Å and 2.37 Å, respectively; Figure 2). The terminal double bonds are quite long (1.37 Å and 1.36 Å), while the C–H linkages are normal. These findings suggest that there is an interaction between the unoccupied d orbital of cobalt and the terminal π orbital of the ligand. The conversion of **J5** to the final [CpCo(butadiene)] complex **L5** could be achieved in two steps via the N-coordinated cobaltacyclopentene **K5**. The migration of the nitrogen atom from cobalt to carbon materializes through the carbenic transition state **TS_{J5-K5}** ($\Delta H_{298}^{\ddagger} = 13.0 \text{ kcal mol}^{-1}$), evidenced by the development of a quite short (1.86 Å) Co–C bond. Reductive elimination to the final complex **L5** requires 14.0 kcal mol⁻¹ to reach η^3 -Cp **TS_{K5-L5}**. Although the first step to **K5** is endothermic by 8.7 kcal mol⁻¹, the second to **L5** is appreciably exothermic by 34.3 kcal mol⁻¹. Contrasting with the behavior of **J5**, complex **G1** is converted exothermically into the σ,π -allylhexadiene complex **H1** ($\Delta H_{298}^{\ddagger} = 5.4 \text{ kcal mol}^{-1}$, $\Delta H_{298} = -28.6 \text{ kcal mol}^{-1}$). Similar to its nitrogen counterpart, **TS_{G1-H1}** exhibits a short Co–C bond (1.81 Å). Reductive elimination to the final complex **I1** requires 29.8 kcal mol⁻¹ to reach η^3 -Cp **TS_{H1-I1}** and is exothermic by 15.9 kcal mol⁻¹.

Importantly, the C/N–H activation mechanisms depicted above lead to the *Z*-configuration of the diene, the *C* or *N*-bound pyridone emerging in the thermodynamically less favorable “inside” position, as also observed experimentally (e.g., for **1** in Scheme 1 and **8** in Scheme 2).^[8] However, the *N*-dienylation of 4-pyridone gave a mixture of the corresponding *Z* and *E* products,^[8] and similar isomerizations have been observed for dienes obtained by C–H activation.^[2,10a] Consequently, possible pathways leading to **1** in the *E* configuration were computed (Scheme 6). Thus, the carbenic Co^V hydride **M** can be obtained either directly by reaction between 2-pyridone and the cobaltacyclopentadiene **A**, or through *endo* complex **C10** by intramolecular N···H···Co transfer. The complex **M** subsequently rearranges to the CpCo(*E*-diene) framework via **TS_{M-N}**, which lies 15.0 kcal mol⁻¹ above **M**. These two routes, however, require prohibitive activation energies compared to that found for **C5**→**J5** (35.6 and 41.7, respectively, vs. 4.4 kcal mol⁻¹). These high barriers appear to be endemic for all *endo* systems.^[32] The computed data support the assumption that *Z*/*E* isomerizations, when encountered experimentally, are the result of (presumably acid-catalyzed) processes of the initial cyclization products.^[8]

The observation of relatively facile (by 4–5 kcal mol⁻¹) N–H versus C–H activation, exemplified by **C5**→**L5** and **C1**→**I1** in Scheme 5, is general not only for all *exo* complexes in Figure 1, but all four C–H bonds in the pyridone frame, for which enthalpies of activation of about 9–10 kcal mol⁻¹ were computed. This result is consistent with the protonic character of the hydrogen being transferred and the acidity of the

