

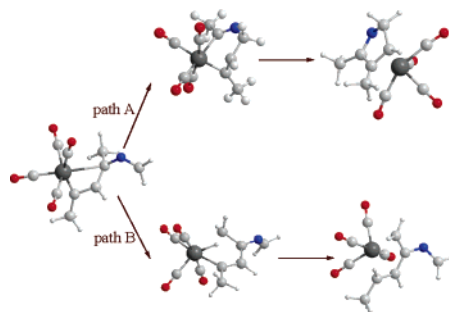
## Irradiation of Imine-Group VI Carbene Complexes in the Presence of Alkynes. 2. Control of Product Distribution

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Received April 6, 2005



The photoreactivity of iminecarbene complexes in the presence of alkynes has been explored. Up to four different reaction paths are available depending on the alkyne and carbene complex substituents, although in each case only one type of product is isolated. *2H*-Pyrrole derivatives are formed mainly from aryl alkynes. When alkyl alkynes are used, the method affords a new type of aza-dendralene product in good yields. Isoquinoline derivatives can also be formed in a two-step one-pot photochemical process when the appropriate substituents are present. Finally, indene derivatives are also available through a benzannulation reaction. To explore the underlying mechanism, we carried out computations using DFT methods. Experimental and theoretical results compare well, which allows control over the reaction and product distribution.

### Introduction

Fischer carbene complexes have shown impressive potential in synthesis due to their extremely versatile behavior.<sup>1–6</sup> The extensive chemistry of this kind of organometallic reagent makes them very useful components in the synthetic toolbox. Cycloaddition reactions are among the most widely explored transformations and represent a valuable route to different kinds of three-, four-, five-, and six-membered cycles.<sup>7–10</sup> More recently,

the photoreactivity of carbene complexes has emerged as an easy and useful method for the synthesis of these compounds, particularly for products that are not accessible under thermal conditions.<sup>11</sup> In a series of papers we have explored the synthetic utility of iminecarbene complexes to yield azadienes,<sup>12</sup> cyclopropanes,<sup>13</sup> triazolines,<sup>14</sup> oxazolines,<sup>14</sup> pyrrolines,<sup>15</sup> and pyrroles and *2H*-pyrroles<sup>16</sup> through cycloaddition reactions with unsaturated compounds. In the particular case of alkyne reactions, we found that there are certain differences between N- and O-substituted carbene complexes. Whereas alkoxy-

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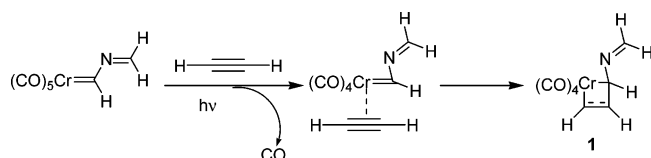
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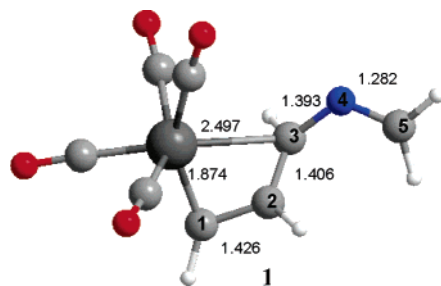
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## SCHEME 1. Formation of Metallacycle 1



