

Weighing Different Mechanistic Proposals for the Dötz Reaction: A Density Functional Study

Maricel Torrent, Miquel Duran, and Miquel Solà*

Contribution from the Institute of Computational Chemistry and Department of Chemistry, University of Girona, E-17071 Girona, Spain

Received April 7, 1998. Revised Manuscript Received September 3, 1998

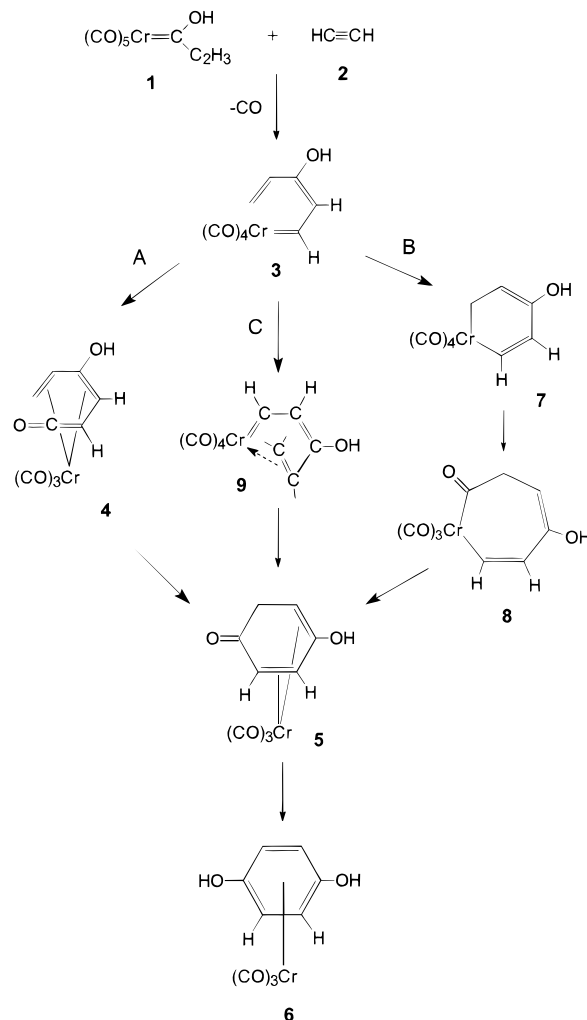
Abstract: Three different routes have been theoretically explored for the benzannulation of heteroatom-stabilized chromium carbene complexes with ethyne (Dötz reaction). The most widely accepted mechanistic proposals assume that the central part of the reaction proceeds through either the vinylketene route (Dötz's hypothesis) or the chromacycloheptadienone route (Casey's suggestion). Our calculations reveal that, from a thermodynamic viewpoint, the latter proposal is surpassed by the former, because conversion of vinylcarbenes into chromacycloheptadienones is computed to be a notably endothermic process. Moreover, a recently postulated new third route is found to be an even better proposal than the one from Dötz's hypothesis since it involves lower energy barriers and more stable intermediates than the vinylketene route postulated by Dötz. The novel findings query revision of the classically assumed paths and are a doorway to new formalisms for the mechanism of the title reaction.

Introduction

The so-called benzannulation or Dötz reaction¹ is an efficient synthetic method that allows α,β -unsaturated pentacarbonyl chromium carbene complexes $(\text{CO})_5\text{Cr}=\text{C}(\text{OR})\text{R}'$ ($\text{R} = \text{H}$, $\text{R}' = \text{C}_2\text{H}_5$, **1**) to react with alkynes $\text{R}^1\text{C}\equiv\text{CR}^2$ ($\text{R}^1 = \text{R}^2 = \text{H}$, **2**) under thermal conditions to give a wide variety of phenol derivatives. Other compounds such as indenenes,² furanes,³ and cyclopentenones⁴ have all been observed as minor products. Whereas the synthetic applications of this type of reactions are well established,⁵ the mechanisms by which they occur have not been fully elucidated yet. Thus, although routes A and B shown in Scheme 1 usually have been invoked for the formation of phenols, there is no general agreement as to which specific path is followed.

An early step common to the two proposed paths, A and B, is the loss of a CO ligand,⁶ followed by the formation of an alkyne–carbene complex.⁷ Theoretical investigations on the alkyne–carbene coupling step indicate that the alkyne insertion is either barrierless⁸ or a low-energy barrier process ($\Delta E^\ddagger =$

Scheme 1



(1) (a) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 644. (b) Dötz, K. H. *Organometallics in Organic Synthesis. Aspects of a Modern Interdisciplinary Field*; de Meijere, A., tom Dieck, H., Eds.; Springer: Berlin, 1988; p 85. (c) Dötz, K. H.; Popall, M. *Chem. Ber.* **1988**, *121*, 665. (d) Wulff, W. D. *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press LTD: Greenwich, CT, 1989; Vol. 1, pp 209–393. (e) Wulff, W. D.; Bauda, W. E.; Kaesler, R. W.; Lankford, P. J.; Miller, R. A.; Murray, C. K.; Yang, D. C. *J. Am. Chem. Soc.* **1990**, *112*, 3642. (f) Wulff, W. D. *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, L., Eds.; Pergamon: New York, 1991; Vol. 5, pp 1065–1113. (g) Wulff, W. D. *Comprehensive Organometallic Chemistry II*; Hegedus, L. S., Ed.; Pergamon: Oxford, 1995; Vol. 12, pp 469–547.

(2) (a) Dötz, K. H.; Neugebauer, D. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 851. (b) Dötz, K. H.; Dietz, R. E.; Kappenstein, C.; Neugebauer, D.; Schubert, U. *Chem. Ber.* **1979**, *112*, 3682. (c) Foley, H. C.; Strubinger, L. M.; Targos, T. S.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1983**, *105*, 3064. (d) Pruskil, I.; Schubert, U.; Ackermann, K.; Dötz, K. H. *Chem. Ber.* **1983**, *116*, 2337. (e) Wulff, W. D.; Tang, P. C.; Chan, K. S.; McCallum, J. S.; Yang, D. C.; Gilbertson, S. R. *Tetrahedron* **1985**, *41*, 5813. (f) Yamashita, A. *Tetrahedron Lett.* **1986**, *27*, 5915. (g) Combie, R. C.; Rutledge, P. S.; Terce, M.; Woodgate, P. D. *J. Organomet. Chem.* **1986**, *315*, 171. (h) Aumann, R.; Jasper, B.; Fröhlich, R. *Organometallics* **1995**, *14*, 231.

3.5 kcal mol⁻¹ [ref 9] – 5 kcal mol⁻¹ [ref 10]). This suggests that alkyne–carbene complexes, provided they exist as discrete intermediates at all, may rearrange directly to the subsequent intermediate, which is postulated to be complex **3**.^{10,11} Remarkably, this early step transformation determines the regioselective features of the overall Dötz reaction,^{12,13} depending upon the specific substitution patterns of alkynes and carbene complexes used. On the other hand, it is not until a later stage following rearrangement of the carbene intermediate **3** that the chemoselectivity toward phenol production is determined. From a mechanistic viewpoint, **3** turns out to be a branching complex from which several diverging routes have been classically postulated (Scheme 1). According to Dötz¹¹ (route A), species **3** would form the η^4 -vinylketene complex **4** upon CO migration into the chromium–carbene bond, followed by electrocyclic ring closure to give the η^4 -cyclohexadienone complex **5**. A 1,3-hydrogen migration would yield tautomeric enol complex **6**, the precursor of the free phenol. By contrast, Casey¹⁴ suggests an alternative mechanism where metalation of the arene ring occurs from complex **3** to form chromacyclohexadiene **7** (route B). This species would then yield chromacycloheptadienone **8** upon carbonylation. Reductive elimination from **8** would give intermediate **5** and from that, **6**.