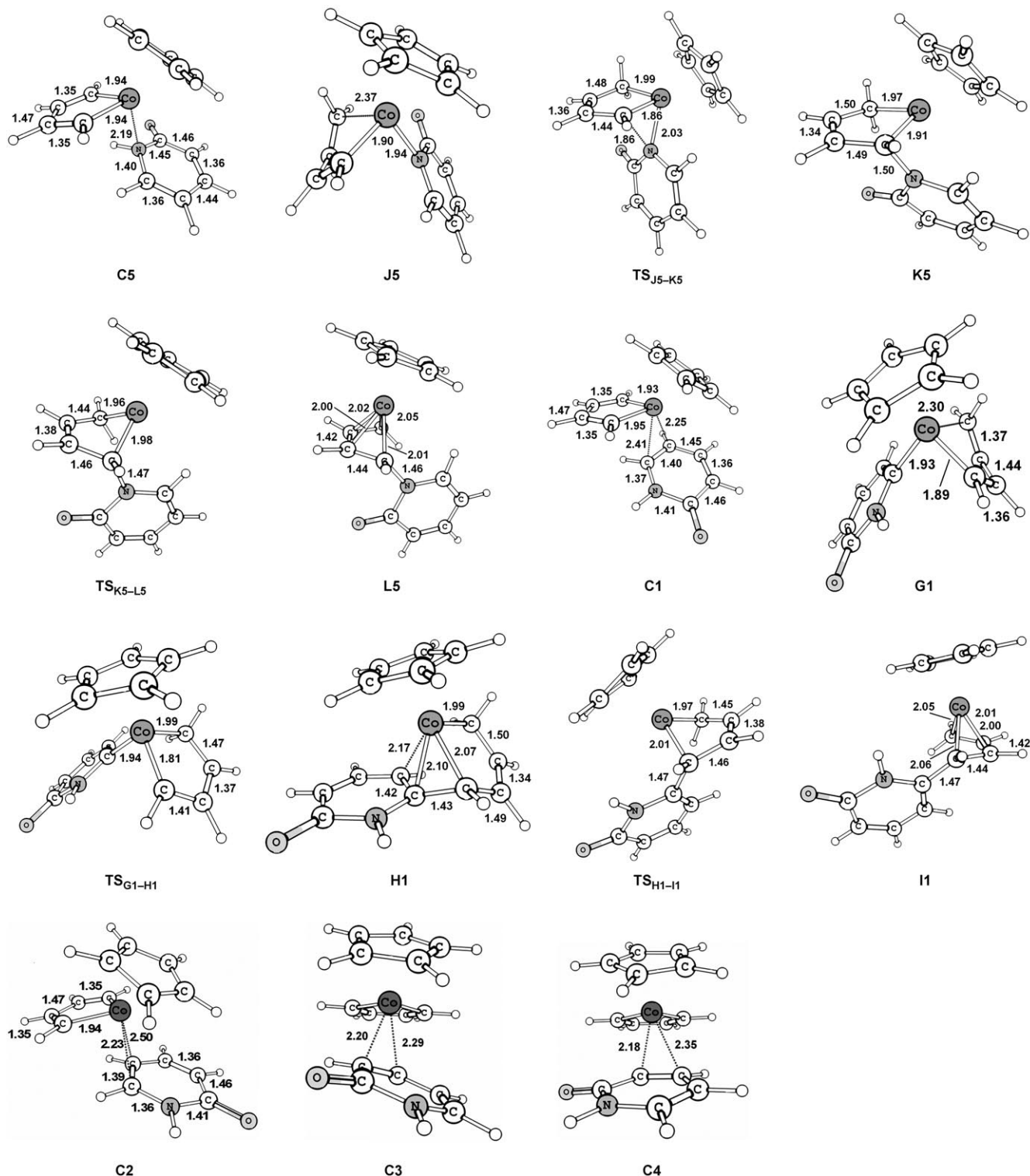
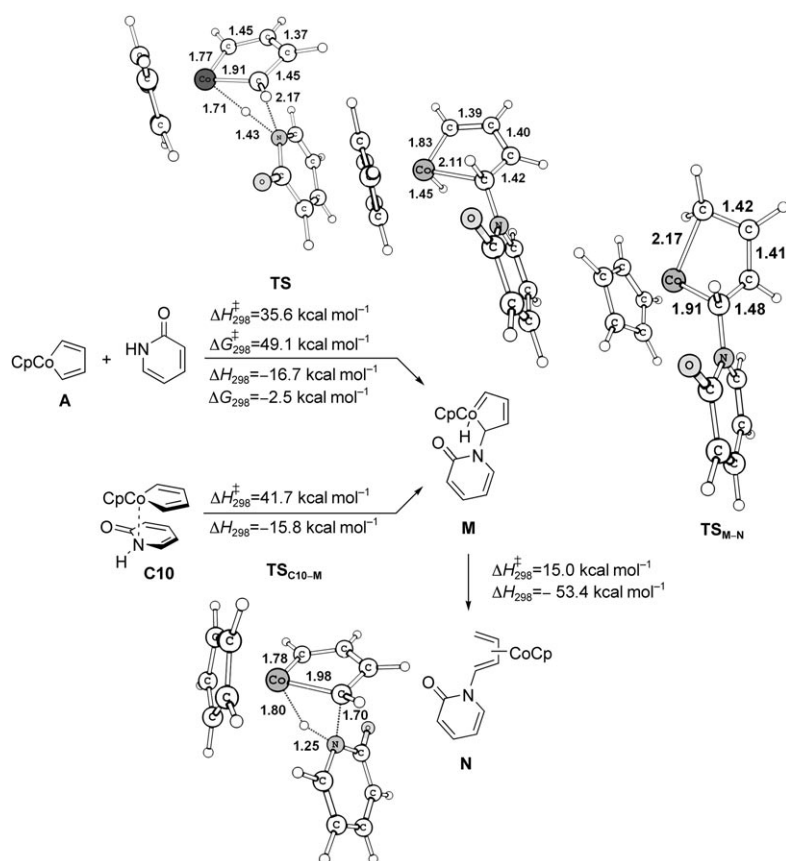


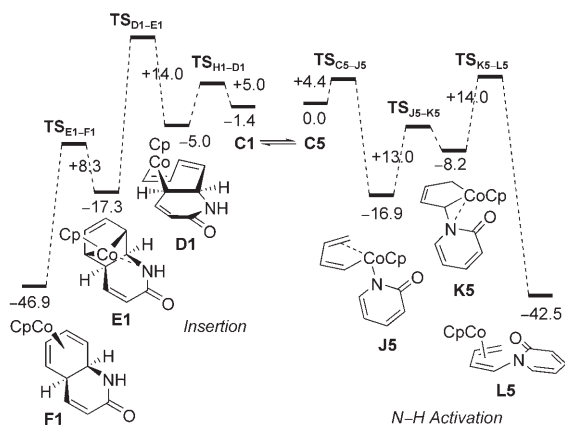
Figure 2. Structures of the various cobalt species depicted in Scheme 5 and Figure 1, with selected bond lengths [Å]. C3 and C4 have been rendered such as to highlight their diastereomeric relationship.

amide hydrogen in 2-pyridone ($pK_a=11.7$). The C–H activation pathway described above follows that previously described for benzene, furan, and thiophene, the first step

being exothermic and kinetically facile (benzene: $\Delta H^\ddagger_{298} = 7.3 \text{ kcal mol}^{-1}$; furan and thiophene: $\Delta H^\ddagger_{298} = 8.7 \text{ kcal mol}^{-1}$).^[11]

Scheme 6. Computational routes to the CpCo(*E*-diene) framework starting from **A** or **C10**.

N–H activation versus [2+2+2] cycloaddition: Although N–H activations are fast, we found that some insertions (on the way to [2+2+2] cycloaddition) could compete, at least initially (vide infra). Indeed, among the eight possible ones, four show moderate activation enthalpies of 3.6 to 5.2 kcal mol⁻¹, as exemplified by **C1** in Scheme 7, $\Delta H_{298}^{\ddagger} = 5.0 \text{ kcal mol}^{-1}$.^[33] However, the energetic gain of forming the

Scheme 7. Energy profile for insertion and N–H activation pathways of 2-pyridone [ΔH_{298} (kcal mol⁻¹) relative to **C5**; the $\Delta H_{298}^{\ddagger}$ values are absolute for the step depicted].

