Correspondence

The Initial Reaction Steps of the Dötz Reaction: A Comment

Sir: Electrophilic Fischer carbene complexes have been widely established as valuable reagents,[1] and the Dötz reaction (benzannulation, e.g. Scheme 1)[2] is of particular synthetic interest.

In a recent paper[3] entitled "Density Functional Study on the Preactivation Scenario of the Dötz Reaction: Carbon Monoxide Dissociation versus Alkyne Addition as the First Reaction Step" Torrent, Duran, and Solá (TDS) carried out DFT calculations on the model reaction of $[(CO)_5Cr{=}C(OH)CH{=}CH_2]$ with $HC{\equiv}CH$ "...with the global objective...to throw some light on the *preactivation scenario* of the benzannulation reaction".

The essential conclusions from their study can be summarized as follows.

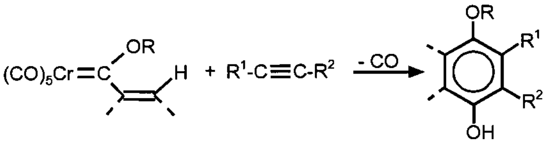
(1) According to the theoretical results, CO elimination followed by complexation and insertion of C_2H_2 (dissociative path) is energetically less favorable than an associative mechanism (insertion of the $C{\equiv}C$ into the $M{=}C$ bond followed by CO dissociation). Loss of CO is claimed to occur one step later than has been usually assumed in earlier mechanistic proposals.

(2) Addition of ethyne to the 18-electron system **1** and insertion of $HC{\equiv}CH$ into the $Cr{=}C$ bond of $[(CO)_5Cr{=}C(OH)CH{=}CH_2]$ (**1**; Scheme 2) to form $[(CO)_5Cr{=}C(H)CH{=}C(OH)CH{=}CH_2]$ (**2**; Scheme 2) is a highly exothermic, nearly barrierless process (or has a very low barrier). Loss of CO from **2** is significantly less endothermic (132.4 kJ/mol) than loss of CO from **1** (144.7 kJ/mol).

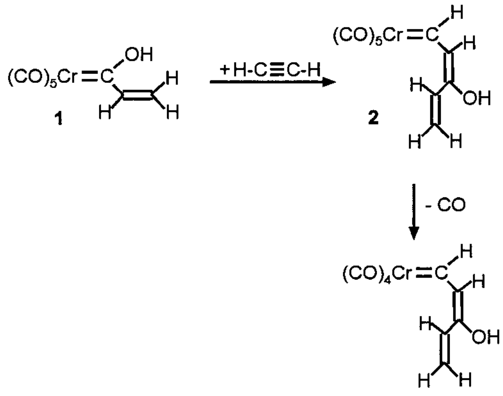
We wish to point out that two of the essential theoretical conclusions (associative initiation of the Dötz reaction and near-barrierless insertion of alkynes into the $Cr{=}C$ bond) do not agree with the experimental facts.

(1) A detailed kinetic study of the prototypical reaction of $[(CO)_5Cr{=}C(OMe)Ph]$ (**3**) with $HC{\equiv}CC_6H_4R$-*p* (**4**; R = H, Me, CF_3)[4] under conditions usually employed in the Dötz reaction[2] (n-Bu_2O, 45.4−73.1 °C) shows that the overall reaction is best represented by the following rate law: $-d[\mathbf{3}]/dt = k_1k_2[\mathbf{3}][\mathbf{4}]/\{k_{-1}[CO] + k_2[\mathbf{4}]\}$. The rate is strongly reduced in the presence of excess CO.[4]

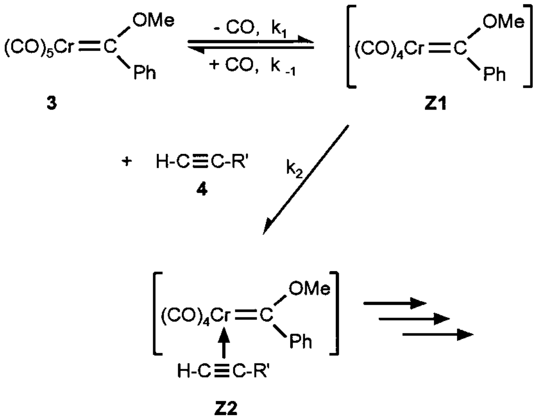
Scheme 1



Scheme 2



Scheme 3



This rate law is not consistent with the associative mechanism but clearly indicates a reversible CO predissociation (Scheme 3).