Validation of these mechanistic suggestions has proven difficult since the rate-limiting step⁶ usually involves ligand loss to open a coordination site for the alkyne to bind. Once bound, fast ring closure occurs to give the observed products.¹⁵ No single reaction has been followed completely through the individual steps of routes A and B illustrated in Scheme 1, although there are now several examples of the addition of

alkynes to carbenes to form vinylcarbenes,¹⁶ and the carbonylation of vinylcarbenes to yield vinylketenes.¹⁷ However, to our knowledge the conversion of a well-characterized vinylcarbene or vinylketene chromium complex into a phenol product has never been achieved.¹⁸

One attempt to determine whether the reaction proceeds through one path or the other has been made by Garret et al.¹⁹ The approach followed by these authors was to generate a coordinatively unsaturated carbene complex at a temperature sufficiently low to retard subsequent reactions so that they could be studied step by step. Unfortunately, no mechanistic distinction was able to be made from this experiment. An alternative strategy for investigating these reaction pathways in more detail was tried by means of the interception of either the vinylketene or the metallacycle precursor. Again, it was impossible to distinguish which mechanistic proposal is the operative one.¹⁹

Wulff and co-workers²⁰ have also evaluated both mechanisms with the same purpose. Consistency to the observed product distribution, together with other experimental data, was taken as the criterion for the mechanistic discussion. Although these authors found that the vinylketene route seemed to explain more satisfactorily all of the data, at that time, they concluded that there was not enough evidence to definitively rule out any of the studied mechanisms.²⁰

From a theoretical point of view, partial support for the mechanism depicted in route A has been provided by extended Hückel molecular orbital calculations¹³ and, more recently, by a detailed density functional theory study.⁹ To the best of our knowledge, no similar theoretical studies exist for the mechanism sketched in route B.

Very recently we have reported a novel mechanistic proposal²¹ for the central part of the benzannulation reaction (route C) that involves the formation of a chromahexatriene intermediate, **9**, connecting complexes **3** and **5**. On the basis of a density functional investigation, we suggested that the reaction could proceed through a coordinated complex such as **9**, and in fact, we were able to characterize the transition states (TSs) corresponding to this route.²¹ Never before had such a hypothesis with the peculiarities mentioned above been formulated. The first results are certainly promising; this notwithstanding, it remains to be seen whether the new findings entail valuable advantages with regard to the previously postulated paths.

From the discussion above, it follows that (i) the assumed/classical elementary reactions involved in the benzannulation

(3) (a) Dötz, K. H. *J. Organomet. Chem.* **1977**, *140*, 177. (b) Wulff, W. D.; Kaesler, R. W. *Organometallics* **1985**, *4*, 1416. (c) Wulff, W. D.; Gilbertson, S. R.; Springer, J. P. *J. Am. Chem. Soc.* **1986**, *108*, 520. (d) Semmelhack, M. F.; Park, J. *Organometallics* **1986**, *5*, 2550. (e) Dötz, K. H. *New J. Chem.* **1990**, *14*, 433. (f) Parlier, A.; Rudler, M.; Rudler, H.; Goumont, R.; Daran, J.-C.; Vaissermann, J. *Organometallics* **1995**, *14*, 2760.

(4) (a) Dötz, K. H.; Trenkle, B.; Schubert, U. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 287. (b) Herndon, J. W.; Tumer, S. U.; Schnatter, W. F. *J. Am. Chem. Soc.* **1988**, *110*, 3334. (c) Duetsch, M.; Vidoni, S.; Stein, F.; Funke, F.; Noltemeyer, M.; de Meijere, A. *J. Chem. Soc., Chem. Commun.* **1994**, 1679. (d) Flynn, B. L.; Silveira, C. C.; de Meijere, A. *Synlett* **1995**, 812. (e) Flynn, B. L.; Funke, F. J.; Noltemeyer, M.; de Meijere, A. *Tetrahedron* **1995**, *51*, 11141.

(5) (a) Dötz, K. H.; Pruski, I.; Mühlemeier, J. *Chem. Ber.* **1982**, *115*, 1278. (b) Dötz, K. H.; Kuhn, W. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 732. (c) Dötz, K. H.; Popall, M. *Tetrahedron* **1985**, *41*, 5797. (d) Dötz, K. H.; Popall, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1158. (e) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081. (f) Dötz, K. H.; Popall, M.; Müller, G.; Ackermann, K. *J. Organomet. Chem.* **1990**, *383*, 93. (g) Bao, J.; Dragisich, V.; Wenglowky, S.; Wulff, W. D. *J. Am. Chem. Soc.* **1991**, *113*, 9873. (h) Hsung, R. P.; Wulff, W. D. *J. Am. Chem. Soc.* **1994**, *116*, 6449. (i) Beddoes, R. L.; King, J. D.; Quayle, P. *Tetrahedron Lett.* **1995**, *36*, 3027. (j) de Meijere, A. *Pure Appl. Chem.* **1996**, *68*, 61. (k) Merlic, C. A.; McInnes, D. M.; You, Y. *Tetrahedron Lett.* **1997**, *38*, 6787.

(6) Fischer, H.; Mühlemeier, J.; Märkl, R.; Dötz, K. H. *Chem. Ber.* **1982**, *115*, 1355.

(7) Dötz, K. H.; Siemoneit, S.; Hohmann, F.; Nieger, M. *J. Organomet. Chem.* **1997**, *541*, 285.

(8) Torrent, M.; Duran, M.; Solà, M. *Organometallics* **1998**, *17*, 1492.

(9) Gleichmann, M. M.; Dötz, K. H.; Hess, B. A. *J. Am. Chem. Soc.* **1996**, *118*, 10551.

(10) Hofmann, P.; Hämmerle, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 908.

(11) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587.

(12) (a) Schubert, U.; Mühlemeier, J.; Schubert, U.; Orama, O. *J. Organomet. Chem.* **1983**, *247*, 187. (b) Wulff, W. D.; Tang, P. C.; McCallum, J. S. *J. Am. Chem. Soc.* **1981**, *103*, 7877. (c) Yamashita, A.; Toy, A. *Tetrahedron Lett.* **1986**, *27*, 3471.

(13) Hofmann, P.; Hämmerle, M.; Unfried, G. *New J. Chem.* **1991**, *15*, 769.

(14) Casey, C. P. *Reactive Intermediates*; Jones, M., Jr.; Moss, R. A., Eds.; Wiley: New York, 1981; Vol. 2, p 155.

(15) For complex **5** see: (a) Tang, P.-C.; Wulff, W. D. *J. Am. Chem. Soc.* **1984**, *106*, 1132. (b) Wulff, W. D.; Bax, B. M.; Brandvold, T. A.; Chan, K. S.; Gilbert, A. M.; Hsung, R. P. *Organometallics* **1994**, *13*, 102.