resulting cobaltacycloheptadienes, such as **D1**, is only modest (from 0.2 to 3.6 kcal mol⁻¹).^[34] Coordinative saturation is achieved by strong puckering, bringing the C_γ–C_δ double bond close to the metal center (e.g. **D1**, Figure 3). The transformation of these complexes into the final products **F** is in accord with the **D**→**E**→**F** pathway in Scheme 3.^[35] The isomerization of cobaltacycloheptadienes into the corresponding cobaltanorbornenes, such as **E1**, requires 9–14 kcal mol⁻¹ depending on the substrate. Cobaltanorbornenes of type **E** are stabilized by the nitrogen atom, when they arise from an *exo* cyclization (e.g. **E1**, Co⋯N 2.02 Å), or by a βH agostic interaction, when they arise from an *endo* cyclization (e.g. **E7**, Co⋯H 1.78 Å). The final isomerization of **E** into the CpCo(η^4 -butadiene) framework **F** is strongly exothermic and kinetically facile (e.g. **E1**→**F1** in Scheme 7:

$$\Delta H_{298}^{\ddagger} = 8.3 \text{ kcal mol}^{-1}; \quad \Delta H_{298} =$$

–29.6 kcal mol⁻¹).

The two double bonds of the pyridone frame appear almost equally reactive with regard to insertion (Table 1). No significant difference between *endo* and *exo* pathways was found, which suggests low diastereoselectivity. Both of these facets are borne out experimentally.^[8] However, while inconsequential to the structure of the final products, the double bonds insert regioselectively, C3 and C5 of the pyridone ring emerging preferentially bound to cobalt in the new metallacycle (Table 1). An explanation for this selectivity is found in the polarization of the inserting carbons which matches that in the cobaltacycle (Figure 4).

The competition between the initial N–H activation and insertion steps, respectively, notwithstanding, the latter pathway to the final product **F** is not competitive with the former ultimately generating **L**, because the subsequent (and rate determining) **TS**_{D–E} is more energetic than **TS**_{K–L}. For example, in the conversions of **C1/C5** in Scheme 7, the difference between the respective rate-limiting **TS**_{D1–E1} and **TS**_{K5–L5} is 3.2 kcal mol⁻¹ in favor of the latter. Therefore for N-unprotected 2-pyridones, the experimental finding of *N*-dienylation is gratifyingly confirmed computationally.^[8]

C–H activation versus [2+2+2] cycloaddition: On blocking the N–H activation pathway by *N*-alkylation, one is left to consider the relative prevalence of the remaining two mech-

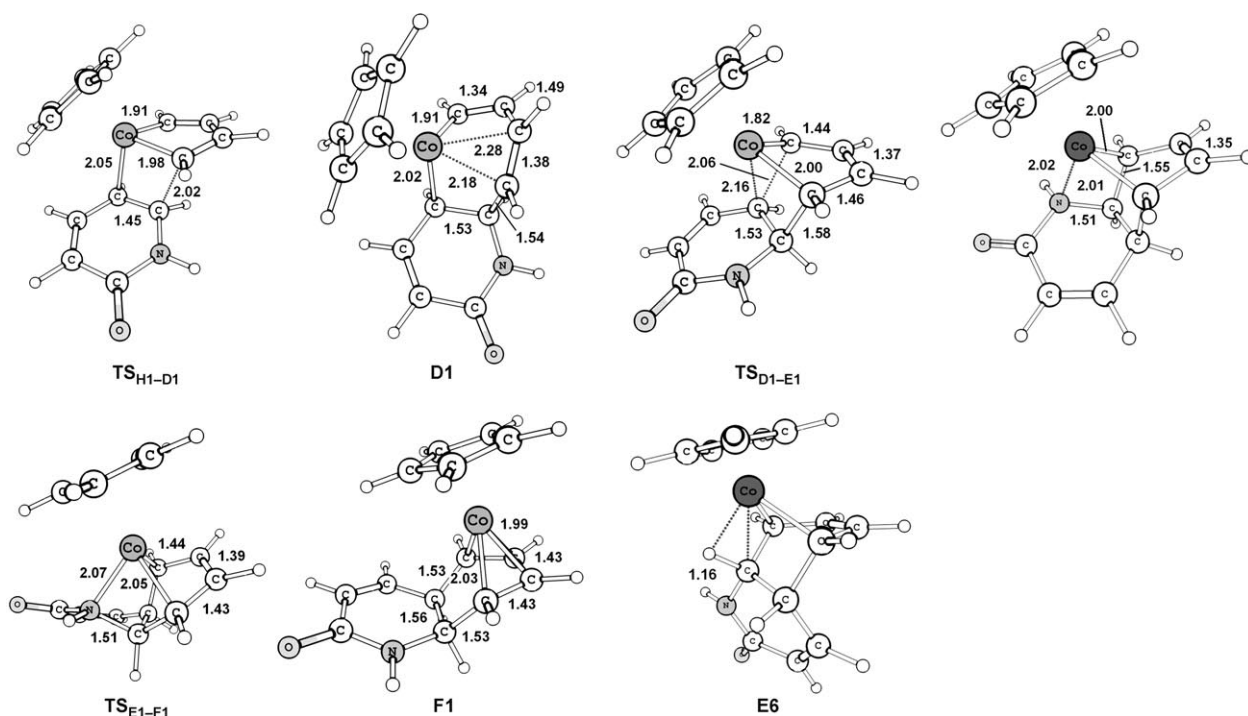


Figure 3. Structures of various cobalt species depicted in Scheme 7 and of **E6**, with selected bond lengths [Å].

Table 1. Regioselectivity of insertion of 2-pyridone in **C**: The labeled position (•) emerges bound to cobalt.