carbene complexes usually yield six-membered cycles after CO insertion, amino and iminecarbene complexes yield five-membered cycles as a result of their different electronic features.<sup>4</sup> Our previous work on the subject demonstrated<sup>16</sup> that the key intermediate along the path connecting reagents to products is a new carbene complex **1** (Scheme 1, Figure 1). This intermediate is formed after a photochemically induced CO extrusion followed by alkyne insertion into the metal–carbon double bond and represents the most stable intermediate along the path. This kind of compound also appears in the proposed mechanism for the Dötz benzannulation<sup>17</sup> and has been found experimentally.<sup>18</sup> In an effort to further explore the synthetic utility of this reaction, we aimed to use different substitution patterns in both carbene complex and alkyne moieties in order to alter the electronic balance in some of the intermediates involved. It was envisaged that changes would cause a detour from the main path leading to pyrrole formation and could lead to a different product distribution. Therefore, any attempt to alter the photo-reactivity of iminecarbene complexes toward alkynes should start with a controlled modification in this intermediate. Careful consideration of the structure of model compound **1** reveals that carbon atoms C1, C2, and C3 are best placed to influence steric or electronic effects in the metallacycle structure. C5, on the other hand, appears to be too remote to have any steric influence on the cycle. However, electronic effects could be important because the iminic carbon C5 is conjugated to the metallacycle.



**FIGURE 1.** Selected geometrical parameters (bond lengths in Å) of model carbene **1**, the key intermediate in the photoreaction of iminecarbene complexes toward alkynes.

As a complementary approach, we decided to carry out a parallel theoretical study into this subject in order to control the effects caused in the intermediates by the modifications of both carbene complex and alkyne. It was believed that this study would enable us to tune the chemical behavior of these compounds through a combined theoretical and experimental approach. Theoretical

calculations on transition metal complexes are now well established as a tool for the study of organometallic species.<sup>19</sup> In this respect density functional theory (DFT) methods are particularly important because of their expediency, which makes them viable for the study of large molecules in a fraction of the time required for post-Hartree–Fock (HF) calculations. An even more important advantage is that, in most cases, the expectation values derived from approximate DFT are in better agreement with experiment than results obtained from HF calculations. In the particular case of group VI carbene complexes, DFT methods have shown remarkable agreement with the experimental results, as they have been able to reproduce experimental findings with considerable accuracy.<sup>20–22</sup> We have also applied this methodology to the study of the photochemical cyclopentannulation of iminecarbene complexes with alkynes in order to overcome the difficulties encountered in the experimental characterization of the intermediates involved.<sup>16</sup>

## Computational Details

All calculations were carried out using the Gaussian 98 program package.<sup>23</sup> Because DFT methods combine the importance of including electron correlation effects and the possibility of dealing with large systems, ground-state molecular geometries were optimized within the nonlocal density approximation (NLDA), including Becke's<sup>24</sup> nonlocal exchange corrections as well as Perdew's<sup>25</sup> inhomogeneous gradient corrections for correlation. The standard split-valence 6-31G\* basis set<sup>26</sup> was employed for C, O, N, and H. The Hay–Wadt effective core potential<sup>27</sup> with the minimal basis set split to [341/2111/41] was used for the chromium atom. Geometry was fully optimized without any symmetry constraint for all model compounds. Optimized structures were characterized as minima or saddle points by frequency calculations, which also allowed the obtaining of ZPE and thermal corrections.

## Results and Discussion

**Dendralene Formation.** As stated above, the first steps along the reaction path consist of the substitution of a CO ligand by an alkyne followed by partial alkyne insertion into the metal–carbon double bond to yield the intermediate shown in Figure 1. C1, C2, and C3 interact with the metal center to a certain extent so the structure for this intermediate is that of a  $\eta^3$  vinylcarbene complex

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**TABLE 1.** Dendralene Formation through Photoreaction of Iminecarbene Complexes with Alkynes

M=Cr 2  
W 3

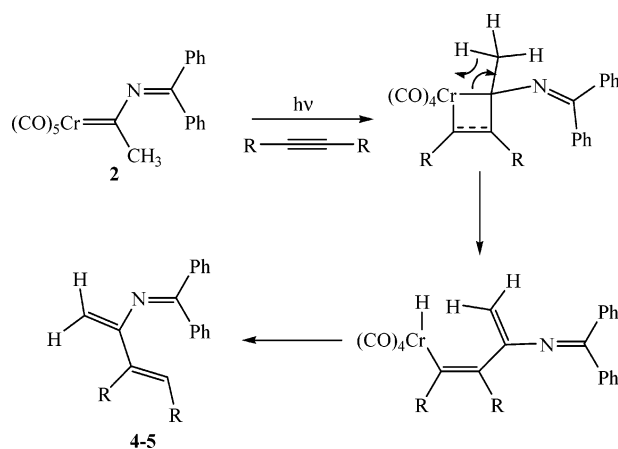
R=Et 4  
Pr 5

entry	carbene	compound	R	t (h)	yield (%)
1	2	4	Et	2	72
2	3	5	Pr	5	45
3	2	4	Et	2	63
4	3	5	Pr	5	51