(16) (a) Mitsudo, T.-A.; Ishihara, A.; Kadokura, M.; Watanabe, Y. *Organometallics* **1986**, *5*, 238. (b) Casey, C. P.; O'Connor, J. M.; Haller, K. J. *J. Am. Chem. Soc.* **1985**, *107*, 3172.

(17) (a) Mitsudo, T.-A.; Sasaki, T.; Watanabe, Y.; Takegami, Y.; Nishigaki, S.; Nakatsu, K. *J. Chem. Soc., Chem. Commun.* **1978**, 252. (b) Wood, C. D.; McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 3210. (c) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 954. (d) Dötz, K. H.; Fügen-Köster, B. *Chem. Ber.* **1980**, *113*, 1449. (e) Dötz, K. H.; Sturm, W. *J. Organomet. Chem.* **1985**, *285*, 205. (f) O'Connor, J. M.; Ji, H.-L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 9846.

(18) Synthesis of η^4 -vinylketene complexes by insertion of Rh(I) and Co(I) reagents into cyclobutenones has been reported, together with the reaction of η^4 -vinylketene cobalt complexes with alkynes to form phenols: Huffman, M. A.; Liebeskind, L. S.; Pennington, W. T. *Organometallics* **1992**, *11*, 255.

(19) Garret, K. E.; Sheridan, J. B.; Pourreau, D. B.; Feng, W. C.; Geoffroy, G. L.; Staley, D. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 8383.

(20) (a) Chan, K. S.; Petersen, G. A.; Brandvold, T. A.; Faron, K. L.; Challener, C. A.; Hyldahl, C.; Wulff, W. D. *J. Organomet. Chem.* **1987**, *334*, 9. (b) Bos, M. E.; Wulff, W. D.; Miller, R. A.; Chamberlin, S.; Brandvold, T. A. *J. Am. Chem. Soc.* **1991**, *113*, 9293.

reaction of chromium carbenes and alkynes still have some crucial aspects which remain unsolved and (ii) the consequences of reopening the mechanistic debate by introducing a novel proposal are self-evident regardless of the final conclusion. Therefore, our aim in the present study is 2-fold: First, a theoretical investigation of the two assumed routes for the formation of phenols is presented with the purpose of offering a better mechanistic understanding. The key issue is whether the reaction proceeds through a vinylketene intermediate (route A) or, instead, via a metallacycloheptadienone complex (route B). As noted above, there is no general agreement as to which path is followed,²² although the isolation of several vinylketene complexes from the reactions of metal carbenes with alkynes²³ and the knowledge that vinylketenes generated from organic precursors undergo benzannulation reactions to form naphthols²⁴ provides support for the vinylketene route. Second, the recently proposed third route²¹ is thoroughly examined in terms of its operativeness with respect to the two already assumed paths. As will be seen, the novel third route emerges as the best alternative. Comparison of the three pathways leads to reinterpretation of the classical mechanisms, and demands revision of the order of the proposed steps.

Computational Details

Density functional calculations were made with the GAUSSIAN 94 program.²⁵ All geometry optimizations and energy differences were computed including nonlocal corrections (Becke's nonlocal exchange correction²⁶ and Perdew's nonlocal correlation correction²⁷). The 6-31G** basis set²⁸ was employed for C, O, and H atoms. For the chromium atom we utilized a basis set as described by Wachters²⁹ (*14s9p5d*)/[*8s4p2d*], using the *d*-expanded contraction scheme (62111111/3312/311). The stationary points were located with the Berny algorithm³⁰ by using redundant internal coordinates and characterized by the correct number of negative eigenvalues of their analytic Hessian matrix; this number must be zero for minima and one for any true TS. We also verified that the imaginary frequency exhibits the expected motion. Only closed-shell states were considered. Kinetic relativistic effects are unimportant for an accurate calculation of chromium complexes³¹ and were neglected in our calculations.

(21) Torrent, M.; Duran, M.; Solà, M. *Chem. Commun.* **1998**, 999.

(22) McCallum, J. S.; Kunng, F. A.; Gilbertson, S. R.; Wulff, W. D. *Organometallics* **1988**, *7*, 2346.

(23) (a) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 954. (b) Dötz, K. H.; Fügen-Köster, B. *Chem. Ber.* **1980**, *113*, 1449. (c) Herrmann, W. A.; Gimeno, J.; Weichmann, J.; Ziegler, M. L.; Balbach, B. *J. Organomet. Chem.* **1981**, *213*, C26. (d) Bkouche-Waksman, I.; Ricci, J. S.; Koetzle, T. F.; Weichmann, J.; Herrmann, W. A. *Inorg. Chem.* **1985**, *24*, 1492. (e) Mitsudo, T.; Watanabe, H.; Sasaki, T.; Takegami, Y.; Watanabe, Y.; Kafuku, K.; Nakatsu, K. *Organometallics* **1989**, *8*, 368. (f) Anderson, B. A.; Wulff, W. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 8615. (g) Anderson, B. A.; Bao, J.; Brandvold, T. A.; Challener, C. A.; Wulff, W. D.; Xu, Y.-C.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 10671.

(24) Moore, H. W.; Decker, O. H. W. *Chem. Rev.* **1986**, *86*, 821.

(25) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andrés, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A.: Gaussian 94 (Revision A.1); Gaussian, Inc.: Pittsburgh, PA, 1995.

(26) Becke, A. D. *Phys. Rev.* **1988**, *A38*, 3098.

(27) Perdew, J. P. *Phys. Rev.* **1986**, *B33*, 8822; *B34*, 7406E.

(28) (a) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939. (b) Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 2797. (c) Pietro, W. J.; Francl, M. M.; Hehre, W. J.; Defrees, D. J.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 5039.

(29) Wachters, A. J. H. *J. Chem. Phys.* **1970**, *52*, 1033.

(30) Peng, C.; Ayala, P. Y.; Schlegel, H. B.; Frisch, M. J. *J. Comput. Chem.* **1996**, *17*, 49.

Results and Discussion

This section is divided as follows: First, the results for the vinylketene route (section A) and for the chromacycloheptadienone route (section B) are presented, followed by a brief comparison of the two studied paths. Once the most classically assumed mechanisms have been pondered, we discuss and compare (section C) the suitability of a novel route involving a chromahexatriene intermediate as an alternative to redefine the standard pathway believed to be operative.

A. The Vinylketene Route. According to Scheme 1, the intermediate that results from alkyne addition to the carbene complex derived by loss of a CO ligand in **1** is the branch point complex **3**. The structure of **3** has been recently reported in a previous study of the initial part of the Dötz reaction.⁸ It was shown that **3**, despite being the actual end product of the ethyne insertion, lies on a flat region of the potential energy surface, and undergoes a small structural rearrangement turning into its isomer, **3a**, which is 6.7 kcal mol⁻¹ more stable. Therefore, the actual branching point of the central part of the benzannulation reaction (and the starting point of the present paper) from which the three routes to be investigated diverge is species **3a** (Figure 1).

To follow the vinylketene route suggested by Dötz, complex **3a** has to convert into **4**. Such a conversion takes place in two steps. First, **3a** isomerizes into **3b** through TS(**3a**→**3b**) (Figure 1), and then turns into **4** (Figure 2) via TS(**3b**→**4**) (Figure 3). No TS connecting directly **3a** and **4** has been found.