$\Delta H^{\ddagger}_{298}$ [kcal mol ⁻¹]		$\Delta H^{\ddagger}_{298}$ [kcal mol ⁻¹]	
<i>exo</i>			
C1 → D1	5.0	C2 → D2	11.5
C3 → D3	5.0	C4 → D4	11.5
<i>endo</i>			
C6 → D6	5.2	C7 → D7	10.2
C9 → D9	3.6	C8 → D8	9.7

D1, D6

D3, D9

D4, D8

D2, D7

Favored

anisms by which 2-pyridone may transform in the presence of CpCo. Inspection of Scheme 5 and 7 reveals that these routes should be competitive. Thus, from **C1**, C–H activation toward **II** faces a rate determining hurdle of 8.9 kcal mol⁻¹ (**TS_{Cl-G1}**), whereas [2+2+2] cycloaddition is marginally more difficult by 1.5 kcal mol⁻¹ (**TS_{D1-E1}**). This finding explains the often puzzling occurrence of products derived via either pathway encountered not only in the present work (e.g., Scheme 1 and 2), but also previous cyclizations with other heteroaromatics.^[2,4a,7,8] In this connection, the observation of a clean switch over from [2+2+2] cycloaddition to C–H activation in the conversions of **3** and **7** in

Scheme 2, provided the opportunity to probe to what extent seemingly minor alterations of the system, in this case changing the tether length, might affect the relative energetics of the competing mechanisms. Thus, these systems were mapped energetically (**C11** and **C12** in Scheme 8).

To begin with, and as expected, coordination of the enone C–C double bond to the metal was prevented by strain, thus ensuring complete regioselectivity. *exo* complexes **C11** and **C12** compare directly to **C1** in the untethered series (see Scheme 5 and 7 for insertion and C–H activation of **C1**). The insertion trajectories from these complexes (on route to [2+2+2] adducts) are analogous to that from **C1** (**C11**: $\Delta H^{\ddagger}_{298} = 5.3$ kcal mol⁻¹; **C12**: $\Delta H^{\ddagger}_{298} = 6.8$ kcal mol⁻¹; **C1**: $\Delta H^{\ddagger}_{298} = 5.0$ kcal mol⁻¹), but are now almost thermoneutral (**C11**: $\Delta H^{\ddagger}_{298} = 0.5$ kcal mol⁻¹; **C12**: $\Delta H^{\ddagger}_{298} = -0.8$ kcal mol⁻¹; **C1**: $\Delta H^{\ddagger}_{298} = -3.6$ kcal mol⁻¹). For *endo* complexes **C13** and **C14**, which compare to **C6** in the untethered series, the effect of adding the tethers has a more detrimental energetic effect. Because of relatively increased strain, *endo* insertions are found disfavored both kinetically (**C13**: $\Delta H^{\ddagger}_{298} = 15.4$; **C14**: $\Delta H^{\ddagger}_{298} = 13.0$ kcal mol⁻¹; **C6**: $\Delta H^{\ddagger}_{298} = 5.2$ kcal mol⁻¹) and thermodynamically (**C13** and **C14**: $\Delta H_{298} = 8.0$ kcal mol⁻¹ each; **C6**: $\Delta H_{298} = -3.3$ kcal mol⁻¹).^[36] Consequently, the final complexed cyclohexadienes arise from initial *exo* complexation of the pyridones, thus rendering the stereochemistry that was also observed experimentally, namely the metal emerging *anti* with respect to the hydrogens at the ring junction (Scheme 2). Similar to the untethered series, the transformation of the cobaltacycloheptadienes **D11** and **D12** into the N-stabilized cobaltanorbornenes **E11** and **E12** requires 13.3 and 14.8 kcal mol⁻¹.

