

Density Functional Study on the Preactivation Scenario of the Dötz Reaction: Carbon Monoxide Dissociation versus Alkyne Addition as the First Reaction Step

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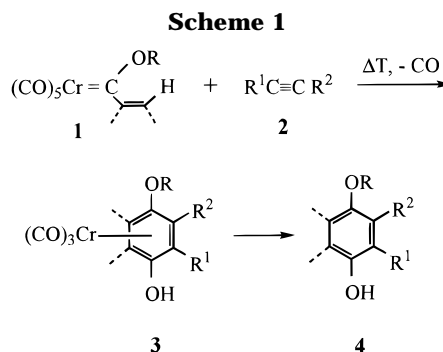
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Two different mechanistic proposals have been investigated theoretically for the initial steps of the chromium-assisted Dötz benzannulation reaction at the nonlocal density functional level of theory. The energy requirements needed for the reaction to start through the usually assumed CO-dissociative mechanism are calculated to be 144.7 kJ mol⁻¹ for (CO)₅Cr=C(OH)(C₂H₃) (**1**). Under the mild thermal experimental conditions, the decarbonylation step may be sometimes a serious bottleneck for the reaction to proceed, even to the extent of completely blocking the formation of the subsequent tetracarbonyl compound (CO)₄Cr=C(OH)(C₂H₃) (**5**), which is supposed to add an alkyne molecule in the second step. An alternative path is suggested, where the alkyne reacts directly with the saturated metal-carbene complex **1** instead of competing with a CO molecule for a position in the coordination sphere of the metal center in **5**. Our calculations reveal that if alkyne addition takes place in **1** before CO loss, then the initial process becomes clearly exothermic (-163.4 kJ mol⁻¹). Moreover, this alternative path makes it easier for CO dissociation to occur as the second step because at this point the complex has more internal energy than **1** to expel a CO ligand. From a comparison of both mechanistic routes, it is concluded that the Dötz reaction better proceeds initially through an *associative* step.

I. Introduction

Complexes of the type (CO)₅M=C(OR)R' (M = Cr, Mo, W), which are also known as Fischer carbene complexes after their discoverer,¹ have found widespread application in organic synthesis in recent years.^{2,3} A major role has been especially played by heteroatom-stabilized chromium complexes of type **1** (Scheme 1).⁴ Among the synthetically useful reactions of chromium carbenes, one of the most prominent is benzannulation.⁵ In particular, the so-called Dötz reaction⁶ is an efficient synthetic method which has already proved its worth numerous times in the fields of antibiotics⁷ and natural product synthesis.⁸ This process allows α,β -unsaturated pentacarbonyl carbene complexes (R' = aryl, alkenyl) such as **1** to react with alkynes **2** under thermal conditions to give a wide variety of phenol derivatives **4**, which can



be easily liberated from Cr(CO)₃-complexed hydroquinone derivatives **3**.

Remarkable improvements have been reported experimentally regarding the optimization of the reaction yield, such as variations in the reaction temperature and solvent,^{9,10} and introduction of special techniques (e.g.,

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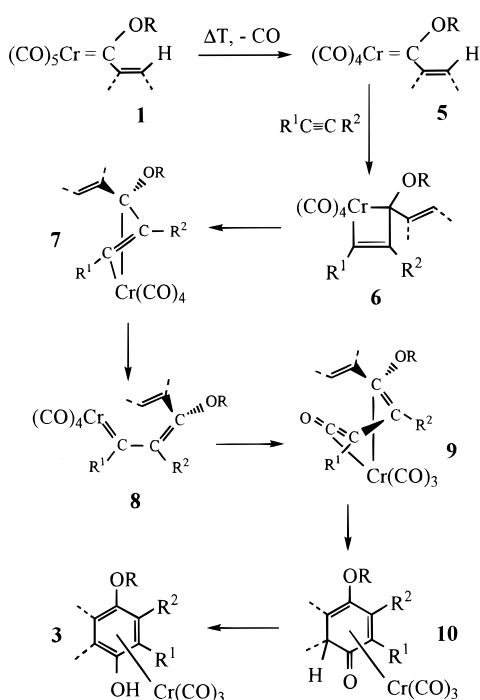
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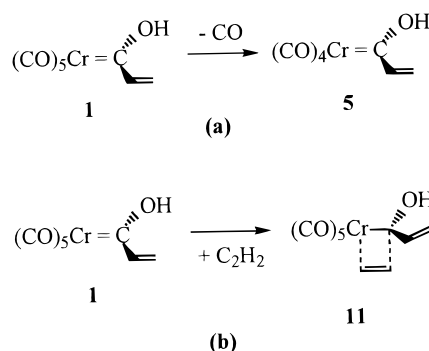
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Scheme 2



Scheme 3



dry state adsorption conditions,¹¹ ultrasonication,¹² and photoirradiation employing a xenon lamp¹³). In contrast, mechanistic aspects of the Dötz reaction are still in an early stage of discussion. The mechanism of the whole scenario for the benzannulation reaction is briefly described in Scheme 2 as it has been usually adopted in the literature.¹⁴ Reflecting the original mechanistic proposals of Dötz in 1975, it was suggested that metal-complexed derivatives **3** are obtained by, first, alkyne coordination to compound **5**, second, rearrangement to the chromacyclobutene **7**, third, migration of CO to yield coordinated ketene **9**, and last, collapse to the phenolic substrate **4**, in the overall transformation of Scheme 1.

Surprisingly or not, no computational studies on the Dötz reaction existed before the 1990s. Even nowadays the knowledge about reaction mechanisms in the area of organic synthesis by means of organometallic catalysts is still rather scarce, but hopefully, recent advances in the methodology of computational chemistry, combined with the increasing performance of computer hardware, are starting to widen the range of molecules which can be calculated.^{15,16} The mechanistic complexity of the Dötz reaction is typical of many other transition-metal-mediated organic transformations, whose size has prevented them from being computationally studied until this decade. This fact partially explains why it was not until 1991 that the first theoretical investigation related to the Dötz reaction was reported

(Hofmann *et al.*¹⁷). Some of the hypotheses that had been previously assumed from experimental data were shown to be incorrect and had to be reformulated. Thus, the extended Hückel molecular orbital calculation performed by Hofmann indicated that planar chromacyclobutenes **6**, usually formulated as initial products of the alkyne carbene coupling step at chromium, were indeed unrealistic intermediates.

Very recently, Gleichmann *et al.*¹⁸ have reported reaction barriers, intermediates, and transition-state structures for the benzannulation reaction of heteroatom-stabilized chromium pentacarbonyl carbene complexes with ethyne. According to their density functional calculations, all reaction steps except the rate-determining CO dissociation are characterized by a pronounced gentle character and low energy barriers. The only important bottleneck seems to be located at the very beginning of the reaction, but once the early activation barrier has been surmounted, the reaction proceeds gently, and the total benzannulation is found to be exothermic.