Isomer **3a** can be considered an η^1 -vinylcarbene, whereas isomer **3b** is better described as an η^3 -vinylcarbene (Figure 1). From an energy point of view, the latter isomer happens to lie 11.8 kcal mol⁻¹ above the former despite the apparently more favorable η^3 -coordination. What accounts for the extra stability found in **3a** is presumably (i) the larger π -electron delocalization due to a higher planarity of the carbene chain than in **3b** and (ii) the agostic interaction between chromium and one of the C₅-H bonds of the terminal alkenyl ligand. (The length of the C₅-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 these kinds of interactions³²). In **3b** such an interaction is impeded because the vacant coordination site available in **3a** around Cr is here fulfilled by the π interaction with the C₂-C₃ double bond (Figure 1). The optimized molecular structure of **3b** (Figures 1 and 2) shows that the vinylcarbene ligand is likely to be coordinated to chromium via three carbon atoms, although the Cr-C distances vary considerably. Within the vinylcarbene ligand, the C₁-C₂ and C₂-C₃ distances are midway between typical carbon-carbon single and double bond values. The C-C-C angles within the vinylcarbene ligand imply *sp*² hybridization about C₂ and C₃ (C₁-C₂-C₃, 122.5°; C₂-C₃-C₄, 126.6°), and also point to notable strain around C₁ (Cr-C₁-C₂, 85.9°). The vinylcarbene is bent with a hinge angle of 132.8° between the Cr-C₂-C₁ and Cr-C₂-C₃ planes. Other interplanar angles within this ligand are [C₃-Cr-C₁/Cr-C₁-C₂] = 25.9°, [Cr-C₂-C₃/C₂-C₃-C₄] = 90.3°, and [C₁-C₂-C₃/C₂-C₃-C₄] = 44.7°. Such angles indicate that delocalized π -bonding between the three carbon atoms linked to the metal would be difficult because none of the *p* orbitals are properly aligned for good orbital overlap due to the orientation of the vinylcarbene substituents. This fact also explains why **3b** is not so stable compared to **3a** as expected for a rigorous η^3 -bonded system. Similar structural details have also been found in other

(31) Jacobsen, H.; Schreckenbach, G.; Ziegler, T. *J. Phys. Chem.* **1994**, *98*, 11406.

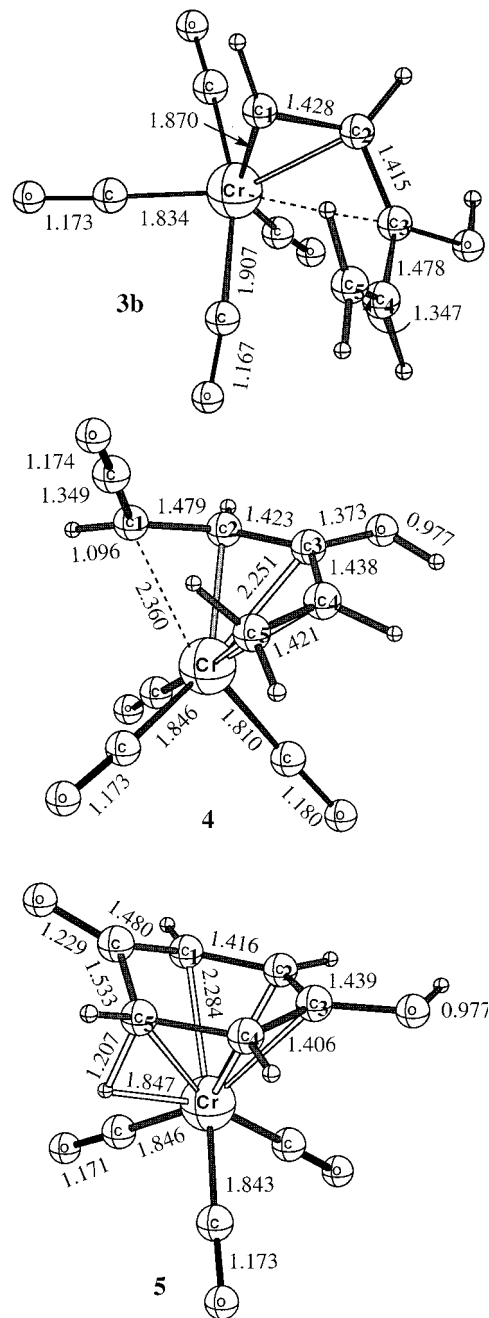
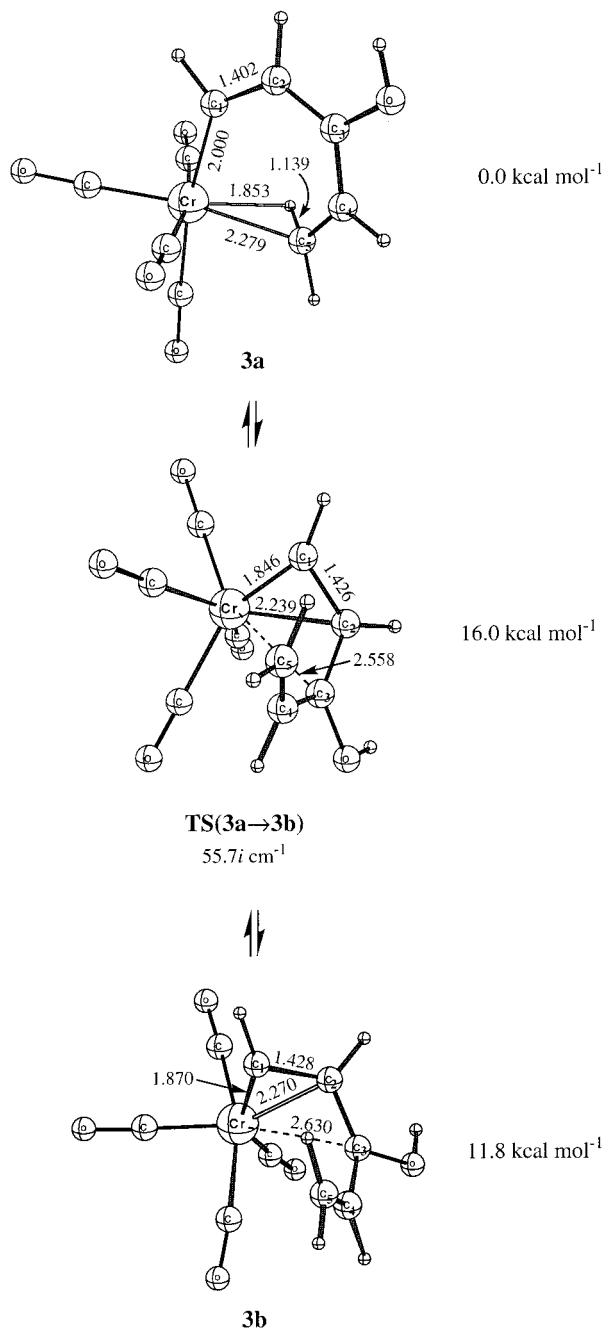


Figure 1. Optimized geometries of η^1 -vinylcarbene complex **3a** (above), η^3 -vinylketene complex **3b** (below), and the transition state connecting them (center). Selected bond distances are given in Å.