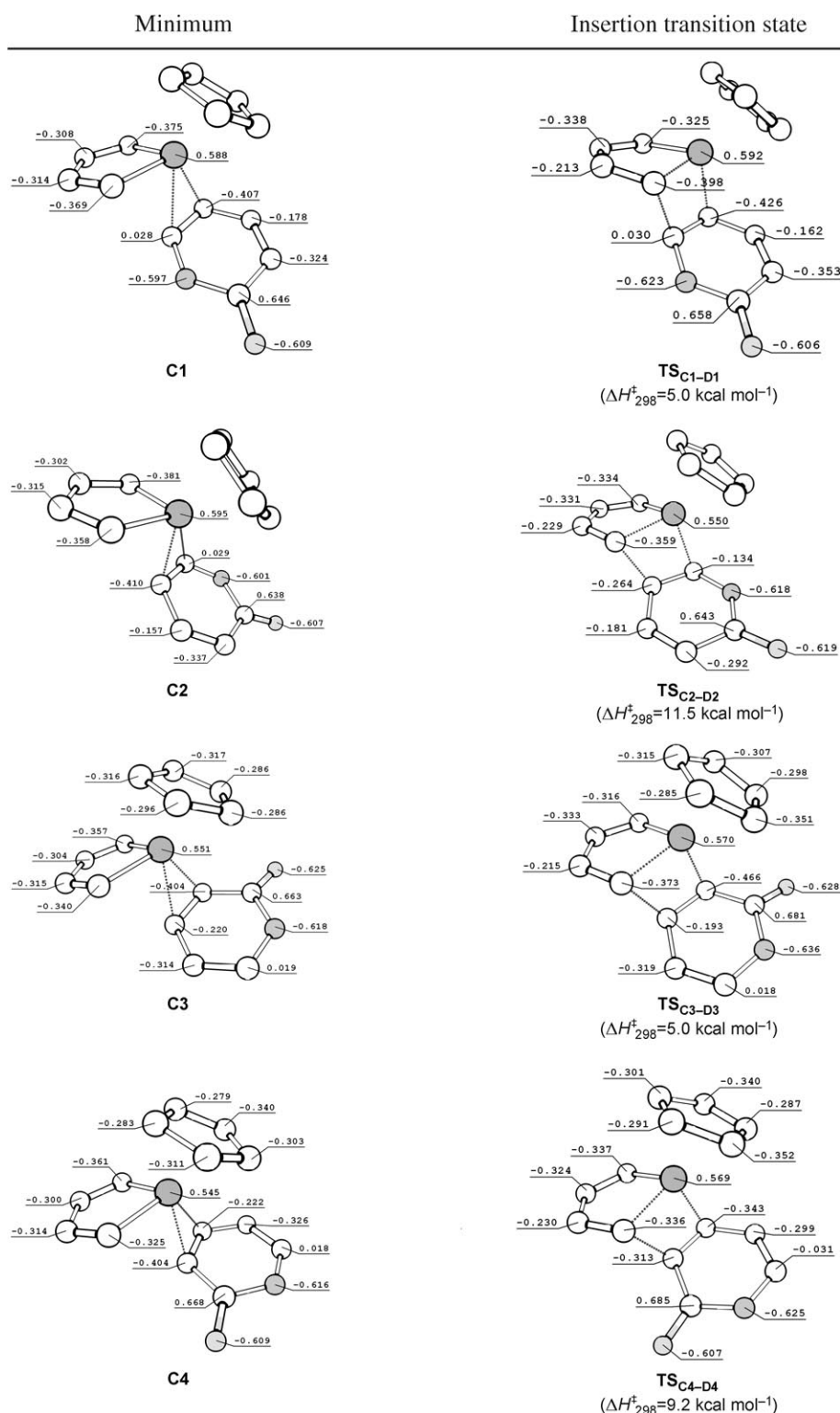


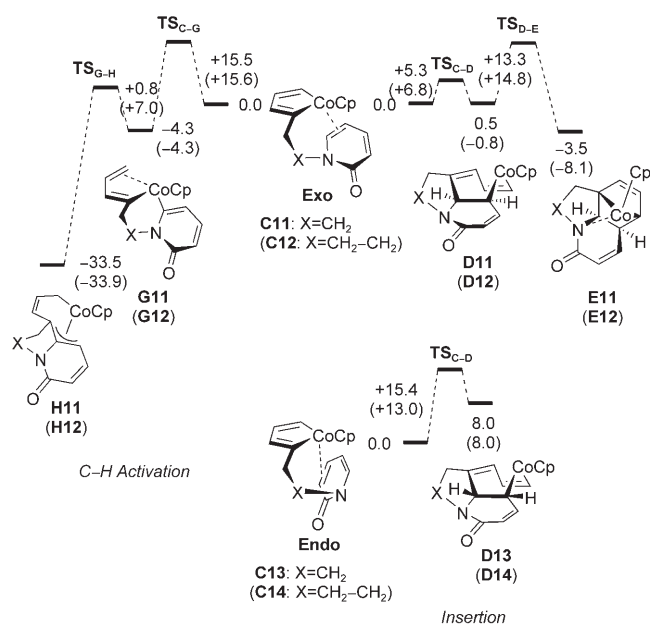
Figure 4. Examples of NBO charges (shown only for *exo* insertions) in the enamine and enone moieties of 2-pyridone, respectively (hydrogen atoms have been omitted for clarity).

Whereas **C1**→**G1** required only $8.9 \text{ kcal mol}^{-1}$, in the tethered series C–H activations show higher barriers: 15.5 and $15.6 \text{ kcal mol}^{-1}$ for **C11**→**G11** and **C12**→**G12**, respectively.

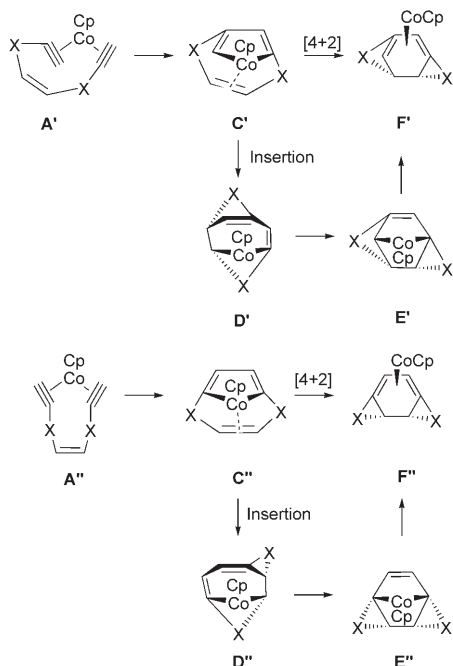
aged,^[11] but appears difficult due to strain. Similarly, in the mechanistic consideration of the formation of **12** from **11**, the classical insertion pathway leading to **D''** seems disfa-

The differences between **TS_{C-G}** and **TS_{D-E}** are $1.7 \text{ kcal mol}^{-1}$ and $1.6 \text{ kcal mol}^{-1}$, respectively, modestly in favor of the insertion pathway, whereas with **C1**, this difference is $1.5 \text{ kcal mol}^{-1}$ in favor of the C–H activation route. Thus, in neither series, as already noted for the simplest systems described in Scheme 5 and Scheme 7, can a clear energetic preference be found for insertion versus C–H activation. As a result, the isolation of only one product in each case (see, for example, Scheme 2) is deemed fortuitous.^[8] Further support for this notion is found in the occurrence of both types of activation of the same substrate in the indole^{4a} and pyrimidinone series.^[7a]

The regiochemical puzzle of the Co-mediated cyclization of pyrazinedione 9: To conclude this study, we turn to the unexpected regio- and stereochemical outcome of the cyclization of *N,N'*-dipentynylpyrazinedione **9**, particularly in view of the “normal” course of the reaction observed for its all-carbon analogue **11** (Scheme 4). The generation of the unsymmetrical fused cyclohexadiene in **10** is quite puzzling when applying the general mechanism depicted on Scheme 3. Thus, the conversion of **9** to **10** would necessitate the unsymmetrical coordination of a bisalkyne complex of type **A'**, which would undergo oxidative coupling to give **C'** (Scheme 9). After insertion, the resulting cobaltacycloheptadiene **D'** would exhibit quite acute anti-Bredt geometry, and so will the next intermediate **E'** [4+2]. Cycloaddition between the coordinated double bond and the diene moiety of the metallacycle could be envis-



Scheme 8. Energy profile for insertion and C-H activation pathways of two- and (in parentheses) three-carbon-tethered 2-pyridones [ΔH_{298} (kcal mol⁻¹) relative to **C11** (**C12**); the ΔH_{298}^\ddagger values are absolute for the step depicted].