The aforementioned theoretical studies have clearly brought significant findings. Some aspects still remain uncertain, however. In particular, one of them involves the elucidation of the mechanistic details of the initial processes of the reaction, because the crucial step for the reaction to proceed occurs precisely at this early stage. From an energetic point of view, one may wonder whether the usually assumed first step (CO dissociation) is always compatible with experimental conditions. Furthermore, one may wonder whether there is any alternative to bypassing such a determining barrier, for instance, by interchanging the two first steps and inserting the alkyne prior to the CO loss. In fact, two different mechanisms can be formulated for the first step (Scheme 3): a dissociative mechanism (a) and an associative mechanism (b).

Most mechanistic proposals found in the literature assume that the reaction starts out from a CO dissociation in **1**, leading to the unsaturated 16-electron species **5** (dissociative mechanism). Although such highly reactive species have rarely been isolated,¹⁹ these proposals are supported by the 16/18-valence-electron (VE) rule.²⁰ Moreover, early experiments have shown that the cycli-

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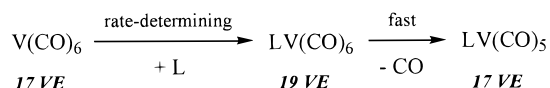
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Scheme 4



zation reaction is blocked in the presence of excess CO, suggesting CO elimination in one of the first steps.^{21–24}

On the other hand, the possibility that the cycloaddition with alkynes might take place initially by direct reaction of coordinatively saturated chromium carbene complexes has not been carefully considered yet, despite the existence of similar reactions with other transition metals. For example, the reactions of $(\text{CO})_5\text{WCHC}_6\text{H}_6$ with alkenes were best explained by direct electrophilic attack of the carbene carbon at the alkene.²⁵

Therefore, another possible mechanistic scenario which could operate in competition with the reported CO loss would be the insertion of an alkyne ligand into the metal coordination sphere prior to CO elimination (associative mechanism). Such a mechanism is not unknown in the field of transition-metal chemistry; e.g., carbonylmetal complexes with a 17-VE shell such as $\text{V}(\text{CO})_6$ undergo substitution via an associative mechanism (Scheme 4), the formation of a 19 VE intermediate being accompanied by a gain in bond energy.²⁶

Moreover, Casey²⁷ showed that the nucleophilic attack of electron-rich ethynes at the carbene carbon atom is faster than ^{13}C O exchange of the starting carbene complex. The rate of reaction was found to depend solely on the concentrations of the carbene complex and ethyne. These results seem to indicate that the first step does not involve CO dissociation. In contrast, they favor the alkyne addition path as the initial step.

A third mechanism for the first step of the Dötz reaction might be a [3 + 2] cycloaddition of the alkyne with the saturated metal-carbene complex **1**. Formation of the phenol product would thus be favored at higher concentrations of alkyne. However, Bos *et al.*,⁹ who have recently suggested a [3 + 2] cycloaddition for the particular reaction of a phenylcarbene complex with diphenylethyne, found that it was inconsistent with the kinetics of the reaction. In effect, experiments revealed that under conditions in which the reaction yielded phenol products, the reaction rate was first order in phenylcarbene complex concentration and was independent of the ethyne concentration. A [3 + 2] cycloaddition could not explain, therefore, the effect of the concentration of diphenylethyne on the distribution of products. Such a hypothetical [3 + 2] cycloaddition will not be analyzed here.

From the above discussion, it follows that the experimental results reported to date on the elementary reactions involved in the initial steps of the Dötz reaction

are not conclusive. This notwithstanding, the few theoretical investigations in this field so far^{17,18} have assumed that the reaction starts with a dissociation of a *cis*-CO molecule, no other alternative mechanistic pathways having been explored yet. The major goal in the present paper is twofold: (i) we shall analyze the traditionally accepted dissociative mechanism for the purpose of clarifying its operativeness and (ii) we shall present an alternative path, which can be more consistent with the known facts²⁷ concerning the initial steps of the Dötz reaction, starting with an associative mechanism. On the whole, the global objective is to throw some light on the preactivation scenario of the benzylation reaction.

II. Computational Details

Considering the importance of electron correlation effects, which are known to be essential for transition-metal systems in organometallic chemistry, it seems reasonable to use a correlated level of calculation able to treat coordination compounds accurately and, at the same time, practical enough for large systems. Encouraged by the success of DFT in recent gas-phase studies involving chromium complexes,^{28–30} we performed the present work using this method.

All DFT calculations were made using the Gaussian 94 program.³¹ Geometries were optimized within the nonlocal density approximation (NLDA), including Becke's³² nonlocal exchange correction as well as Perdew's³³ inhomogeneous gradient corrections for correlation. The 6-31G* basis set³⁴ was employed for C, O, and H atoms. For the chromium atom we used a basis set as described by Wachters,³⁵ (14s9p5d)/[8s4p2d]. An additional 1d polarization function was added to chromium with a 0.3466 exponent. All geometries were fully optimized and energy minima located without any symmetry restrictions.

III. Results and Discussion

This section begins with a description of the starting carbene complex. In the second part we will analyze the dissociative mechanism, dividing the discussion into stereochemical and energetic considerations. The proposal of an alternative path where the reaction proceeds initially through an associative mechanism will be examined in the third part. Finally, the feasibility of both routes will be also weighed up.

A. Chromium Carbene Complex. Chromium carbenes such as **1** can be considered as formed, as in a

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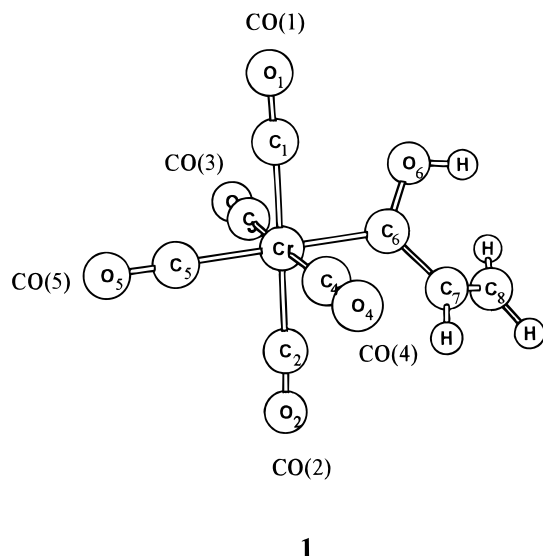


Figure 1. Optimized geometry of complex **1**. Labels numbering CO ligands are indicated in parentheses.