(crystallographically characterized) complexes possessing ligands of this type.¹⁹

Conversion from **3a** to **3b** involves rotation and folding of the organic chain, which can be expected to occur without many hindrances given the unrestricted mobility of the carbene ligand (Figure 1). The corresponding barrier is 16.0 kcal mol⁻¹. Despite this barrier, an equilibrium between **3a** and **3b** is conceivable under reaction conditions. Indirect support for the feasibility of this interconversion is provided by a recent investigation by Barluenga et al.³³ where the isolation and X-ray characterization of a chromium vinylaminocarbene complex similar to **3** has been reported for the first time. These authors concluded that the isolated species should be better described as an intermediate between a rigorous η^1 - and an η^3 -bonded system. (They referred to it as an η^1 : η^3 -vinylcarbene complex.) Mayr et al.³⁴ have also reported the isolation of a tungsten vinylcarbene complex

Figure 2. Optimized geometrical parameters for the intermediates involved in route A: η^3 -vinylcarbene complex **3b** (above), η^4 -vinylketene complex **4** (center), and η^4 -cyclohexadienone complex **5** (below). Bond distances are given in Å.

whose characteristics (in solid state) are intermediate between those of rigorously η^1 -bonded vinylcarbene ligands (found in coordinatively saturated metal complexes^{15a,35}), and those of more strongly η^3 -bonded ligands (found, e.g., in low-valent iron complexes³⁶). In view of these results, the coexistence of isomers **3a** and **3b** should not be discarded, especially in the gas phase. Although there is a small barrier between the two conformations, it is reasonable to assume that their interchange is still possible.

Figure 2 illustrates the optimized structures of the three main intermediates following **3a** in the vinylketene route. The crucial species is complex **4**. This is a key intermediate in many mechanistic proposals and was originally suggested by Dötz.^{23b} The metal-carbon bond to the ketene carbon (2.360 Å) is slightly larger (0.2–0.3 Å) than the typical value for vinylketene complexes that have been structurally characterized.^{23c} Also the

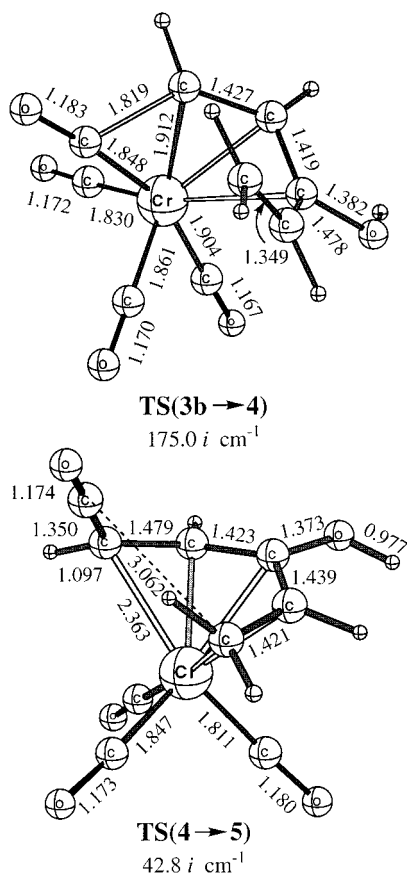


Figure 3. Optimized geometry for the TS structures connecting intermediates **3b**–**5** in route A. Bond distances are given in Å.

O–C–C bond angle of the coordinated ketene (175.0°) is ca. 30° less bent than usual.^{34,37} Intermediate **4** differs from the structure identified in a previous work for an η^4 -phenylketene,⁹ where coordination was found to occur at the C₁=C(O) bond. Analysis of the bond distances in **4** reveals that this is an η^4 -vinylketene complex with the metal bound to the C₂=C₃ and C₄=C₅ bonds. Although the initial input geometry structure does involve a Cr–C₁ linkage, the optimization process invariably leads to a minimum where such an interaction is unfavorable and eventually gets lost. Investigation of the MOs in the fragment O=C=C₁(H)–C₂(H)=C₃(OH)–C₄(H)=C₅H₂, however, shows that the best donor ability in the free ketene corresponds to the π orbital with larger contributions on C₂=C₃ and C₄=C₅ bonds, which explains why coordination is preferred on these atoms over C₁ and C(O). Moreover, in the previously identified η^4 -phenylketene,⁹ there are only two aliphatic C=C double bonds (C₄=C₅ is aromatic), and consequently, no election different from C₁=C(O) and C₂=C₃ is possible for an η^4 coordination in that case.

(32) (a) Goddard, R. J.; Hoffmann, R.; Jemmis, E. D. *J. Am. Chem. Soc.* **1980**, *102*, 7667. (b) Zaera, F. *Chem. Rev.* **1995**, *95*, 2651. (c) Hall, C.; Perutz, R. N. *Chem. Rev.* **1996**, *96*, 3125.

(33) (a) Barluenga, J.; Aznar, F.; Martín, A.; García-Granda, A.; Pérez-Carreño, E. *J. Am. Chem. Soc.* **1994**, *116*, 11191. (b) Barluenga, J. *Pure Appl. Chem.* **1996**, *68*, 543.

(34) Mayr, A.; Asaro, M. F.; Glines, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 2215.

(35) (a) Dötz, K. H.; Kuhn, W. *J. Organomet. Chem.* **1983**, *252*, C78. (b) Kuo, G. H.; Helquist, P.; Kerber, R. C. *Organometallics* **1984**, *3*, 806. (c) Casey, C. P.; Miles, W. H.; Tukada, H. *J. Am. Chem. Soc.* **1985**, *107*, 2924.

(36) (a) Klimes, J.; Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 205. (b) Nakatsu, K.; Mitsudo, T.; Nakanishi, H.; Watanabe, Y.; Takegami, Y. *Chem. Lett.* **1977**, 1447.

(37) Templeton, J. L.; Herrick, R. S.; Rusik, C. A.; McKenna, C. E.; McDonald, J. W.; Newton, W. E. *Inorg. Chem.* **1985**, *24*, 1383.

Scheme 2

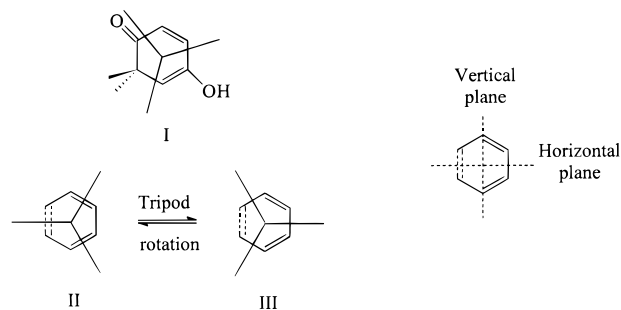


Table 1. Reaction Energies, ΔE , and Activation Energies, ΔE^\ddagger (in kcal mol⁻¹), for All Steps in Routes A–C

route	step	ΔE	TS	ΔE^\ddagger
A	3a → 3b	11.8	TS(3a→3b)	16.0
	3b → 4	–18.1	TS(3b→4)	6.9
	4 → 5	–24.3	TS(4→5)	0.3
B	3a → 8	25.0	TS(3a→8)	
	8 → 5	–55.7	TS(8→5)	
C	3a → 9	–11.2	TS(3a→9)	1.8
	9 → 5'	–19.5	TS(9→5')	12.9