and not a new  $\eta^1$  carbene complex formed after complete alkyne insertion. At this point, the use of alkynes with the electron-withdrawing or electron-donating groups previously used<sup>16</sup> to stabilize the newly formed complex becomes unnecessary. We therefore explored the photoreactivity of iminecarbene complexes toward alkyl-substituted alkynes. The results of this study are shown in Table 1.

As can be seen, the presence of alkyl groups induces a completely different photoreactivity of the iminecarbene complexes, yielding a new type of acyclic product instead of 2*H*-pyrrole derivatives. Compounds **4** and **5** are 2-aza-[3]dendralenes, which are N-substituted analogues of cross-conjugated trienes. It would appear that such a structure should be ubiquitous, but in fact few strategies are available even for the all-carbon system. Until recently, these kinds of compounds, which are also known as dendralenes, had only been observed in low yields during transition-metal-catalyzed reactions of alkynyl allenes. This situation changed recently when the first synthesis of the dendralene family of hydrocarbons was reported.<sup>28</sup> Since then, several syntheses of compounds with this structure have been published<sup>29–31</sup> and their chemistry as building blocks<sup>32</sup> and industrially interesting products<sup>33</sup> has been studied. Despite this recent interest, the influence of heteroatom substitution in the dendralene moiety has not yet been explored. Cross-conjugated azatrienes could be formed through the mechanism shown in Scheme 2, with the key step consisting of an H abstraction from the methyl group to yield a new structure with an interaction between the hydrogen atom and the metal center. Although such a mechanism has been invoked previously to explain similar results,<sup>34</sup> proof of its contribution has not been found. In an effort to clarify mechanistic aspects of this process we approached the problem using the computational methods described above.

The only difference between these results and those reported previously concerns the different electronic

**SCHEME 2.** Formation of Dendralene Products

nature of the alkyne substituents. For this reason we computed the paths connecting model compound **6** [intermediate for the photoreaction between  $\text{Cr}(\text{CO})_5=\text{C}(\text{Me})-\text{N}=\text{CH}_2$  and propyne] with the corresponding products of ring expansion (pyrrole, path A) and  $\beta(-\text{H})$  elimination (dendralene, path B). The results of the calculations are shown in Scheme 3.

Path A connects the metallacyclobutene **6** (analogue of **1** with a methyl group at C3) with the pyrrole derivative. Once the transition state **TS-6a** is passed through, no intermediates were found along the path until the final product **6a**. Our previous results<sup>16</sup> showed the presence of a shallow minimum with a metallacyclohexadiene structure when a simplified model was considered and this had a barrier of only 0.2 kcal/mol prior to pyrrole formation. This barrier is lifted when a more appropriate model like **6** is used. More specifically, this barrier disappears completely and an intermediate cannot be located along the path when any substituent is bonded to C3. This atom corresponds to the carbenic carbon in the starting carbene complexes and always bears a substituent, meaning that this lack of an intermediate should be a general feature. The IRC calculation for path A is shown in Figure 2, and in this case model **1** was used for simplicity. On the other hand, path B corresponds to triene formation. This path involves only one step given that the postulated intermediate, with a bond between the hydrogen atom and the metal center, really represents the transition structure leading to the dendralene. **TS-6b** is characterized by an imaginary frequency as high as 937  $\text{cm}^{-1}$ , which is typical of a hydrogen motion. The global process consists of the transfer of a hydrogen atom from the methyl substituent in C6 to C1, and this proceeds through a transition state in which this hydrogen clearly interacts with the metal center. The path was further explored by means of by an IRC computation. Selected geometrical parameters of **TS-6b** are shown in Figure 2.