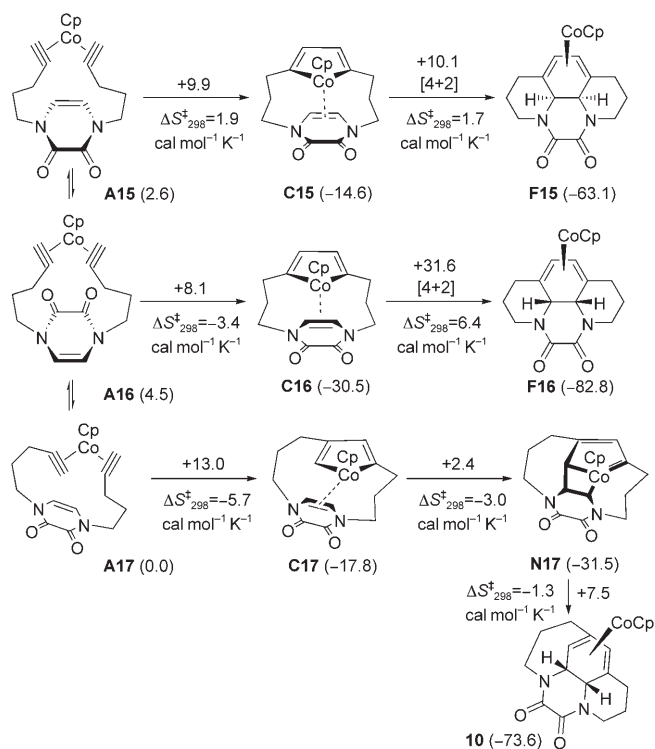


Scheme 9. Possible routes to unsymmetrical (**A'** → **F'**) and symmetrical (**A''** → **F''**) CpCo-complexed cyclohexadienes from ynenynes.

vored for two reasons: 1) in the insertion transition state, the coordinated double bond must be rotated into parallel alignment with the Co-C_α bond of the metallacycle, a motion impeded by the presence of its tethers; 2) cobaltacycloheptadiene **D''** exhibits a presumably energetically unfavorable bridgehead double bond. Here, the [4+2] cycloaddi-

tion might be the only feasible pathway to **F''**, although a relatively high activation barrier may be anticipated.^[37]

Both *exo* and *endo* symmetrical (**A15** → **C15** and **A16** → **C16**, respectively), but only the *endo* unsymmetrical (**A17** → **C17**) oxidative cyclizations could be modeled in the pyrazinedione series, the *exo* version of the latter invariably converging to its *endo* counterpart (Scheme 10, Figure 5).



Scheme 10. Competitive pathways to symmetrical and unsymmetrical cyclohexadienes in the cyclization of **9**. [ΔH_{298} (kcal mol⁻¹) relative to **A17**; the ΔH_{298}^\ddagger values are absolute for the step depicted].

Making the reasonable assumption that all rotamers of **A** are in rapid equilibrium, the rate determining steps to **C** are very close in (enthalpic) energy (**C15**: 12.5; **C16**: 12.6; **C17**: 13.0 kcal mol⁻¹). While all of these steps are exothermic, **C17** progresses on to the next intermediate with remarkable ease ($\Delta H_{298}^\ddagger = 2.4$ kcal mol⁻¹), perhaps the key to the understanding of the outcome of this cyclization. As anticipated, for **C15** and **C16**, insertion of the coordinated double bond could not be modeled. However, their direct transformations to **F15** and **F16**, respectively, could be achieved via [4+2] cycloaddition. This step requires 10.6 and 31.6 kcal mol⁻¹, respectively, and is strongly exothermic for both. On the other hand, the much lower energy pathway for **C17** obviates both direct [4+2] cycloaddition and insertion (neither one of which was calculable) and proceeds through a new step: A formal valence tautomerization to generate the polycyclic cobalt carbene **N17**. The geometry of this complex is reminiscent of the transition structures **TS_{D-E}**, exemplified in Figure 3, but now the tethers constrain the struc-