metal carbonyl,³⁶ by bonding a singlet $\text{Cr}(\text{CO})_5$ fragment and a singlet carbene fragment. The 1-hydroxy-2-propenylidene ligand, $\text{C}(\text{OH})(\text{C}_2\text{H}_3)$, is a better σ -donor than CO. Also, it has a single π -acceptor orbital, which is better than either of the two π -acceptor orbitals of CO; however, the CO ligand is a stronger π -acceptor than the carbene ligand because it can accept electron density into two different π^* orbitals.³⁷ The $\text{Cr}=\text{C}$ (carbene) bonding is similar to that of a metal carbonyl; the carbene donates in a σ fashion to the metal, and the metal back-donates to the carbene ligand in a π fashion. One might expect a decrease in the C(carbene) σ electron density, which partially explains the electrophilicity of the carbene carbon atom observed in Fischer-type complexes.³

The aforementioned facts are in agreement with the experimental dipole moment value of 4 D [$(\text{CO})_5\text{Cr}^{\delta-}\leftarrow\text{C}^{\delta+}$] measured for $(\text{CO})_5\text{Cr}=\text{C}(\text{OCH}_3)\text{CH}_3$, which indicates a lack of charge on the carbene carbon atom and suggests an electrophilic reactivity of the carbene site.³⁸ To our knowledge, no experimental dipole moment is available for compound **1**. Our calculations yield a dipole moment of 5.3 D and reveal that charges on the carbene fragment (-0.215) are smaller than charges on the CO ligands (-0.318 to -0.368). These results predict a similar electrophilic reactivity for **1** and confirm the assigned σ -donor/ π -acceptor strength for CO and the carbene ligand.

The optimized geometry of complex **1**, together with the definitions of structural parameters, is displayed in Figure 1. Calculations indicate that in the optimized structure **1** the H atom bonded to O_6 prefers to adopt a *cis* conformation. In fact, free rotation around the $\text{C}_6\text{--O}_6$ bond axis is expected at room temperature, as has been experimentally observed for a similar carbene complex.³⁹ In the solid state, the methoxymethylcarbene complex is found to be in its *trans* conformation

Scheme 5

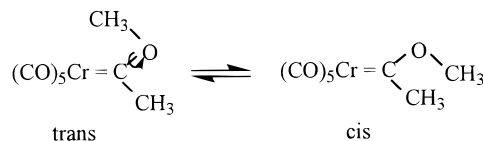


Table 1. NLDA-Optimized Geometrical Parameters for the Most Stable Conformation of $(\text{CO})_5\text{Cr}=\text{C}(\text{OH})(\text{C}_2\text{H}_3)^a$

param ^a	this work	ref 18 ^c	ref 28 ^d
$d(\text{Cr}=\text{C}_6)$	1.993	2.03	1.99
$d(\text{Cr}-\text{C}_1)$	1.898	1.89	1.92
$d(\text{Cr}-\text{C}_2)$	1.893	1.89	1.93
$d(\text{Cr}-\text{C}_3)$	1.900	1.89	1.92
$d(\text{Cr}-\text{C}_4)$	1.893	1.89	1.93
$d(\text{Cr}-\text{C}_5)$	1.899	1.89	1.95
$d(\text{C}_1-\text{O}_1)$	1.166	1.16	1.16
$d(\text{C}_2-\text{O}_2)$	1.169	1.16	1.16
$d(\text{C}_3-\text{O}_3)$	1.166	1.16	1.16
$d(\text{C}_4-\text{O}_4)$	1.168	1.16	1.16
$d(\text{C}_5-\text{O}_5)$	1.167	1.16	1.16
$d(\text{C}_6-\text{O}_6\text{R})$	1.344		1.36
$d(\text{C}_6-\text{R}')$	1.477	1.47	1.51
$\angle(\text{C}_6=\text{CrC}_1)$	89.9		
$\angle(\text{C}_6=\text{CrC}_2)$	91.5		
$\angle(\text{C}_6=\text{CrC}_3)$	89.0		
$\angle(\text{C}_6=\text{CrC}_4)$	87.6		
$\angle(\text{C}_6=\text{CrC}_5)$	178.5		
$\angle\text{C}_1\text{CrC}_6\text{O}_6$	-29.3		
$\angle\text{C}_1\text{CrC}_6\text{C}_7$	153.0		

^a Bond angles and dihedral angles are given in degrees, and bond distances in Å. ^b Labels for each atom are as depicted in Figure 1. ^c Optimized geometrical parameters for **1** as reported by Gleichmann *et al.* ^d Optimized geometrical parameters for $(\text{CO})_5\text{Cr}=\text{CMe}(\text{OMe})$ as reported by Ziegler *et al.*

(Scheme 5), whereas in solution at -40 °C and higher temperatures, both *cis* and *trans* forms occur, the rotational energy barrier³⁹ being only $\Delta E = 52$ kJ mol⁻¹. A similar behavior can be predicted for **1**.

Geometrical parameters from Table 1 are in good agreement with those previously reported^{18,28} for similar carbene systems, also at the NLDA level. From experimental studies of various carbene complexes, it has been observed that the $\text{M}=\text{C}$ (carbene) bond is significantly shorter than an $\text{M}-\text{C}$ single bond but longer than the $\text{M}-\text{C}(\text{CO})$ bond in metal carbonyls.³⁸ Values from Table 1 fit such a pattern and reflect the importance of the $\text{Cr}(d\pi)\rightarrow\text{C}(\pi$ in carbene or π^* in CO) back-donation. The greater elongation found in the $\text{M}=\text{C}$ (carbene) bond as compared to the $\text{M}-\text{C}(\text{CO})$ bond can be ascribed to the weaker π -acceptor character of carbene as compared to CO.

Another point concerns the C–O bonding in $\text{Cr}(\text{CO})_6$ compared to the carbonyl bonding in **1**. Due to the aforementioned weaker π -acceptor character of the carbene as compared to CO, back-donation from metal to the carbonyl orbital of π^* symmetry takes place to a further extent in **1** than in $\text{Cr}(\text{CO})_6$. As a result, a slightly larger C–O bond length is found for **1** (1.166–1.169 Å) in relation to $\text{Cr}(\text{CO})_6$ (1.164 Å) at the present level of calculation.

As can be seen from Table 1, the bond length between the carbene C_6 atom and its alkenyl substituent (C_7) is midway between that of a C–C single bond (1.54 Å) and that of a C=C double bond (1.34 Å). Electron delocalization along conjugated bonds as well as π back-donation in the formation of complex **1** from $\text{Cr}(\text{CO})_5$

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and $\text{C}(\text{OH})(\text{C}_2\text{H}_3)$ are the major factors responsible for the shortening of the $\text{C}_6\text{--C}_7$ bond. Also the bond distance between C_6 and O_6 is shorter than a typical C--O single bond (1.43 Å).⁴⁰ In this case, what largely accounts for the shortening of the bond are electrostatic effects. Support for the latter statement comes from a charge analysis performed on both the optimized structure of the free carbene $\text{C}(\text{OH})(\text{C}_2\text{H}_3)$ and **1**.