As can be seen in Scheme 3, the two paths starting from the same metallacycle **6** yield the pyrrole and the triene through two different transition structures with an energy difference of less than 1 kcal/mol. Moreover, the preferred product should be the 2*H*-pyrrole derivative because the transition state leading to it has a lower energy barrier. This suggests that the influence of the substituents must be important in the fate of metalla-

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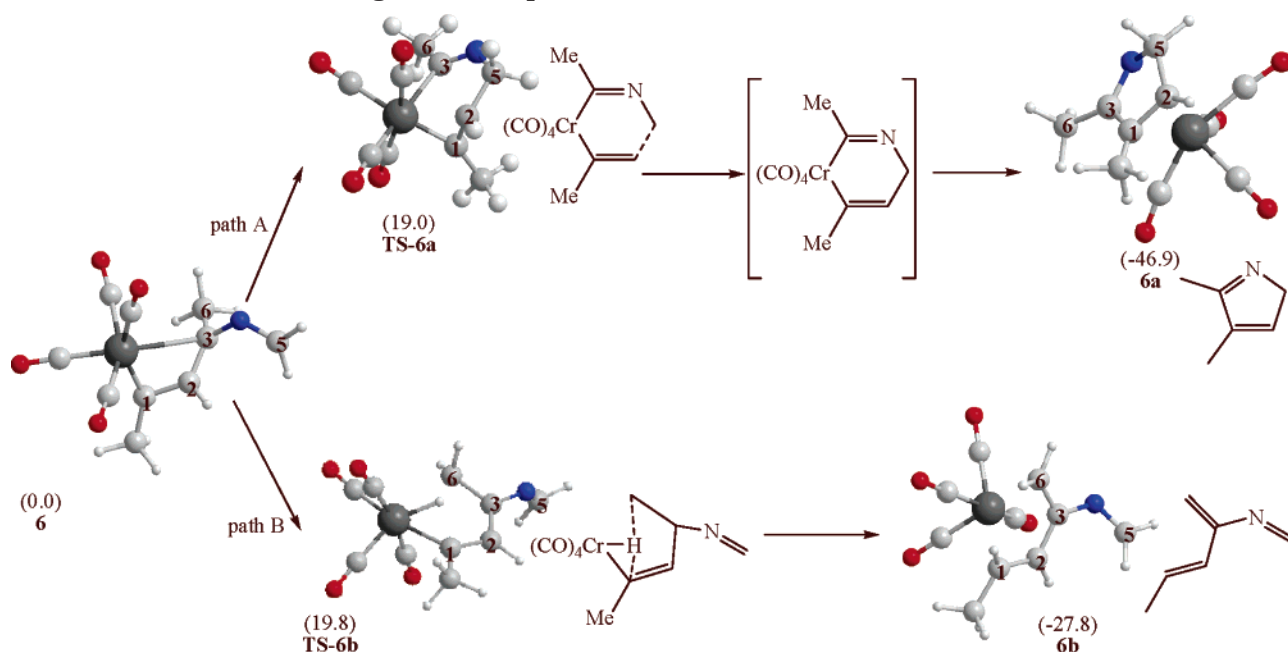
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SCHEME 3. Two Paths Starting Form Compound 6<sup>a</sup>

<sup>a</sup> Relative energies (kcal/mol) in brackets.

cyclobutene intermediates such as **6**, as only the dendralene product was detected in the crude reaction mixture when alkyl-substituted alkynes were used. To calculate this influence on both pyrrole and dendralene formation, we computed paths A and B for different carbene complexes of increasing substitution. We first assessed the effect of iminic carbon substitution by computing compounds **7** and **8**. The results of these calculations are shown in Table 2.