Addition of CO to the solvent-stabilized intermediate **Z1** is faster than addition of the alkyne ($k_{-1}/k_2 = 200$ (R = H), 180 (R = Me), and 230 (R = CF_3)).[4] The activation parameters for the CO elimination are $\Delta H^\ddagger = 108 \pm 2$ kJ/mol and $\Delta S^\ddagger = 26 \pm 6$ J/(mol K) and are similar to those of the *dissociatively initiated* substitution of PR_3 for CO in the methoxymethylcarbene complex $[(CO)_5Cr{=}C(OMe)Me]$ to give *cis*-$[(CO)_4(PR_3)Cr{=}C(OMe)Me]$ ($\Delta H^\ddagger = 108.8{-}115.5$ kJ/mol, $\Delta S^\ddagger = 3.3{-}25.9$ J/(mol K)).[5] For an associative reaction appreciably negative $\Delta S^\ddagger$ values are to be expected.

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10.1021/om980958r CCC: $18.00

A tungsten complex related to **Z2**, *cis*-[(CO)$_4$(PhC≡CPh)W=C(OMe)Ph], has been shown to collapse above −20 °C to give mainly the annulation product 1-methoxy-2,3-diphenylindene and [W(CO)$_6$].[6] The carbene complex was obtained by irradiation of a solution of [(CO)$_5$W=C(OMe)Ph] and PhC≡CPh in hexane at −30 °C.[6]

At 45 °C, $\Delta G^{\ddagger}$ is 99.7 kJ/mol, and the half-life $\tau_{1/2}$ is 2460 s. Five half-lives (96.9% consumption of the starting complex) amount to 3.42 h, which is well *below the time span* usually required for the Dötz reaction (6−24 h at 45 °C). Therefore, the statement[3] that a mechanism involving dissociation of CO from **1** is "...only feasible when photodissociation is used" does not hold. Of course, CO dissociation and consequently the Dötz reaction can be accelerated by photodissociation[7] or sonification.[8]

The insertion of an alkyne ((diethylamino)propyne (**5**)) into the metal−carbene bond of **3** and of several tungsten carbene complexes [(CO)$_5$W=C(OMe)C$_6$H$_4$R-*p*] (R = CF$_3$, Br, H, Me, OMe) has also been studied kinetically.[9] In contrast to the Dötz reactions, the insertion follows a *second-order rate law*: $-\mathrm{d}[\mathbf{3}]/\mathrm{d}t = k[\mathbf{3}][\mathbf{5}]$. As expected, the activation entropy is *highly negative* ($\Delta S^{\ddagger} = -142 \pm 16$ J/(mol K), in octane). Thus, the reaction characteristics for the Dötz reaction and for these insertion reactions are completely different. The insertion of alkynes into the M=C bond of [(CO)$_5$M=C(OR)R′] complexes[1a,12] is confined to π-donor-substituted alkynes. The insertion of alkynes such as acetylene, phenylacetylene, tolane, and alkylalkynes into the M=C bond of [(CO)$_5$M=C(OR)R′] complexes has not been observed.

(2): According to the DFT calculations by TDS the insertion of the alkyne into the chromium−carbene bond proceeds with nearly no barrier. Therefore, an almost instantaneous formation of the insertion product on mixing solutions of the carbene complexes and alkynes is to be expected. When the reaction of **3** with tolane, phenylacetylene, etc. is monitored by IR spectroscopy, only the starting complex and the product complex are observed, in addition to some decomposition products. The formation of an intermediate cannot be detected. At 4 °C, the calculated half-life for CO dissociation from **3** in *n*-Bu$_2$O is 13.7 days.[11] When **3** is kept in a solution of HC≡CPh (95-fold excess) in *n*-Bu$_2$O, the reaction is almost complete after 50 days. In the course of the reaction, there is no spectroscopic indication for the formation of any insertion product as an intermediate, either of [(CO)$_5$Cr=C(H)C(Ph)=C(Ph)OMe] or of [(CO)$_5$Cr=C(Ph)C(H)=C(Ph)OMe].[11]