Two arrangements can be in principle differentiated for complex **1**, namely the staggered conformation S (the plane of carbene bisects two carbonyls' plane), and the eclipsed conformation E. These configurations are related by a rotation of the carbene ligand around the $\text{Cr}=\text{C}_6$ axis of the complex. Previous studies on metal carbene complexes^{28,40,41} have revealed that this rotation is essentially free, with rotational barriers being ca. 2 kJ mol^{-1} . The preference for an E or S arrangement is determined by the substituents of the carbene ligand as well as by the $\text{M}=\text{C}$ bond distance.^{28,29} Thus, when the carbene ligand is rotated into the staggered conformation, the steric repulsion is reduced. A small reduction in orbital interaction is also observed, since the overlap of mainly the empty 2p orbital at carbon with the chromium 3d orbital decreases, causing an elongation of the $\text{Cr}=\text{C}$ bond. As pointed out by Jacobsen and Ziegler,²⁸ the preference for the E or S conformation depends on the balance of these two effects (steric repulsion and orbital interaction). Thus, the bulkier the carbene ligand, the greater the steric repulsion, and therefore, an S arrangement is expected to be more favored. This is the case for complex **1**, where steric repulsions counterbalance orbital interactions, and the molecular geometry turns out to be more stable in an S-like conformation by 4.1 kJ mol^{-1} rather than in an E conformation. The torsional angles $\angle\text{C}_1\text{CrC}_6\text{O}_6$ and $\angle\text{C}_1\text{CrC}_6\text{C}_7$ from Table 1 indicate that, on average, the plane of carbene ligand has rotated ca. 28° in relation to the vertical plane. If a simpler carbene complex had been considered, then Pauli repulsions would have been likely weaker, allowing a smaller rotation angle and favoring a more eclipsed conformation. This is the case for $(\text{CO})_5\text{Cr}=\text{CH}(\text{OH})$, whose E structure was reported to be more stable than its S structure.⁴⁰

B. Dissociative Mechanism. This section deals with the mechanistic proposal which claims a decarbonylation as the first step in the Dötz reaction.

1. Stereochemistry of CO Elimination: Geometrical Analysis. The ease of CO elimination in metal-pentacarbonyl complexes is related to the donor–acceptor capacity of the involved ligands. With respect to the relative donor–acceptor properties of the carbene and carbonyl ligands, a preference for the elimination of a *cis* CO group is expected. This idea has been proven by CO exchange studies.⁴² Nevertheless, under experimental conditions, it is difficult to determine for a given system which of the four *cis* CO ligands is exchanged with free CO molecules. Depending on the particular CO ligand actually removed from **1**, the resulting species, **5** (a 16-electron species), can either be suitable to interact with an ethyne molecule **2** or be unable to

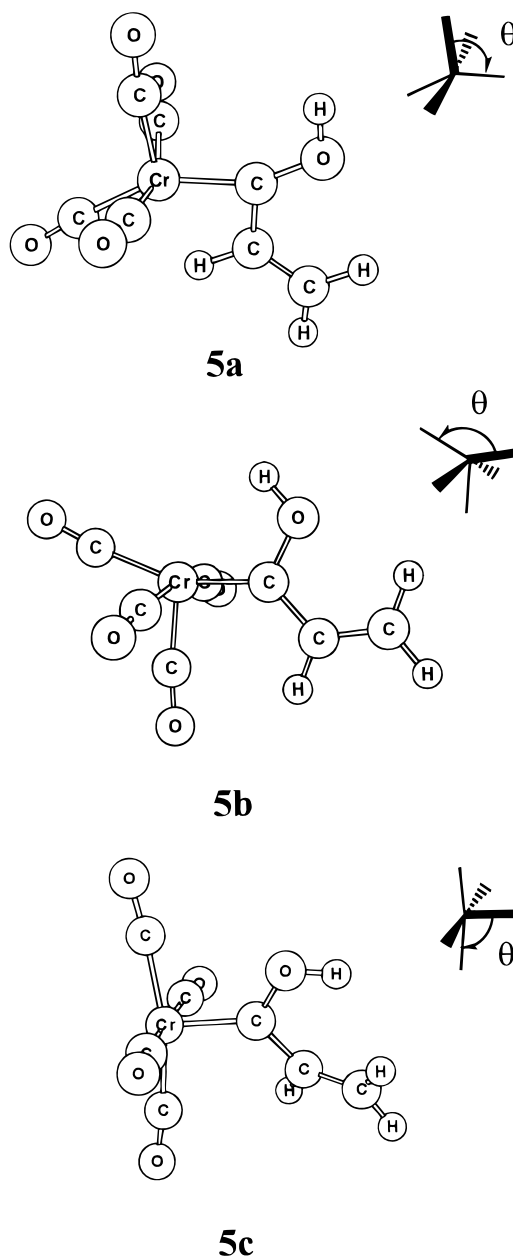


Figure 2. Optimized structures for the three different isomers of tetracarbonylcarbene complex **5**, $(\text{CO})_4\text{Cr}=\text{C}(\text{OH})(\text{C}_2\text{H}_3)$, obtained from **1** by removing one CO ligand. Apical positions are indicated by boldface lines.

undergo the cyclization reaction because the vacant site is blocked by a solvent molecule (or occupied again by another CO group).

Because of the lack of experimental data in connection with this point, we have explored all possibilities (i.e., five CO dissociation processes) in order to avoid missing relevant intermediates. Hence, the relative energies of the optimized structures that spring from **1** by removing $\text{CO}(1)\text{--CO}(5)$ ligands, one at a time, have been computed. A priori, one would expect that five such decarbonylation processes led to five different complexes. However, due to the S-like conformation of the starting carbene complex, only three different dissociation products are indeed found (Figure 2). Removal of either $\text{CO}(1)$ or $\text{CO}(3)$ ligands yields complex **5a**. Complex **5b** comes from dissociating either $\text{CO}(2)$ or $\text{CO}(4)$. Finally, the loss of the *trans* CO leads to complex **5c**. Notice

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Table 2. NLDA-Optimized Bond Distances (in Å) and Bond Angles (in deg) for Intermediates 5a–c^a