The influence of iminic carbon substitution can be understood mainly in terms of steric interactions, in that the structures for both metallacycle and transition states are virtually the same for compounds **6**–**8**. Transition states for path B (dendralene formation) represent equal barriers as a result of the lack of electronic or steric effects because the phenyl rings are too far away from the reactive center. However, when path A (pyrrole formation) is considered, aromatic rings at C5 make the approach of C2 and C5 more difficult. Thus, when larger groups are involved (**6** → **7** → **8**), steric interactions give rise to higher energy barriers in path A. Since C5 corresponds with the iminic carbon in the starting complexes and is always bonded to two alkyl or aryl groups,<sup>12,16</sup> the steric interaction that leads to higher energy barriers for path A when the alkyne has alkyl substituents should be a general feature. However, the product distribution in the photoreaction (i.e., pyrrole vs dendralene) depends only on alkyne substituents and not on carbene complexes, meaning that steric effects are not the only aspects to be considered. In an effort to clarify further the preference for dendralene formation, we computed paths A and B for different metallacycles formed after insertion of mono- and disubstituted alkyl and aryl alkynes. The results of these calculations are shown in Table 3.

Several conclusions can be drawn from the information in Table 3. First, the effect of disubstituted alkynes is different depending on the nature of the substituent. In

the case of the methyl group, the second substituent leads to stabilization in both paths A and B (**8** vs **9**). However, in the case of Ph, the introduction of a second ring increases the energy of both transition structures (**10** vs **11**). Note that in the case of monosubstitution the regiochemistry of the insertion has been determined previously.<sup>16</sup> Second, a change in the electronic nature of the alkyne substituents (Me vs Ph) causes a preference for a different path. In the case of methyl groups (**8**, **9**) path B (dendralene formation) is favored over path A. This situation changes when the alkyne bears aryl groups in that path A (pyrrole formation) becomes the preferred route. These data are in complete agreement with the experimental results and can be understood by considering more closely the structures involved. Some geometrical parameters for the key structures are shown in Figure 3.

As can be seen, metallacycles **11** and **9** show slight differences, but these are clear enough to explain the experimental results. The influence of the aromatic rings makes the C1–C2 bond longer in **11** (1.484 Å) than in **9** (1.458 Å). In the same way, the Cr–C3 bond increases in length from **9** (2.789 Å) to **11** (2.838 Å), which causes methyl group C6 to be farther from the metal center. As a result, the path describing the required motion for the hydrogen atom is longer in **11**. For this reason, the transition structures differ mainly in the distances between the migrating H and the closest atoms, Cr and C6. Both distances are shorter in **TS-9b** (Cr–H = 1.671 Å in **TS-11b** and 1.656 Å in **TS-9b**, H–C6 = 1.450 in **TS-11b** and 1.443 Å in **TS-9b**). This difference causes path B (dendralene formation) to be lower in energy. As far as path A (pyrrole formation) is concerned, we previously demonstrated<sup>16</sup> that a higher degree of conjugation contributes to the stabilization of the species along the reaction path. As a result, the presence of phenyl substituents in the alkyne leads to pyrrole formation, whereas alkyl substituents favor the formation of