Geometrical analysis of complex **5** reveals that the short distances between the metal and the carbon atoms in the ring (mean value: 2.312 Å) are consistent to those reported for other (η^6 -arene)tricarbonylchromium complexes,³⁸ and, as shown in Figure 2, favor an agostic interaction between the metal and one of the hydrogen atoms α to the carbonyl group of the ring. The lack of aromatization in complex **5** induces a puckering of the six-membered ring, and the Cr(CO)₃ tripod adopts an anti-eclipsed conformation to the OH– group as shown in **I** (Scheme 2). Barriers to rotation about the metal–arene bond in several Cr(CO)₃ complexes of selected trienes have been studied recently by Baldrige and Siegel.³⁹ According to these authors, conformations **II** and **III** (Scheme 2) are predicted to be energetically equal whenever triene symmetry includes the vertical and horizontal mirror plane (as, e.g., in benzene). When triene lacks a vertical mirror plane, then conformation **III** becomes the major form. Although complex **5** is not a triene, its preferred conformation can be estimated to resemble **III** rather than **II**. The actual conformation adopted by the tripod in **5**, **I**, is likely to deviate from the predicted structure, **III**, because of the agostic interaction in one of the carbon atoms α to the carbonyl group.

The reaction energies and activation barriers for the mechanistic sequence **3a** → **3b** → **4** → **5** (route A) are collected in Table 1. Once the isomer suitable for this route, **3b**, is formed from its precursor **3a**, a CO migration takes place in the step **3b** → **4** followed by a ring closure in the step **4** → **5**. The activation barrier for the conversion **3b** → **4** (6.9 kcal mol⁻¹) corresponds to the energy required for a CO ligand to migrate into the Cr=C₁ double bond. Such a low barrier can be rationalized by weighing up bond-breaking and bond-making processes. An early loss of the η^3 -interaction in **3b**, together with a distortion of the octahedral framework around chromium in order to approach the coming CO ligand, are partially counterbalanced by the formation of new bonds, even though the latter process is slightly behind the former. Support for this statement is provided by inspection of the transition state **TS(3b→4)**, whose optimized geometry is depicted in Figure 3. To

(38) Djukic, J.-P.; Maisse, A.; Pfeffer, M.; Cian, A.; Fischer, J. *Organometallics* **1997**, *16*, 657.

(39) Baldrige, K. K.; Siegel, J. S. *J. Phys. Chem.* **1996**, *100*, 6111.

improve orbital interactions, the CO group that is shifted should be cis and parallel to the π orbital of the carbene ligand. However, the carbonyl migration into the Cr=C bond is disfavored by the repulsion between the CO lone pair and an occupied d orbital of the metal. Slightly higher barriers have been computed for similar carbonyl migrations into M–C single bonds (M = late⁴⁰ and middle⁴¹ transition metals).⁴²

In the next step, conversion from **4** to **5** is kinetically very favorable, with a smooth activation barrier of only 0.3 kcal mol⁻¹. The corresponding transition state, TS(**4**→**5**), is depicted in Figure 3. The last step is notably exothermic (–24.3 kcal mol⁻¹). This is in agreement with a previous study of the vinylketene route by Gleichmann et al.⁹ where it was reported that η^4 -cyclohexadienone complexes such as **5** are the most stable and strongly exothermic intermediates in the phenol formation. However, in that study,⁹ no η^4 -vinylketene intermediate was found despite checking for the existence of such a complex. The authors reported a direct conversion from a vinylcarbene similar to **3** to **5** (–46.4 kcal mol⁻¹) and calculated an activation energy of 5.3 kcal mol⁻¹ for this global step. Our computed activation barrier (if we only consider the conversion **3b** → **4**) is slightly higher (6.9 kcal mol⁻¹) but still in good agreement with the barrier reported by Gleichmann et al.⁹ Nevertheless, according to our study, there is evidence for two additional intermediates. In the present work, intermediates **3b** and **4** are found to be real minima of the potential energy surface.

B. The Chromacycloheptadienone Route. According to Scheme 1, the main intermediates postulated for the conversion of **3** to **5** through route B are chromacyclohexadiene **7** and chromacycloheptadienone **8**. No minimum has been located on the potential energy surface having the geometrical traits shown by the six-membered species labeled **7**. Complex **7**, as it is depicted in Scheme 1 (i.e., with two short Cr–C distances), turns out to be a fictitious intermediate. Different input geometries lead systematically directly to complex **3a**. Opening of the chain and stabilization through agostic interaction (as in **3a**) are invariably the preferred trends observed along any optimization process starting with Cr–C bonds in the range 1.85–1.95 Å. It is inferred from our calculations that **7** does not exist as a real stationary point, and that chromacycloheptadienone **8** does directly derive from complex **3a**. This is consistent with a recent isotopic study by Hughes et al.⁴³ where metallacyclohexadiene complexes similar to **7** were suggested to be excluded as intermediates along the reaction pathway of the Dötz and related reactions.

Figure 4 displays the optimized geometry of the only intermediate for the conversion of **3** to **5** through route B. Seven-membered rings involving a metal such as **8** are rather odd, but not completely unknown in the field of organometallic chemistry. Similar complexes were isolated and reported a long time ago from the reaction of nickel hydrides.⁴⁴ Interestingly, complex **8** keeps its character of 16-electron species through a $d\pi$ interaction between chromium and the O–C bond of the

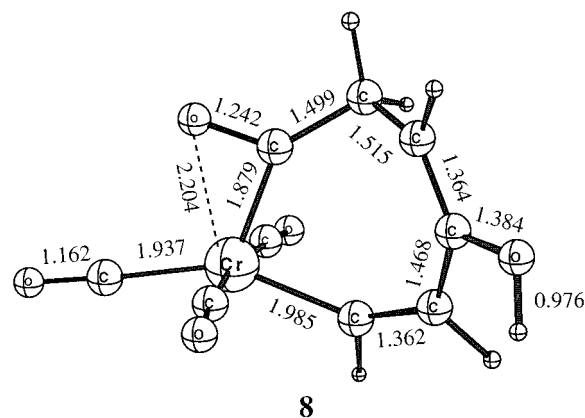


Figure 4. Optimized geometrical parameters for the main intermediate involved in route B: chromacycloheptadienone complex **8**. Bond distances are given in Å.

migrated CO ligand. As seen from Figure 4 (and as usual in this kind of interaction⁴⁵), the O–C bond (1.242 Å) is slightly longer than the typical C–O double bond at this level of calculation (1.229 Å). Such a lengthening arises from the stretching induced by both donation to the metal from the π orbital of CO and back-donation to the π^* orbital of CO from the metal. However, complex **8** is not very stable. Folding and steric strain generated in the nonaromatic seven-membered ring partially account for instability. Thus, the conversion of **3a** into **8** (Table 1) turns out to be a notably endothermic process. Likewise, release of the strain by turning the seven-membered ring into a six-membered one (step **8** → **5**) is accompanied by a substantial release of energy (55.7 kcal mol⁻¹).