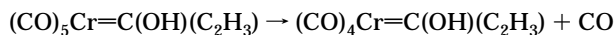
param	compd		
	5a	5b	5c
$d(\text{Cr}=\text{C}_6)$	1.980	1.875	1.900
$d(\text{Cr}-\text{C}_1)$		1.820	1.895
$d(\text{Cr}-\text{C}_2)$	1.802		1.878
$d(\text{Cr}-\text{C}_3)$	1.892	1.895	1.903
$d(\text{Cr}-\text{C}_4)$	1.892	1.895	1.903
$d(\text{Cr}-\text{C}_5)$	1.884	1.898	
$d(\text{C}_1-\text{O}_1)$		1.176	1.170
$d(\text{C}_2-\text{O}_2)$	1.179		1.175
$d(\text{C}_3-\text{O}_3)$	1.169	1.167	1.168
$d(\text{C}_4-\text{O}_4)$	1.169	1.167	1.168
$d(\text{C}_5-\text{O}_5)$	1.171	1.169	
$d(\text{C}_6-\text{O}_6)$	1.359	1.331	1.353
$d(\text{C}_6-\text{C}_7)$	1.467	1.450	1.482
$\angle(\text{C}_6=\text{CrC}_1)$		106.0	95.2
$\angle(\text{C}_6=\text{CrC}_2)$	101.3		97.2
$\angle(\text{C}_6=\text{CrC}_3)$	90.7	94.0	87.7
$\angle(\text{C}_6=\text{CrC}_4)$	90.7	94.0	87.7
$\angle(\text{C}_6=\text{CrC}_5)$	164.8	152.4	
ligand lost	CO(2 or 4)	CO(1 or 3)	CO(5)

^a Labels for each CO are as depicted in Figure 1.

that in both **5a** and **5b** the 1-hydroxy-2-propenylidene ligand has rotated from its original position until it becomes totally coplanar with the *trans* CO ligand, whereas in **5c** the carbene ligand still keeps its original S-like conformation. The rotation experienced by the carbene fragment in **5a** and **5b** arises from the net balance between electronic and steric factors. This is the reason only two products (instead of four) are found when, one at a time, the four *cis* CO ligands are removed.

Geometrical parameters for **5a–c** are collected in Table 2. For many pentacoordinate transition-metal complexes, it is not easy to determine which part of an observed conformational preference is due to electronic effects and which part is set by the steric requirements of the coordinated ligands. With regard to electronic effects, there exists an additional problem concerning the choice between a trigonal bipyramid (TB) or square pyramid (SP) (both connected by a Berry pseudorotation), or even other intermediate conformations, which is quite usual in a flat potential energy surface.⁴³ In the particular case of d⁶ tetracarbonyl complexes involving also a fifth π -acceptor ligand, the TB geometry is not as favorable as the SP.⁴³ Species **5a–c** thus all have in common an SP structure. However, each species has undergone a different geometrical change; i.e., each has adopted a different pyramidalization bond angle, θ (see Figure 2 for definition). The major perturbation occurs in **5b** ($\theta = 165^\circ$), the apical site being occupied by the carbene ligand. Notice that in **5a** ($\theta = 106^\circ$) the carbene ligand remains in a basal position of the "flat" square pyramid. Only structure **5c** can be considered to stay nearly unaltered ($\theta = 96^\circ$).

Structural rearrangements happen to be crucial in explaining the relative stabilities of the products and, therefore, the relative energies of CO dissociation. Table 3 collects the calculated energies required for each decarbonylation reaction: **1** \rightarrow **5** + CO(*n*) (*n* = 1–5). The cleavage of CO(5) requires the highest energy,

Table 3. Calculated CO Bond Dissociation Energies (BDE) in kJ mol⁻¹ for the Different CO Ligands

ligand lost	product	BDE
CO(2) or CO(4)	5a	144.7
CO(1) or CO(3)	5b	171.9
CO(5)	5c	188.6

immediately followed by the removal of CO(1) (or CO(3)). Unlike **5b**, the product **5c** is unable to gain some extra stability by means of further structural rearrangements. The energetic cost is smaller for the dissociation of CO(2) (or CO(4)) because of the favorable agostic interaction in **5a**, which renders some stability to the product. The bond distance between Cr and the H atom located on C₇ is only 2.056 Å, whereas the C₇–H bond length is remarkably longer than the C₈–H distances (1.126 vs 1.094 Å). This points to the existence of an agostic interaction between the metal center and the H atom in **5a**, which would be responsible for an important gain of stability (ca. 30 kJ mol⁻¹ in similar complexes⁴⁴). In contrast, structure **5c** becomes hardly misshapen by relaxation and, consequently, is less stabilized. The situation of **5b** is midway between those of **5a** and **5c**. In **5b** the distance between Cr and the H atom bonded to O₆ is 2.897 Å, suggesting some kind of favorable interaction that is still weaker than in **5a**.

Gleichmann *et al.*¹⁸ have recently calculated the CO bond dissociation energy (BDE) for compound **1**. They have also found that *trans*-CO dissociation is a highly endothermic process (202 kJ mol⁻¹). Regarding *cis*-CO dissociation, only two different products have been reported, but whereas one of them is similar to **5a**, the other does not resemble **5b** and is better described as an η^3 -allylidene complex. The compound analogous to **5a** is found to be 34 kJ mol⁻¹ more favorable than the *trans*-CO dissociation (our results being in good agreement) and 43 kJ mol⁻¹ less stable than the η^3 -allylidene complex. According to this, the most favorable direct dissociation product of both studies would seem to be the η^3 -allylidene complex. However, this structure has the disadvantage of being inaccessible to ethyne insertion in the next step of the Dötz reaction unless further rearrangement occurs. In effect, unlike the case for **5a** and **5b**, there is no vacant coordination site available in an η^3 -allylidene complex for the ethyne molecule to approach. As pointed out by Gleichmann *et al.*,¹⁸ the consequence would be a too highly energetic attack of the ethyne on the carbon atom. The only way to overcome this inaccessibility of ethyne insertion into the η^3 -allylidene complex is precisely by giving up the intramolecular η^3 bonding, the resulting species being no longer the direct product of *cis*-CO dissociation referred to as an η^3 -allylidene complex. Therefore, compound **5a** of the present paper turns out to be the most stable and suitable dissociation product according to the proposed dissociative mechanism.

2. Energetic Considerations. In principle, the energy required to remove a carbonyl ligand from Cr(CO)₆ can be a good reference for the reaction under study. The experimental first BDE of Cr(CO)₆ has been

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measured⁴⁵ to be ca. 154 kJ mol⁻¹. Our calculated BDE is 187 kJ mol⁻¹; a value of 192 kJ mol⁻¹ has been previously reported by Ziegler⁴⁶ (also computed at the NLDA level), and a more accurate value of 170.6 kJ mol⁻¹, including BSSE corrections, has been later quoted by Rosa *et al.*⁴⁷ Interestingly the substitution of one of the six CO ligands by a carbene ligand is expected to make the decarbonylation process even more endothermic. Thus, the first BDE of **1** is predicted to exceed the aforementioned calculated amount of 187 kJ mol⁻¹. This notwithstanding, not all dissociation energies shown in Table 3 follow this trend. The reason originates from the previously discussed favorable interactions occurring in products **5a** and **5b**. Although it is difficult to quantify the gain in energy furnished by such interactions, the comparison with Cr(CO)₆ makes clear that some kind of additional stability exists (probably ranging 20–50 kJ mol⁻¹).

