Novel mechanistic proposal for the Dötz reaction derived from a density functional study: the chromahexatriene route

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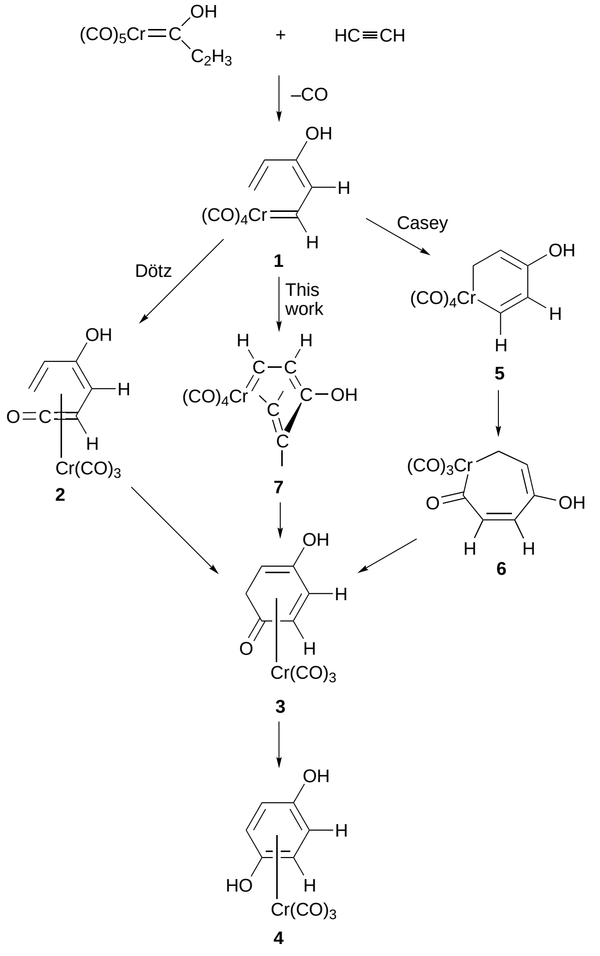
A new mechanism for the Dötz reaction of vinylcarbene complexes with ethyne proceeds through a chromahexatriene intermediate instead of a vinylketene with smooth energy changes and low energy barriers.

One of the most important synthetic transformations leading to C–C bond formation involves the reaction of chromium carbenes with alkynes. This process, a formal [3 + 2 + 1] cycloaddition known as the benzannulation or Dötz reaction,[1] generates substituted phenols by sequential coupling of the alkyne, the carbene and one carbonyl ligand at a [$Cr(CO)_3$] template. The major interest in this reaction is its utility in organic and organometallic synthesis.

The most widely accepted mechanism[2] assumes that the reaction starts with a reversible decarbonylation followed by alkyne coordination, yielding η^3-vinylallylidene complexes **1** (Scheme 1). Two diverging routes have been postulated from this point. According to Dötz,[2] complexes **1** form η^4-vinylketenes **2** by CO insertion into the chromium–carbene bond, followed by electrocyclic ring closure to yield η^4-cyclohexadienones **3**, which can finally turn into the direct precursor of the phenol derivative **4** after enolization and aromatization. As suggested by Casey,[3] an alternative possibility is that metallation of the arene ring occurs in complex **1** to form **5**, which subsequently undergoes carbonylation to yield **6**. Reductive elimination from **6** gives intermediate **3**, where both scenarios merge again.



Scheme 1 Postulated routes for the benzannulation reaction

It has proven difficult to validate these mechanistic suggestions since the rate-limiting step typically involves CO ligand loss to open a coordination site for the alkyne to bind. Once bound, rapid ring closure occurs to give the observed products. No single reaction has been followed completely through the individual steps illustrated in Scheme 1, although there are now several examples of isolation and structural characterization of presumed intermediates relevant to η^3-allylidene complexes[4] and η^4-vinylketene complexes.[5] Additional support for the Dötz route has also been provided by extended Hückel molecular orbital[6] and recent quantum chemical calculations.[7] However, most steps are still only postulated. Thus, although kinetic investigations[8] strongly support the assumption for the CO loss as one of the first reaction steps, most of the subsequent intermediates have so far escaped experimental observation.