Up to this point, we have brought enough evidence to weigh the two most assumed mechanisms, and to answer one of the questions made in the Introduction. From the results shown herein, it can be inferred that route A is favored over route B. Comparison of the energies for the two paths (Table 1) clearly indicates that the reaction will better proceed through the vinylketene route. No TSs are reported for the pathway proposed by Casey; this notwithstanding, thermodynamic data are conclusive enough to choose route A, not B, as the more operative path of the two: As seen from Table 1, the reaction energy for the formation of intermediate **8** is larger than any of the activation energies involved in route A.

C. The Chromahexatriene Route. Once route B is ruled out and the choice of route A as the preferred one is justified, it remains to be seen whether this mechanism can be either strengthened by the support of new breakthroughs or surpassed by novel proposals. It is the purpose of the present section to evaluate an alternative proposal.

The mechanism outlined in route C has been suggested very recently.²¹ Unlike Dötz's route, the new proposal does not claim CO migration in the first step but formation of a chromahexatriene intermediate **9** through rearrangement (Figure 5), which subsequently inserts a CO ligand in the second step, **9** → **5'**. Intermediate **9** can be regarded as a five-membered chelate ring if the midpoint of the coordinated double bond is taken as one ring member. This complex exhibits a weak $d\pi$ interaction between the C₄–C₅ bond and the Cr center. The relative strength of such interaction is further reflected by a trans effect observed for the CO ligand trans to the chelation site. The Cr–CO_{trans} distance in **9** (1.857 Å) is significantly shorter than that for the remaining Cr–CO_{cis} ligands (mean value: 1.889 Å), which arises from the fact that the terminal alkene cannot compete

(40) (a) Sakaki, S.; Kitaura, K.; Morokuma, K.; Ohkubo, K. *J. Am. Chem. Soc.* **1983**, *105*, 2280. (b) Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1985**, *107*, 7230. (c) Koga, K.; Morokuma, K. *J. Am. Chem. Soc.* **1986**, *108*, 6536. (d) Versluis, L.; Ziegler, T.; Baerends, E. J.; Ravenek, W. *J. Am. Chem. Soc.* **1989**, *111*, 2018.

(41) (a) Berke, H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 7224. (b) Ziegler, T.; Versluis, L.; Tschinke, V. *J. Am. Chem. Soc.* **1986**, *108*, 612. (c) Axe, F. U.; Marynick, D. S. *Organometallics* **1987**, *6*, 572.

(42) van Leeuwen, P. W. N. M.; Morokuma, K.; van Lenthe, J. H., Eds. *Theoretical Aspects of Homogeneous Catalysis*; Kluwer: Dordrecht, 1995.

(43) Hughes, R. P.; Trujillo, H. A.; Gauri, A. J. *Organometallics* **1995**, *14*, 4319.

(44) Clark, H. C.; Shaver, A. *Can. J. Chem.* **1975**, *53*, 3462.

(45) Solà, M.; Ziegler, T. *Organometallics* **1996**, *15*, 2611.

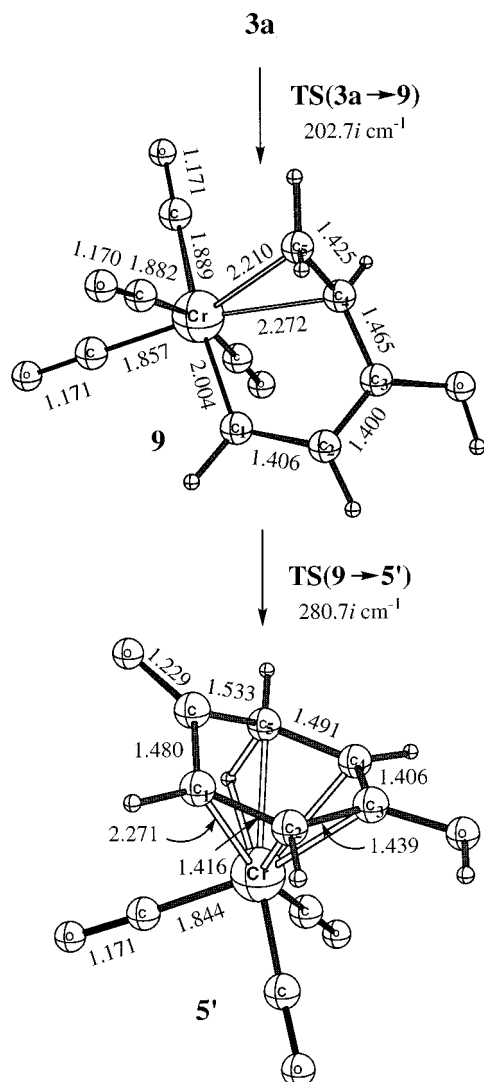


Figure 5. Optimized geometrical parameters for the chromahexatriene intermediate involved in route C, together with the subsequent η^4 -cyclohexadienone complex from CO insertion into the ring. Bond distances are given in Å.

successfully with the *trans*-CO ligand for back-bonding from the metal. The trend followed by the distance between Cr and the *trans*-CO ligand from **3a** to **5'** can be taken as a measure of the change in electron back-donation from Cr to CO all along the path. Further mechanistic details of this pathway, together with the optimized TS structures, have been given elsewhere.²¹ The point here is whether the novel route is feasible and can compete with the usually assumed pathways, in particular, with the apparently preferred route A.

Notice that intermediates **5** (route A) and **5'** (route C) are enantiomers; therefore, from an energy point of view they are entirely comparable because they have identical energies. Moreover, both of them can be obtained from any of the presented routes: Having one or the other depends only on which of the *cis*-CO ligands migrates (which in turn is set by the particular folding acquired by **3a** and **3b** while being formed). Eventually, both enantiomers lead indistinctly to complex **6**, the next reaction intermediate, through tautomerization. Enol complex **6** (Figure 6) turns out to be 18.4 kcal mol⁻¹ more stable than the keto form **5** (or **5'**). The energy barrier for this 1,3-hydrogen migration is expected not to go beyond 10 kcal mol⁻¹, taking into account that the ground-state

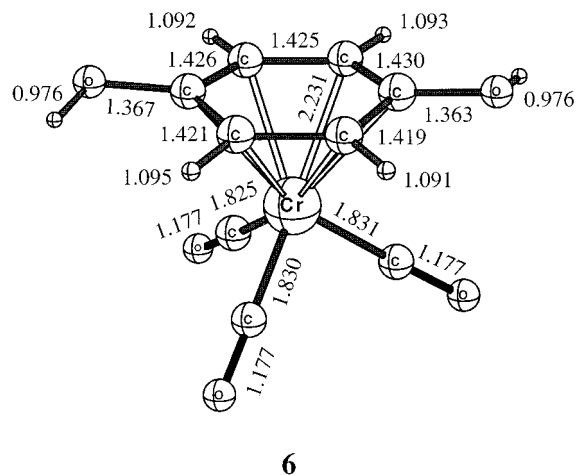


Figure 6. Optimized geometry of enol tautomer **6**. Bond distances are given in Å.