Our results from Table 3 are in line with those reported by Gleichmann *et al.*¹⁸ for compound **1**. Hence, the BDE for the *trans* CO ligand, CO(5), has been computed to be 188.6 kJ mol⁻¹, compared to their 202 kJ mol⁻¹. With regard to the *cis*-CO ligands, only two dissociation products were also reported, the first one (a tetracarbonyl carbene complex similar to **5a**) with a BDE of 168 kJ mol⁻¹ and the second one (an η^3 -allylidene complex structurally very different from **5a** and **5b**) having a BDE of 125 kJ mol⁻¹. However, as mentioned, the η^3 -allylidene complex was found to be an unsuitable intermediate because it had no vacant coordination site available for ethyne to insert unless the intramolecular η^3 bonding was lost.¹⁸

To this end, the decarbonylation of **1** is found to need quite extreme conditions (more than 144 kJ mol⁻¹ to reach the least unfavorable dissociation product **5a**). Because experiments are carried out under mild conditions (moderate temperatures:^{4,9} 45–55 °C), it is difficult to see how CO loss can take place at this stage, as suggested by earlier mechanistic proposals which assume that CO dissociates in the first step. Given the high energy required to get the subsequent unsaturated complexes (such as **5a–c**), these 16-electron species are better considered unusual intermediates. In fact, in experiments performed under thermal conditions, tetracarbonyl complexes have thus far escaped direct observation. They have only been detected in some photochemical studies.^{22–24} However, even under extreme conditions, their existence is not always clear (as in the experimental observations by Bell *et al.*,⁴⁸ who investigated the CO photodissociation of the organometallic species (CO)₅W=C(OMe)Ph in noncoordinating solvents without being able to stabilize any transient species), especially when intramolecular chelation¹⁹ is not possible. In the case of the carbene complex studied here, intramolecular interactions cannot take place: chelation in **5** through either the vinyl fragment or the OH group would result in a small, tight ring and,

consequently, in an even more unstable complex. Only the aforementioned agostic interactions are relevant. A different route, alternative to the dissociative mechanism, must then exist at least when the reaction proceeds in the gas phase or in noncoordinating solvents.

Known facts from similar reactions also support the query about the feasibility of CO dissociation in situations which demand too much energy. For instance, a nonlocal density functional study on the decarbonylation of HCo(CO)₄ has recently revealed⁴⁹ that bond energies are as large as $\Delta E(\text{Co}-\text{CO}_{\text{eq}}) = 169$ kJ mol⁻¹ and $\Delta E(\text{Co}-\text{CO}_{\text{ax}}) = 207$ kJ mol⁻¹. Despite the lack of experimental data, the authors of this study concluded that it was understandable that very high temperatures were required to generate a sufficient concentration of HCo(CO)₃. From the experimental side, a kinetic study on the reaction of a methoxyphenylcarbene complex with tolan revealed a long time ago that a relatively high activation enthalpy ($\Delta H^\ddagger = 108 \pm 2$ kJ mol⁻¹) and a positive activation entropy ($\Delta S^\ddagger = 26 \pm 6$ J mol⁻¹ K⁻¹) were required for the reaction to proceed through a CO dissociative mechanism.⁵⁰ Such a mechanism is only feasible when photodissociation (or other techniques^{12,13}) is used. This is not the case for the procedures usually employed in the Dötz reaction.

C. Associative Mechanism. From the above discussion, it follows that there must exist an alternative (and energetically less demanding) route leading to **8**. Otherwise, one could not explain how the reaction can proceed under mild conditions when the large energy requirements are not reduced by chelation. As mentioned above, a good alternative mechanistic pathway could be the insertion of ethyne into the coordination sphere of chromium in complex **1** (Scheme 3b). In principle, this mechanism would involve the formation of the seven-coordinated complex (CO)₅Cr[C(OH)(C₂H₃)]-(η^2 -C₂H₂) (**11**), which is not completely unknown in the field of coordination chemistry. A characteristic of this type of complex is the variety of geometries that ligands can adopt around the metal center, as reported by Balakrishna *et al.*,⁵¹ who have recently elucidated the structures of several seven-coordinated derivatives of group 6 metal carbonyls.

Starting from reactants **1** and **2** (Figure 3), we have searched for the existence of a weak complex or early intermediate along the potential energy surface. The initial distances between Cr and one of the alkyne C atoms and between C₆ and the other C atom in the alkyne have been 3.95 and 3.65 Å, respectively. The C–C axis in **2** has been taken to be nearly coplanar with the Cr–C axis in **1** (initial tilt angle of ca. 20° to avoid any possible collapse of alkyne with one of the *cis* CO ligands). We have found that, when ethyne is placed somewhere close to **1**, one of the carbon atoms in the organic reactant nucleophilically attacks the metal center. This is followed by a second nucleophilic attack of C₆ on the other C in ethyne, leading to the formation of the four-center metallacycle **11**. However, structure

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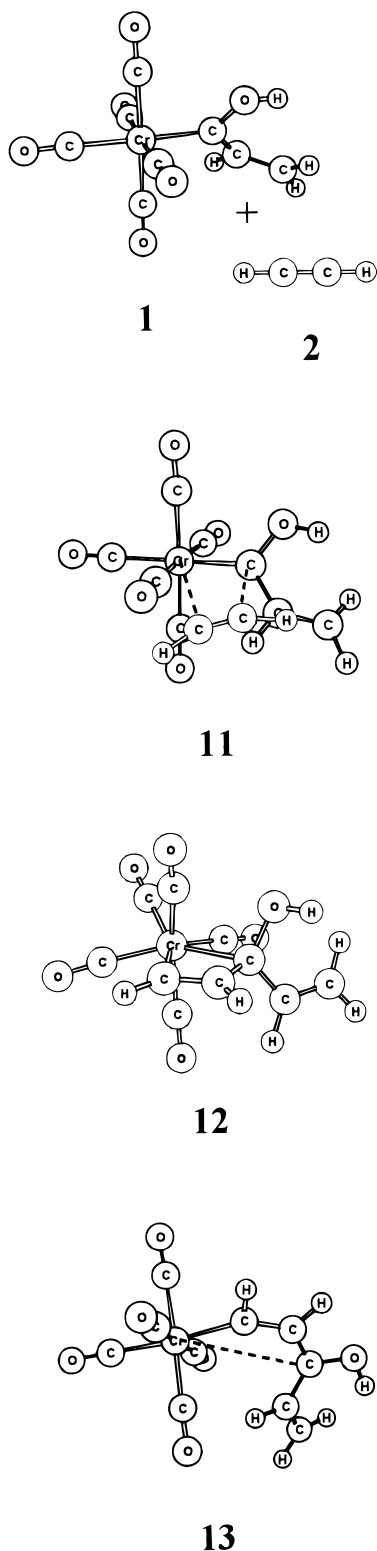


Figure 3. Course of the ethyne association with the saturated complex **1** to yield pentacarbonyl complex **13**.