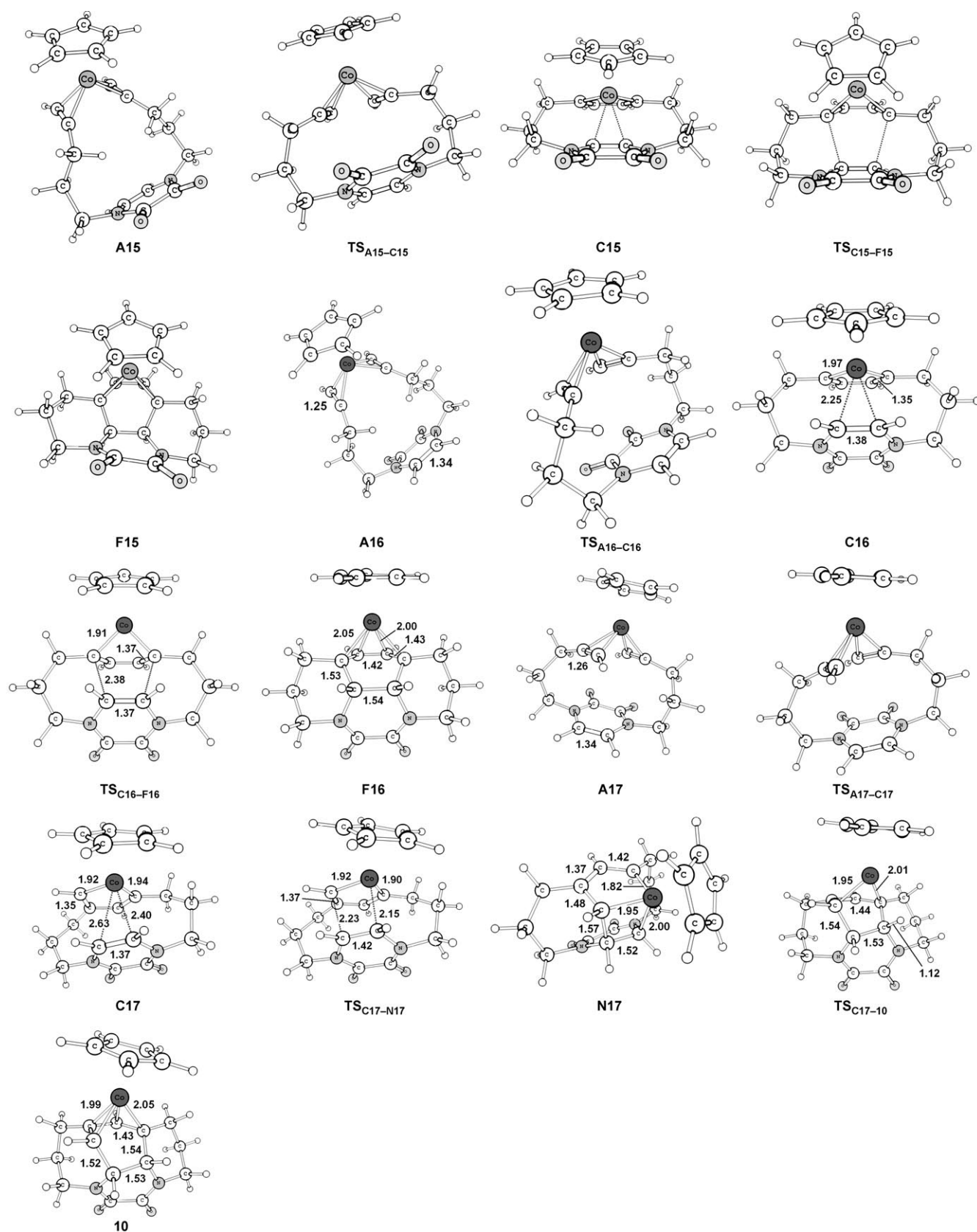


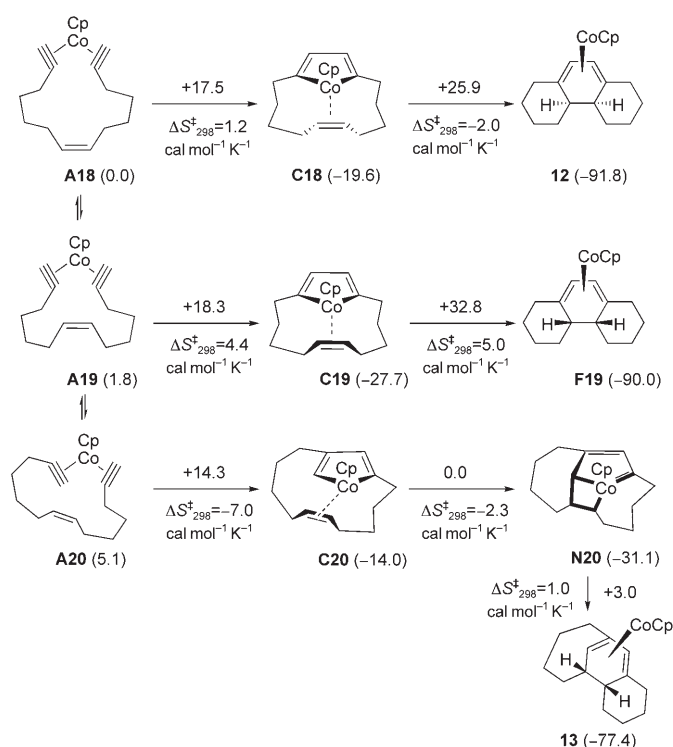
Figure 5. Structures of various cobalt species depicted in Scheme 10 and Scheme 11, with selected bond lengths [Å].

ture such as to render it a minimum. In the mechanism of the Ru-catalyzed cocyclization of ethene with acetylene, the same kind of intermediate was proposed.^[38] Moreover, a related 1-iridabicyclo[3.2.0]hepta-1,3,6-triene has been characterized by an X-ray diffraction study.^[39] The conversion of **N17** into **10** requires 7.5 kcal mol⁻¹ and is appreciably exothermic by 42.1 kcal mol⁻¹. The geometry of the transition state closely resembles that of the cobaltanorbornenes **E** exemplified by **E6** in Figure 3. Even the β-H agostic interaction is perceivable through the relatively long β C–H bond (1.12 Å).

Intrigued by the close calculated barriers leading to **10** and its isomers in Scheme 10, the role of entropy as a deciding factor for the exclusive observation of **10** was probed. However, at room temperature, the conditions under which **9** was cyclized, the generation of **C15** is now distinctly favored [$\Delta S_{298}^{\ddagger} = 1.9$ cal mol⁻¹ K⁻¹; $\Delta G_{298}^{\ddagger}$ (relative to **A17**) = 11.9 kcal mol⁻¹], at the expense of **C16** ($\Delta S_{298}^{\ddagger} = -3.4$ cal mol⁻¹ K⁻¹; $\Delta G_{298}^{\ddagger} = 13.6$ kcal mol⁻¹) and **C17** ($\Delta S_{298}^{\ddagger} = -5.7$ cal mol⁻¹ K⁻¹; $\Delta G_{298}^{\ddagger} = 14.7$ kcal mol⁻¹), respectively (Scheme 10). Testing the possibility that an experimental switch over in product formation from **10** to **F15** might be detected at higher temperatures, the experiment was performed at 139°C in boiling xylene and with [CpCo(CO)₂], the conditions under which **11** led to **12** (Scheme 4). However, there was no change in its result. It appears that the calculations overestimate the barrier to oxidative coupling of **A17** and/or underestimate the corresponding values for its rotamers by at least 3–4 kcal mol⁻¹.