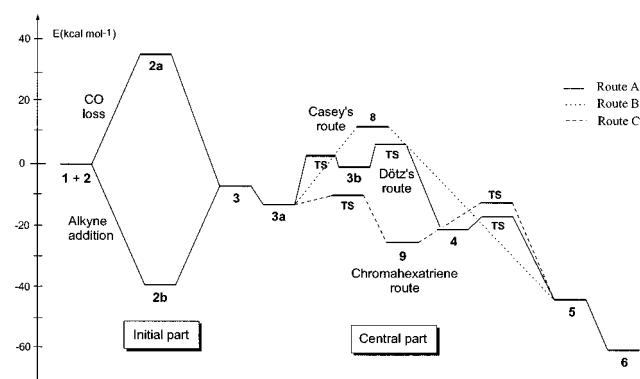


Figure 7. Energy profile for the whole benzannulation reaction: comparison of the profiles for the three studied mechanisms (route A, solid line; route B, dotted line; route C, dashed line). Relative energies are in kcal mol⁻¹.

barrier for a similar tautomerization⁴⁶ has been computed to be ca. 4 kcal mol⁻¹. The aromatization energy **5** \rightarrow **6** is smaller than expected for a "pure" aromatization reaction because of the additional stability of **5** (arisen from the above-mentioned agostic interaction), which makes this species lower in energy than a "purely nonaromatic" species.

The results of the present paper are summarized in Figure 7. It gathers the energy profile for the three routes studied here and fits them into the whole framework of the benzannulation reaction. Details concerning the initial part of the reaction (species **1** to **3**) have been reported elsewhere⁸ with use of the identical basis set and method of calculation as in the present work. As can be seen from the graph, the lowest energy path starting with **3** (central part of the reaction) flows along the dashed line. As already seen in Table 1, one of the most costly processes in the global reaction **3** \rightarrow **5** (or **5'**) turns out to be CO migration. Therefore, the ideal mechanistic path is the one that minimizes the amount of energy required to insert a CO ligand into the ring. Interestingly, the particular orientation of the carbene ligand in **9** makes the migration of CO very accessible ($C_{CO}-C_5 = 2.559$ Å and $C_{CO}-C_1 = 2.638$ Å): During the process each of the two π^* orbitals of CO can interact simultaneously with the $C_4=C_5$ and $Cr=C$ π orbitals. Therefore, CO migration in **9** is favored over CO migration in **3**, and, consequently, on the whole, the energy profile for route C has the advantage of being globally smoother (Figure 7).

(46) Guallar, V.; Moreno, M.; Lluch, J. M.; Amat-Guerri, F.; Douhal, A. *J. Phys. Chem.* **1996**, *100*, 19789.

Indeed, inspection of the energy profile for route C as compared to route A (Table 1) shows that the conversion of the branch point, complex **3a**, into intermediate **9** is more favorable ($\Delta E = -11.2$ kcal mol⁻¹; $\Delta E^\ddagger = +1.8$ kcal mol⁻¹) than the conversion of **3a** into **4**, which occurs via **3b** ($\Delta E = -6.3$ kcal mol⁻¹; $\Delta E^\ddagger = +18.7$ kcal mol⁻¹) from both thermodynamic and kinetic points of view. Concerning the second step, formation of **5** from **4** is predicted to have, as aforementioned, an activation barrier not higher than 0.3 kcal mol⁻¹ whereas formation of **5** (or **5'**) from **9** has a barrier of +12.9 kcal mol⁻¹. However, the latter barrier is lower than the most prominent in route A (+18.7 kcal mol⁻¹), which turns out to be the main bottleneck of the two routes.

One final question remains in connection to the viability of route C. Is there any evidence for the existence of chromahexatriene complexes such as **9** or are they merely hypothetical complexes? In case they can exist, then, are they an endpoint of the reaction or can they be seen as a real precursor of η^4 -cyclohexadienone complexes? Evidence supporting the existence of **9** is provided by a recent investigation by Barluenga et al.,³³ where a chromahexatriene similar to **9** was isolated (from the reaction of a tetracarbonyl vinylcarbene of a chromium(0) complex with dimethyl acetylenedicarboxylate) and characterized by ¹H and ¹³C NMR spectroscopy. Moreover, these authors also found that the synthesized chromahexatriene was not stable in solution at room temperature, and decomposed to yield the most common final product in the Dötz reaction with aminocarbenes, after demetalation and a 1,5-hydrogen shift.^{33a} This is consistent with the energy profile for route C depicted in Figure 7, which indicates that the reaction does not end at **9**, such intermediate connecting to a more stable intermediate that leads to the final free phenol.

Conclusions

Two main conclusions can be drawn from the present investigation. First, the results shown herein indicate that, from a thermodynamic point of view, Casey's mechanistic proposal for the central part of the benzannulation reaction should be rejected. The conversion of vinylcarbenes into chromacycloheptadienones is computed to be a highly endothermic process, more energy-demanding than any of the steps postulated by Dötz in the vinylketene route. Such a conclusion is not in contradiction with previous experimental attempts made to distinguish the two mechanisms.^{19,20}

Second, our study shows that the novel proposal involving a chromahexatriene intermediate emerges as a concurrent alternative in the context of the two previously assumed mechanisms. Comparison of the new route to the one suggested by Dötz reveals that, when the classical order of the two central steps is reformulated by postponing CO migration (as in route C), the reaction proceeds through a lower-energy barrier path. It

suggests that, instead of assuming CO migration as the first step from the branching point followed by structural rearrangement (route A), the mechanism could be best formulated as inverting these two processes. It obviously means replacing the vinylketene intermediate by the one capable of undergoing CO migration in the second step, i.e., the chromahexatriene intermediate **9**, for which experimental support exists.³³

Moreover, it is worth reminding that, although experimental evidence has been provided also for the formation of η^4 -vinylketene complexes, such species have never been observed during a benzannulation reaction itself.⁴⁷ It can only mean that either (i) η^4 -vinylketene complexes are actual intermediates, but they are not observed because of their easy, almost barrierless conversion to **5**, or (ii) they are not observed because the actually operating mechanism does not take place through η^4 -vinylketene complexes, other intermediates being involved instead. Results shown in this work do not rule out the former hypothesis. However, the intermediacy of a chromahexatriene complex as it has been presented here has expectations good enough to take the second hypothesis into thorough consideration. According to this, the novel route comes out as a potentially suitable alternative to redefine the classical mechanism.

Further research is under way to broaden the scope of the aforementioned conclusions. Given the similarity in energies for the investigated routes, the use of different substrates may alter the relative order of the barriers and, therefore, modify the mechanistic behavior of the reactants, making the reaction proceed through other pathways. In fact, reaction mechanisms are only scientific postulates open to revision whenever new insights emerge. It is very difficult to really prove a particular mechanism; a mechanistic hypothesis can be eliminated only when it does not satisfy experimental observations. Keeping this idea in mind, we hope our study contributes to widen the range of concurrent, competing alternatives, and stimulates further rigorous study of this reaction.

Acknowledgment. Support from DGES Project No. PB95-0762 is gratefully acknowledged. One of us (M.T.) thanks the Generalitat de Catalunya for financial help through CIRIT Project No. FI/94-5001. We also acknowledge the Centre de Supercomputació de Catalunya (CESCA) for a generous allocation of computing time.

Supporting Information Available: Cartesian coordinates of all optimized adducts, intermediates, transition structures, and products (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA981162M

(47) (a) Anderson, B. A.; Wulff, W. D. *J. Am. Chem. Soc.* **1990**, *112*, 8615. (b) Chelain, E.; Parlier, A.; Rudler, H.; Daran, J.-C.; Vaissermann, J. J. *Organomet. Chem.* **1991**, *419*, C5.