11 is not a real minimum of the potential energy surface and, during the process of optimization, undergoes [2 + 2] ring closure to yield the intermediate chromacyclobutene **12**, where the Cr–C₆ bond has been remarkably elongated (0.31 Å longer than in **1**). Notice that neither **11** nor **12** are minima but are structural representations of intermediates along the path. Efforts to locate a stationary point in the path between **1** and

13 have been made by means of partial optimization and small linear transit calculations. All attempts have failed in locating a stable intermediate, since all structures have been easily turned into **13**. These results indicate that the reaction may well proceed directly from the reactants to **13** without the intermediacy of a chromacyclobutene complex. This is in agreement with an experimental study by Garrett *et al.*,⁵² where it has been also reported that, although a chromacyclobutene complex had generally been proposed as a common intermediate in the mechanism of the Dötz reaction, there is no direct evidence for its involvement. Theoretical calculations by Hofmann *et al.*¹⁷ and, more recently, by Gleichmann *et al.*¹⁸ have also failed in finding similar metallacyclobutene intermediates. This notwithstanding, we cannot yet discard the existence of a shallow well somewhere around the reactant region, or even the existence of a tiny barrier (and a transition state) following the hypothetical well. However, whether an intermediate exists or not, what is clear is that the reaction may be roughly considered barrierless (or at least has a very low barrier). After having explored the potential energy surface, we can conclude that **13** is the real intermediate of the carbene–alkyne coupling step. Any energy barrier leading to **13** through an associative mechanism (route **B** in Figure 4) should be irrelevant in light of the large amount of energy required to eject a CO ligand from **1** and yield **5** (route **A** in Figure 4).

Let us now turn our attention to the energetics of the associative mechanism. The addition of ethyne to **1** is computed to be a highly exothermic process. As seen from Figure 4, compound **13** lies 163.4 kJ mol⁻¹ below the reactant molecules. This compound can be considered a new pentacarbonylchromium carbene, similar to **1**. The only difference between **1** and **13** is that the latter has a 3-hydroxy-2,4-pentadienylidene ligand instead of the initial 1-hydroxy-2-propenylidene ligand. A larger carbene fragment in **13** causes a labilization effect on the cis-CO ligands. This is assessed by comparing the orbital energies of 1-hydroxy-2-propenylidene to those of the 3-hydroxy-2,4-pentadienylidene ligand: in the latter, the energy of the HOMO has been raised by 0.42 eV and the energy of the LUMO has been lowered by 1.05 eV (due to larger π conjugation). Consequently, not only is 3-hydroxy-2,4-pentadienylidene a better σ -donor than 1-hydroxy-2-propenylidene, but it also turns into a better π -acceptor as well. Both features make the CO neighbors of the new carbene fragment become more labile ligands. Therefore, cis-CO dissociation from **13** is expected to be easier than from **1**. Furthermore, at this point of the reaction, complex **13** has more internal energy than reactant **1** to expel a CO ligand. Internal energy rearrangements through molecular vibrations may assist in the loss of a CO molecule from **13**, especially in the gas phase at low external pressures, where the number of collisions is reduced.

Why then does not **8** react rapidly with CO to form **13** again, which is 132.4 kJ mol⁻¹ downhill? In fact, at high CO pressures this is likely what happens. Displacement of the equilibrium from **8** to **13** does, fur-

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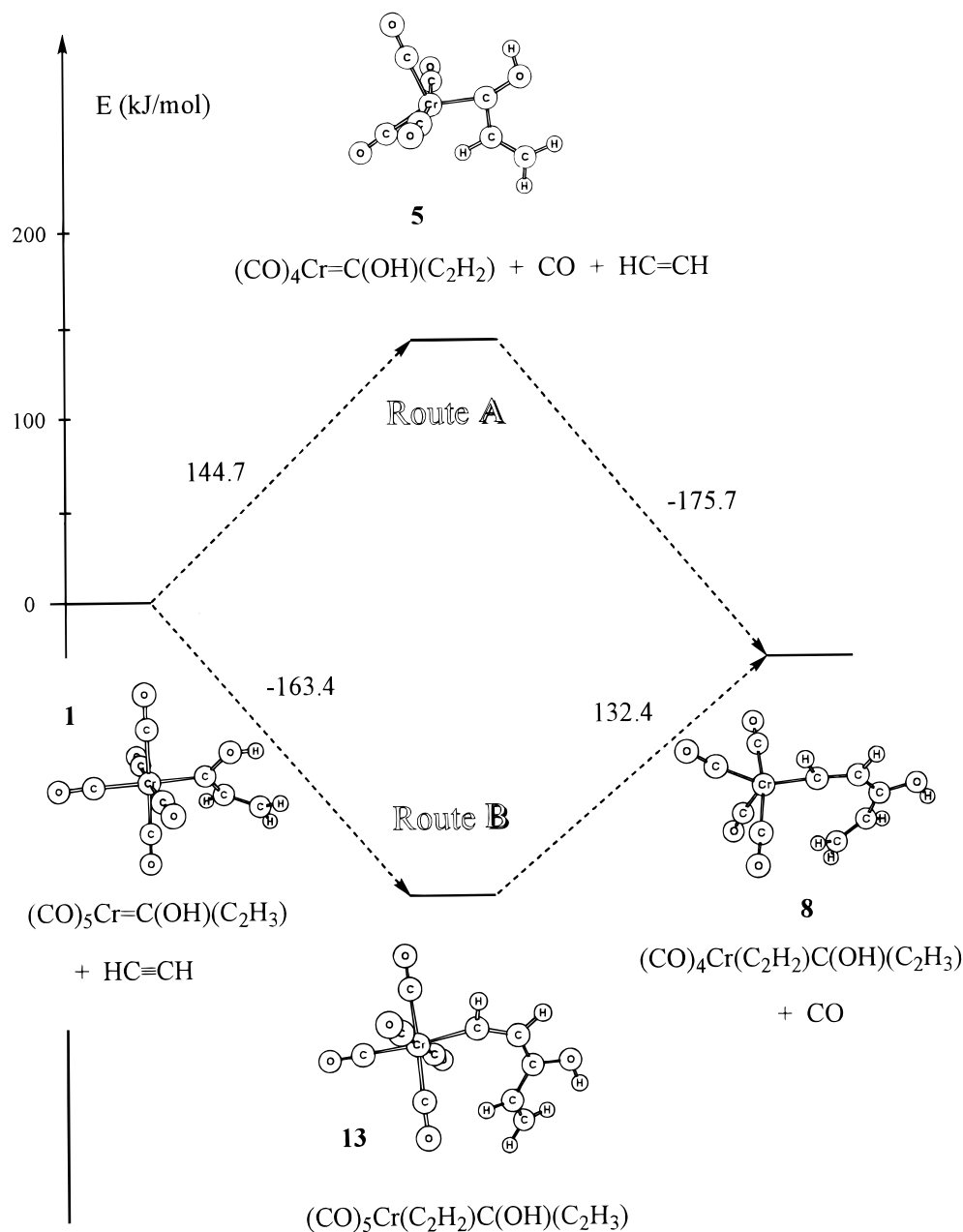