Possible reasons for the discrepancy between experiment and the mechanistic picture derived by TDS from theory might be related to the fact that the calculated data are those of a hypothetical gas-phase reaction. However, the Dötz reaction has to be performed in the condensed phase. Both the reaction rate and the product distribution are considerably solvent-dependent. Usually, polar solvents (e.g. di-*n*-butyl ether, diethyl ether, THF, etc.) or polarizable solvents (e.g. benzene and toluene) are employed to stabilize the reactive intermediates. In the prototypical reaction of **3** with PhC≡CPh the yield of the benzannulated product arising from the coupling of "C(OMe)Ph", CO, and PhC≡CPh is 62% in *n*-Bu$_2$O (45 °C, 3 h)[2] but drops to 38% when the reaction is carried out in heptane (80 °C, 30 min).[12a] Presumably, the coordinating, intermediate-stabilizing solvent can be replaced by an appropriate substituent in the carbene ligand, e.g. by the *o*-OMe group in [(CO)$_5$Cr=C(OMe)-C$_6$H$_4$OMe-*o*].[12b,c] Gas-phase calculations necessarily neglect any stabilizing factors of the solvent.

In addition, the transition state and its energy for the postulated associative reaction between [(CO)$_5$Cr=C(OH)CH=CH$_2$] (**1**; Scheme 2) and HC≡CH, leading to [(CO)$_5$Cr=C(H)CH=C(OH)CH=CH$_2$] (**2**; Scheme 2) has not been characterized by TDS. The high exothermicity of the overall process from **1** to **2** does not automatically imply a small activation barrier.

[(CO)$_4$Cr=C(OH)CH=CH$_2$], the product of CO loss from **1**, can coordinate a double bond of the α,β-unsaturated carbene ligand to the metal, as predicted by theory[13a,b] for [(CO)$_4$Cr(η^3-C$_3$H$_4$)] or [(CO)$_4$Cr(η^3-CH(OH)=CH$_2$)][13c] and confirmed by the X-ray structure of an η^3-allylidene complex.[14] Indeed, the η^3-allylidene structure has been found by TDS[3] to be the lowest energy isomer for the CO dissociation product [(CO)$_4$Cr=C(OH)CH=CH$_2$] but has been discarded as a possible intermediate because of "...the disadvantage of being inaccessible to ethyne insertion..." and "...because there is no vacant coordination site available in an η^3-allylidene complex...". This conclusion is only valid if the energy required for double-bond decoordination is large. However, Hess et al.[13c] found in their DFT study that the decoordination of the double bond only costs 10−13 kcal/mol[18c] and that "...the η^3-allylidene complex as a direct product of *cis*-CO dissociation will give up its intramolecular η^3-bonding in order to become accessible for ethyne insertion. Such a process is reversible, as shown by Barluenga.[14]" In an earlier paper,[15] TDS themselves have shown that the barrier for an interconversion of such η^3- and η^1-forms is only ca. 2 kcal/mol. For isolobal tungsten systems, this barrier is known from experiment to be small.[16]

Absolute energies from DFT calculations for critical points of energy surfaces should be checked by higher level calculations.[17] Also, computed gas-phase energies often do not allow a 1:1 mapping of the energetics in the condensed phase.[18] Therefore, computed Cr−CO dissociation energies should be regarded as an upper

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limit, which in reality are reduced by interaction of the unsaturated intermediate with the solvent. It is conceivable that the double bond of [$(CO)_5Cr{=}C(OH)CH{=}CH_2$] (**1**) can play the solvent's role, thus facilitating CO loss by leading to the above-mentioned η^3-allylidene structure.[13c]

Conclusions

In summary, a large body of experimental observations indicates that the initial reaction steps of the Dötz reaction involving (carbene)pentacarbonylchromium complexes proceed by a dissociative mechanism (CO dissociation followed by alkyne addition). The associative sequence suggested on a theoretical basis (alkyne insertion followed by CO dissociation), although certainly an interesting alternative, does not agree with the experimental data available.

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(18) For very recent examples, where experimental solution chemistry (kinetics, labeling studies) and experimental/theoretical gas-phase work (electrospray MS/quantum chemistry) is available and proves different mechanistic pathways to be operative, see: (a) Luecke, H. F.; Bergman, R. G. *J. Am. Chem. Soc.* **1997**, *119*, 11538. (b) Hinderling, C.; Plattner, D. A.; Chen, P. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 243. (c) Hinderling, C.; Feichtinger, D.; Plattner, D. A.; Chen, P. *J. Am. Chem. Soc.* **1997**, *119*, 10793.

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