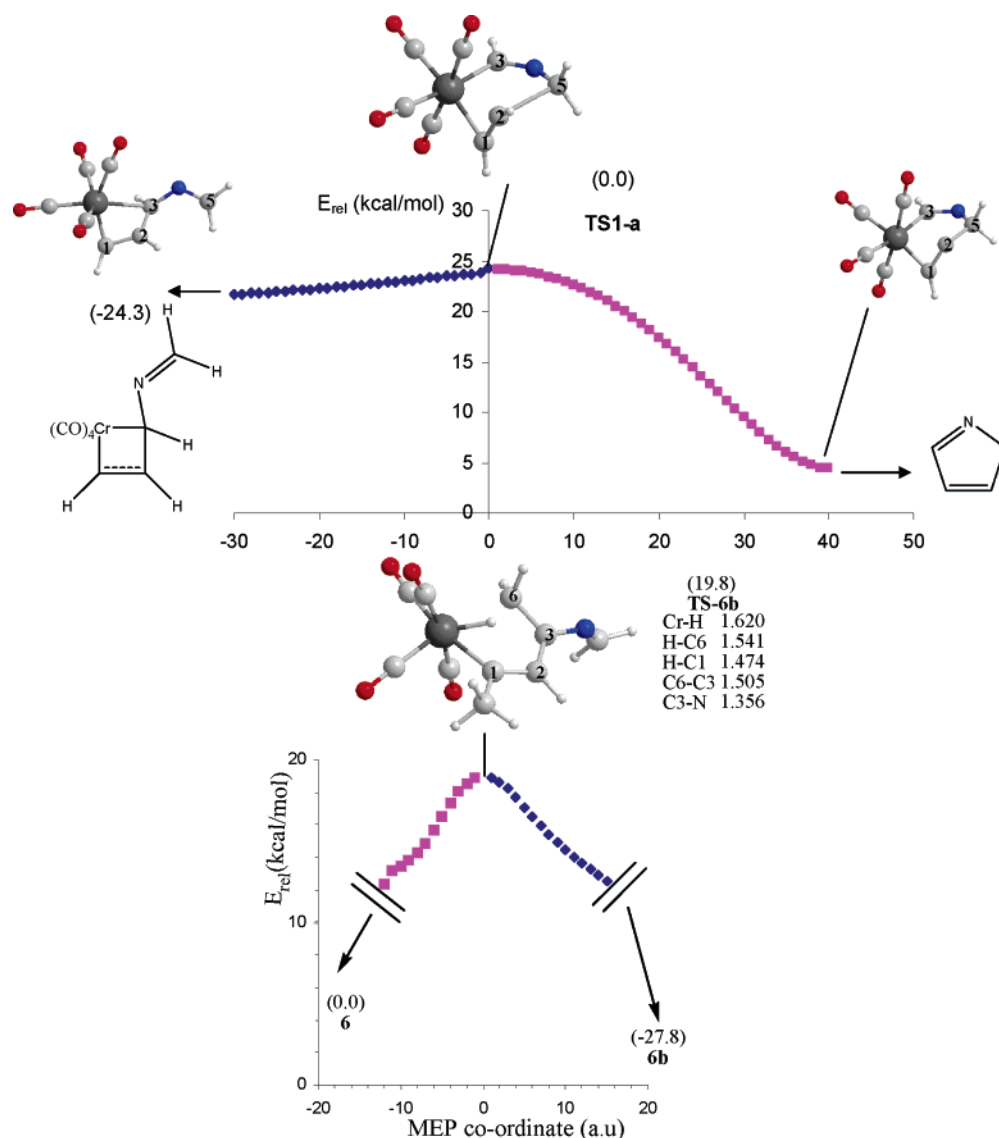
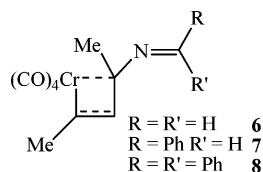


FIGURE 2. Intrinsic reaction coordinate (IRC) calculations for TS-1a and TS-6b.

TABLE 2. Energies of Calculated Structures for Compounds 6–8 Relative to the Corresponding Metallacycle

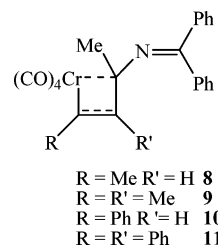


compound	pyrrole formation	dendralene formation
(0.0) <b>6</b>	(19.0) <b>TS-6a</b>	(19.8) <b>TS-6b</b>
(0.0) <b>7</b>	(21.2) <b>TS-7a</b>	(19.8) <b>TS-7b</b>
(0.0) <b>8</b>	(21.3) <b>TS-8a</b>	(19.8) <b>TS-8b</b>

dendralene-type products. The higher energy obtained for both paths in the case of **11** compared with **10** is due to the greater steric demand of a second phenyl ring, a demand that is not fully compensated by increasing the conjugation.