According to our calculations,[9–14‡] vinylallylidene complex **1** is a branching point from which the reaction may go on through a third energy path, different from the ones mentioned above. The new proposed pathway also leads to η^4-cyclohexadienone **3**, but, instead of inserting a CO ligand into the Cr–carbene bond, complex **1** can better create first a π-interaction with the terminal C–C double bond yielding a chromahexatriene complex, which undergoes CO insertion in the next step.

The advantage of such a structural arrangement taking place before CO insertion can be seen from Fig. 1. Complex **1** (usually described as an η^3-vinylallylidene[2]) is found to be more favorable in an η^1-coordination (as depicted in Fig. 1) by 11.8 kcal mol^{-1}. The most outstanding feature of η^1-vinylallylidene complex **1** is the agostic interaction between chromium and one of the C_5–H bonds of the terminal alkenyl ligand. The length of the C_5–H bond is *ca.* 0.05 Å larger than the usual distance for a C(sp^2)–H bond, and clearly corresponds to the ones observed for this kind of interactions.[15] The vacant coordination site in complex **1** created after release of a CO ligand *cis* to the carbene fragment remains temporarily blocked by the C_5–H group, and the reaction is prevented from going backwards to the reactants. Once **1** is formed, the ring chain evolves to a more stable conformation through a dπ interaction between chromium and the C_4–C_5 olefinic bond, the release of energy being 11.2 kcal mol^{-1} (Fig. 1). An early, small energy barrier in the path from **1** to **7** (1.8 kcal mol^{-1}) arises from the loss of the agostic interaction while C_4 has not approached the metal center enough (Cr–C_4 = 3.248 Å in **1**, 3.055 Å in TS1, and 2.272 Å in **7**). A crucial feature of complex **7** as compared to complex **1** is the shortening of the distance between C_5 and the CO ligand to be transferred to the Cr–C_5 bond (C_5–CO = 3.517 Å in **1**, and 2.559 Å in **7**), which facilitates CO insertion in the subsequent step (C_5–CO = 2.262 Å in TS2, and 1.533 Å in **3**). Intermediate **7** is directly comparable to η^2-alkenylamino(aryl)carbene complexes of W[16] and Mn,[17] as well as to the more recently