Figure 4. Energy diagram for two different pathways: route **A**, starting with a dissociative mechanism (above), route **B**, beginning with the alkyne addition (below). Energies are given in kJ mol^{-1} .

thermore, explain the experimental fact that the Dötz reaction is blocked by additional CO.^{21–24} However, at lower CO pressures, the reaction is expected to proceed to some extent toward products instead of reverting to reactants. The preference for such a behavior will depend on how favorable the conversion of **8** to a close isomer of **8** is. Indeed, **8** is found to be located in a flat region of the potential energy surface with many local minima of similar energy. In a more extensive study involving the central part of the Dötz reaction, we have seen⁵³ that **8** experiences a small structural rearrangement in the subsequent step to turn into its isomer **8a** (Figure 5), which is 28.0 kJ mol^{-1} more stable. The new agostic interaction in **8a**, despite not being strong, temporarily blocks the vacant site necessary for a CO

ligand to insert into the metal sphere. This is sufficient to establish an equilibrium: as long as the vacant site remains inaccessible, the reaction moves forward without any further energetic cost since all subsequent steps are clearly exothermic and have low barriers. In contrast, appropriate attacks of CO can easily replace the agostic interaction, making the reaction go backward to **8** and, from that point, directly to **13**.

To sum up, it is clear that the usually assumed CO dissociation from the chromium Fischer carbene complex **1** does not always satisfy the energy requirements needed for the reaction to proceed, especially near room temperature. If we take into account mild experimental conditions, route **A** (Figure 4) becomes too demanding ($E \geq 144.7 \text{ kJ mol}^{-1}$ in the first step). The reaction more likely proceeds through an alternative path (route **B**), which involves addition of the alkyne with the starting pentacarbonyl complex $(\text{CO})_5\text{Cr}=\text{C}(\text{OR})\text{R}'$ as the first

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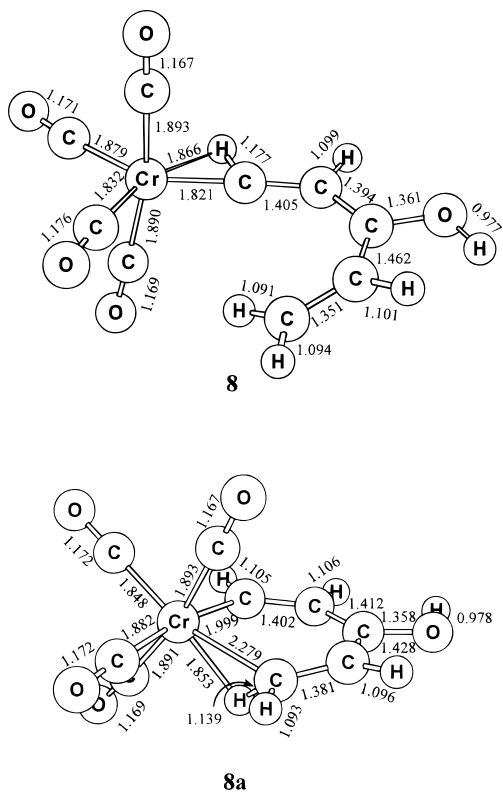


Figure 5. Optimized geometry of intermediates **8** and **8a**. Bond distances are given in Å.

step. Route **B** has the advantage of facing the CO loss in the second step: the new carbene complex coming from an exothermic alkyne addition ($(\text{CO})_5\text{Cr}=(\text{CH})_2\text{C}(\text{OR})\text{R}'$) will always require less energy than the reactant in route **A** to yield the tetracarbonylchromium complex **8**. According to our results elimination of a CO ligand becomes more favorable when it takes place *after* ethyne addition. Therefore, loss of CO is claimed to alternatively occur one step later than has been usually assumed from earlier mechanistic proposals in the literature. Note that such a conclusion is not in contradiction with some experiments, suggesting decarbonylation in *one of the initial steps*.^{21–24}

Conclusions

Although early experiments and mechanistic proposals have suggested that the Dötz reaction begins with CO elimination followed by complexation of C_2H_2 , our gas-phase theoretical results indicate that such a reac-

tion sequence is not always suitable. Calculated reaction energies for the loss of CO from **1** are too large to predict decarbonylation as the first step when the reaction proceeds in the gas phase or in noncoordinating solvents, because it would lead to a highly reactive unsaturated intermediate with a large barrier. Such an endothermic process is in contradiction with mild experimental conditions.

The possibility, however, of stabilizing such unstable intermediates in specific cases through a coordinating solvent or intramolecular solvation (using bulkier substituent groups on the carbene carbon) prevents us from generalizing that, in solution, CO dissociation as the first step must be definitively discarded. If the reaction was performed at high temperatures or in coordinating solvents or via photolysis, then the dissociative mechanism could be still operative. When such conditions are not met, then CO loss is likely to occur immediately *after* the carbene–alkyne coupling process, as shown by the associative mechanism we have examined for the Dötz reaction.

From the present study, the nucleophilic attack of alkynes on carbene complexes is not always believed to require a vacant coordination site at the metal center, provided by the loss of a CO ligand. This is in agreement with a previous study by Casey.²⁷ The alkyne is thought to be bonded directly to the carbene atom and $\text{Cr}(\text{CO})_5$ center, instead of competing with a CO for a position in the coordination sphere of the chromium atom. In light of our gas-phase results, such a coupling reaction is clearly exothermic, and far more likely.

We think that the main conclusions reached in the present work should not be altered in a significant way by the use of a higher level theoretical method. In fact, the main purpose of the present investigation, which has been to evaluate the feasibility of different paths, is based on a comparison. It makes the study less dependent on the methodology than in the cases where extremely accurate results are required. The message of this paper is clear enough for us to be sure that even if more sophisticated techniques had been taken into account the same conclusions would have been drawn.

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