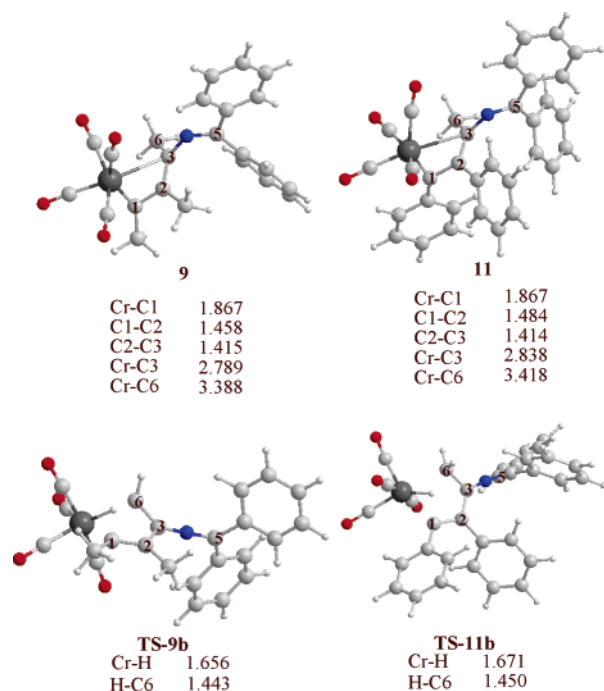
**Carbene Complex Modification: Four Different Routes.** Once the importance of the alkyne substituents and the generation of a new kind of product with the

TABLE 3. Energies of Calculated Structures for Compounds 8–11 Relative to the Corresponding Metallacycle



compound	pyrrole formation	dendralene formation
(0.0) <b>8</b>	(21.3) <b>TS-8a</b>	(19.8) <b>TS-8b</b>
(0.0) <b>9</b>	(19.7) <b>TS-9a</b>	(17.4) <b>TS-9b</b>
(0.0) <b>10</b>	(9.6) <b>TS-10a</b>	(10.8) <b>TS-10b</b>
(0.0) <b>11</b>	(18.3) <b>TS-11a</b>	(21.6) <b>TS-11b</b>

dendralene structure had been assessed, we aimed to study the effect of different carbene complexes on product distribution. In the previous section, we described how a change in the iminic substituents had no effect on path B (dendralene formation). All substituents studied to date



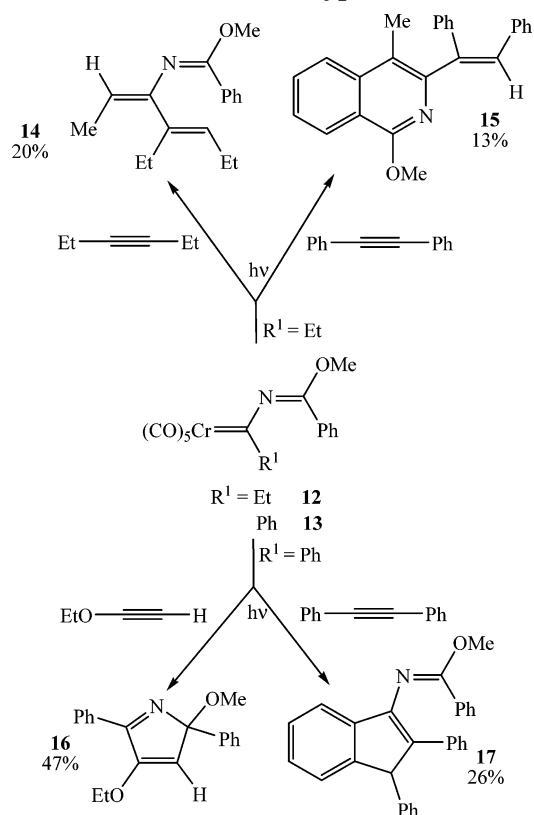
**FIGURE 3.** Selected geometrical parameters (bond lengths in Å) for intermediates **9** and **11** and the corresponding transition structures for dendralene formation, **TS-9b** and **TS-11b**.