To gain further understanding of the system, a complementary set of computations was executed on its all-carbon analogue **11**, which, tantalizingly, had been converted to **12** (Scheme 4), the relative of **F15** (Scheme 10), at 139°C (with simultaneous irradiation). Thus (Scheme 11, Figure 5), relative to the most stable rotamer **A18**, which requires 17.5 kcal mol⁻¹ of rate determining activation to undergo oxidative coupling, the TSs for the same process from **A19** and **A20** are higher in energy by 2.6 and 1.9 kcal mol⁻¹, respectively, in agreement with experiment. The subsequent steps are mechanistically identical to those depicted in Scheme 10. Hence, **C18** and **C19** continue by direct [4+2] cycloadditions to **12** and **F19**, respectively, with sizeable, but, as a result of the exothermicity of their formation, not rate determining barriers. On the other hand, **C20** could be connected to the polycyclic cobalt carbene **N20** through an enthalpically barrierless rearrangement, eventually furnishing **13**. Consideration of entropy, which is sizeably negative for $\text{TS}_{\text{A20} \rightarrow \text{C20}}$, makes **A20** even less competitive at experimental temperatures. However, contemplation of a potential overestimation of $\text{TS}_{\text{A20} \rightarrow \text{C20}}$ relative to the other two, similar to that noted above for $\text{TS}_{\text{A17} \rightarrow \text{C17}}$, namely 3–4 kcal mol⁻¹, raises the possibility that this reaction occurs in an enthalpic window in which the influence of entropy may be decisive.

Inspired by this speculation, compound **11** was exposed to [CpCo(C₂H₄)₂] at lower temperatures than those of the original preparation depicted in Scheme 4. Gratifyingly, at 20°C, **12** was formed admixed with a new isomer in the ratio 1:2



Scheme 11. Competitive pathways to symmetrical or asymmetrical cyclohexadienes in the all-carbon series [ΔH_{298} (kcal mol⁻¹) relative to **A18**; the $\Delta H_{298}^{\ddagger}$ values are absolute for the step depicted].

(64%), improved to 1:4 (62%) on running the reaction at -78°C (with simultaneous irradiation). That this isomer is **13** (Scheme 11) is compellingly indicated by NMR spectroscopy, particularly ¹³C NMR spectroscopy of the (inseparable) mixture.^[40] Thus, in addition to the signals for **12**, the ¹H NMR spectrum shows a new Cp singlet at $\delta = 4.51$ ppm (5H) and a doublet at $\delta = 4.60$ ppm, the latter in the diagnostic region of an internal complexed diene proton. Two narrow multiplets at $\delta = 2.66$ and 2.55 ppm are indicative of the two *endo* tertiary cyclohexadiene protons, the remainder of the spectrum consisting of unresolved multiplets. The ¹³C NMR spectrum contains, in addition to the (minor) eight peaks for **12**, only peaks assignable to **13**. Specifically, there are eight methylene carbon signals between $\delta = 20.6$ and 34.2 ppm, two *C_{tert}*-H absorptions at $\delta = 40.6$ and 41.0, and the two sets of internal ($\delta = 72.8$ and 92.4 ppm) and terminal ($\delta = 53.9$ and 70.5 ppm) complexed diene carbon resonances. A control experiment ascertained that **12** and **13** are stable to and not interconverted under either conditions of their formation.

The results described in this section constitute an especially pleasing demonstration of the utility of calculations in explaining and stimulating experiments. They also highlight new details of the cobalt-mediated [2+2+2] cycloaddition of alkynes to alkenes, in particular the finding that the normally energetically prohibitive Diels–Alder-like cycloaddition (e.g., **C18**→**12**) can be enforced by rendering the normal insertion pathway too strained, and that similar

strain activation, as in **C20**, enables a new mode of addition, ultimately providing **10** and **13**, respectively.

Conclusion

DFT computational estimates have provided a rationale for a number of previously not understood experimental results arising when pyridones and pyrazinones are attacked by alkynes in the presence of [CpCoL₂]. Focusing on 2-pyridone as the prototype, reaction with the cobaltacyclopentadiene intermediate formed by coupling two alkyne units can follow three distinct pathways: N–H activation, C–H activation, and [2+2+2] cycloaddition. The first is kinetically favored and proceeds by N···H···C migration to furnish *N*-dienylated 2-pyridones. When this option is blocked by *N*-alkylation, either insertion (on the way to the cycloaddition product) or C···H···C transfer may occur through energetically close-lying trajectories. In the former, the two double bonds of the heterocycle are equally reactive, and diastereoselectivity is prevalent only when the 2-pyridone and cobaltacyclopentadiene are tethered. H-migration is best described as a metal-assisted proton transfer and gives dienylpyridones with the *Z*-configuration. Prompted by the experimental finding that *N,N'*-dipentynylpyrazinedione transforms into an asymmetrical, formally anti-Bredt, CpCo-complexed cyclohexadiene, the energetics of this system were computed and compared with those of tetradeca-7-ene-1,13-diyne. Placing the reacting double bond between the alkyne fragments obstructs the normal insertion process of the cycloaddition making a Diels–Alder-like pathway possible for symmetrically bound ynenynes. In the case of their unsymmetrically ligating rotamers, the ensuing distortions allow a relatively low energy new mechanism for cyclization to prevail, featuring a polycyclic Co^V carbenic intermediate. This result highlights once more the extraordinary versatility of cobalt in its reactions with unsaturated substrates.

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- [15] For ethene (and presumably other acyclic alkenes), a lower energy pathway to **I** could be computed proceeding via β -hydride elimination from **D**, rather than direct vinyl–H activation. This pathway is precluded for the heterocycles under discussion.
- [16] Although insertion of these heterocycles to provide fused analogues of **D** was energetically feasible, the β -hydride elimination step could not be computed.^[11]
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- [27] Cobaltacyclopentadiene complexation to the carbonyl oxygen is most favored by approximately 20 kcal mol⁻¹ relative to **C3**. However, this must be a reversibly formed dead end, since direct pathways to the products of cycloaddition and insertion from this complex could not be computed.
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- [34] With ethene, this transformation was found to be substantially more exothermic by 13.0 kcal mol⁻¹.^[12]
- [35] **F** can also be obtained directly via reductive elimination of **D**. However, these one step processes require higher activation energies than their two-step counterparts. For instance, 20.8 kcal mol⁻¹ are necessary for the direct transformation of **D1** into **F1** (Scheme 7), whereas reaching the cobaltanorbornene **E1** requires only 14.0 kcal mol⁻¹ (the subsequent generation of **F1** being relatively fast). Similarly, **C7**→**E7** is faster than **C7**→**F7** (9.2 vs. 17.3 kcal mol⁻¹).
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