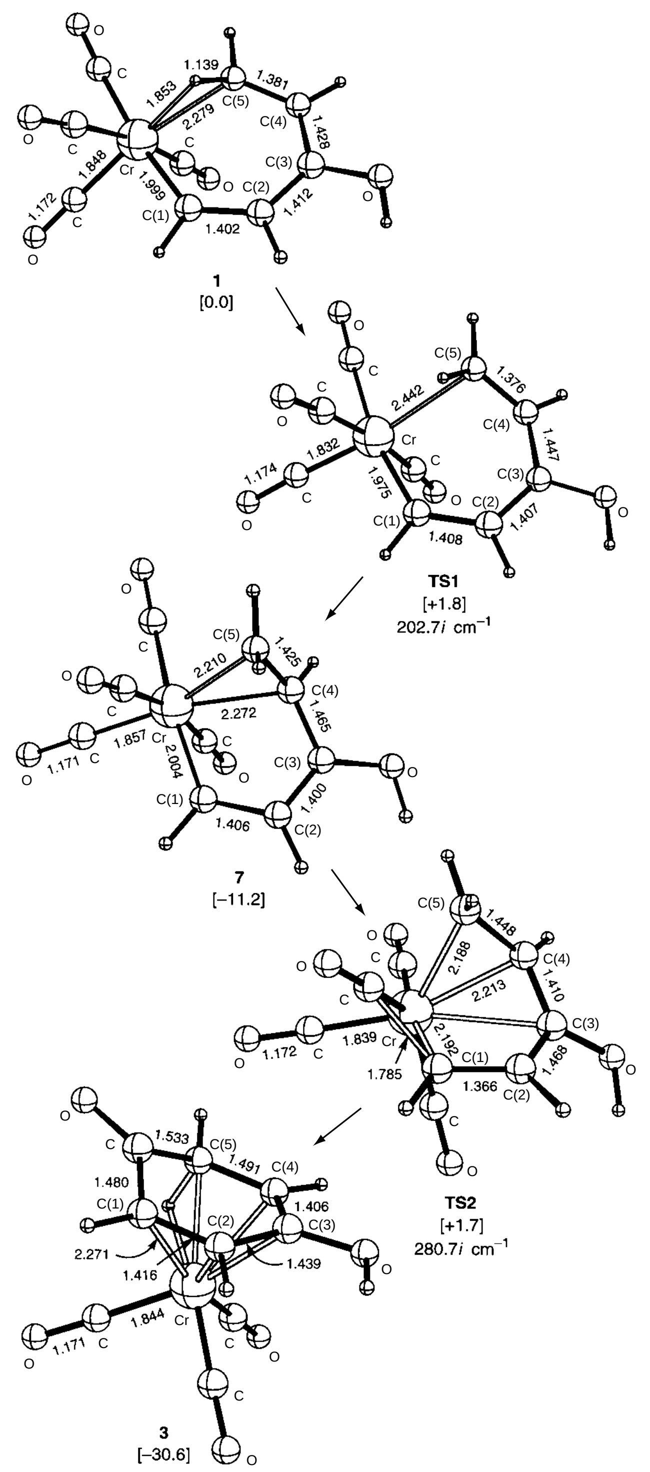


Fig. 1 Geometries of all stationary points and energies relative to complex **1**. Selected bond distances are given in Å, and energies (in square brackets) in kcal mol^{-1}. Compounds **1**, **7** and **3** correspond to minimum energy structures; their absolute energies are −1767.313742, −1767.331596 and −1767.362571 au, respectively. **TS1** (−1767.310883 au) and **TS2** (−1767.310945 au) are first-order saddle points.

reported structure of an alkynylarylcarbene complex of tungsten.[18] In the field of organochromium chemistry, a similar olefin coordination has been also observed for an alkene-[19] and some alkyne-carbenechromium[20] complexes. The strongest support for the existence of **7**, however, probably comes from a recent investigation by Barluenga *et al.*,[4] where a chromahexatriene similar to **7** has been isolated and characterised by ^{1}H and ^{13}C NMR spectroscopy. Experimental data from this study demonstrate that the alkenyl ligand is attached to the metal center through the C_4–C_5 double bond.

Interestingly, chromahexatriene **7** is not an endpoint of the reaction because it connects to a more stable intermediate, as shown in Fig. 1. Distortion of the $Cr(CO)_4$ umbrella mainly accounts for the energy required to reach **TS2** (12.9 kcal mol^{-1}). This is largely compensated by the formation of an agostic interaction in **3**, together with the new Cr–C coordinated bonds in the formed ring. Species **3** with such an agostic interaction has a known precedent in related cationic manganese cyclohexenyl complexes.[21] The fact that the reaction does not end at **7** is consistent again with the experimental results reported by Barluenga *et al.*[4] These authors found that the synthesised chromahexatriene was not stable in solution at room temperature, and decomposed to yield the most common final product in the Dötz reaction with aminocarbenes.[4]

Additional theoretical work on the routes proposed by Dötz and Casey is presently in progress in our laboratory. Preliminary results indicate that the chromahexatriene mechanism presented here seems to be the most favorable of the three proposed routes. Whether this conclusion can be generalised to substrates other than vinyl carbene complexes is the subject of further research.§

Notes and References

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‡ Calculations have been carried out with the GAUSSIAN 94 series of programs[9] using the DFT methodology with the non-local BP86 functional.[10] All geometries have been fully optimised. We have also verified that the imaginary frequency for each transition state exhibits the expected motion.

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