(aryl, alkyl, H atom) have little steric influence and are similar in electronic nature. This situation is demonstrated by the X-ray structures obtained for this type of compound.<sup>5,6</sup> However, the use of substituents with a substantially different electronic nature could affect the structure and chemical behavior to a greater extent. For this reason, we explored the effect of replacing one of the phenyl rings in the iminic carbon with a strong electron-donating group such as the methoxy group. The synthesis of these compounds was achieved by heating the corresponding carbene in the presence of the appropriate nitrile.<sup>35</sup> Preliminary results obtained after irradiation of these carbene complexes in the presence of a number of alkynes are shown in Scheme 4.

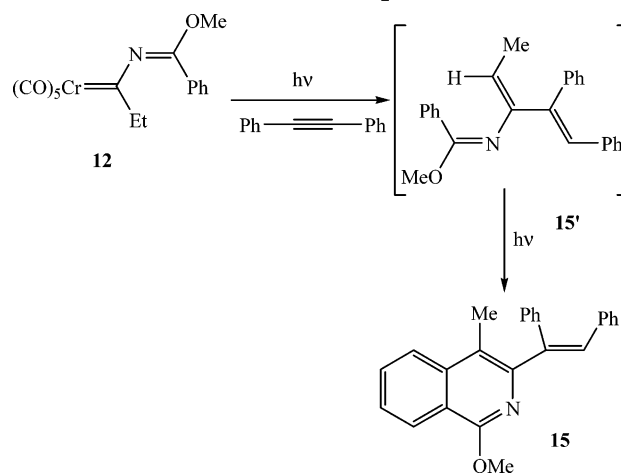
As can be seen, products with four different structures can be formed in the photoreaction of chromium iminocarbene complexes with alkynes, with the nature of the product depending on the nature of the carbenic carbon and alkyne substituents. As both of these substituents are easily modified, we could use the same basic reaction to yield very different products. However, to fully control the potential of these reactions, we must first understand the reasons for the observed differences and how the substituents affect the reaction mechanism.

The first photoproduct in Scheme 4 (**14**) has a cross-conjugated structure similar to that of the dendralene compounds described in the previous section. Since compound **12** has the hydrogen atoms needed for this transformation, the formation of **14** must occur through the same mechanism as discussed above. Compound **15** seems to be formed through a completely different mechanism. Moreover, the isoquinoline structure has not

#### SCHEME 4. Four Different Types of Products



#### SCHEME 5. Formation of Isoquinoline 15



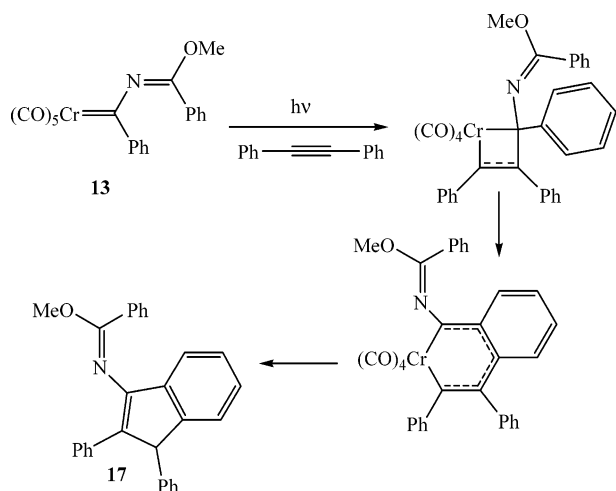
been previously obtained in the context of Fischer carbene chemistry. However, a careful look at **15** reveals that the isoquinoline substructure has been formed exclusively from the carbene moiety and the alkyne acts only as a substituent. In fact, **15** must have been produced after cyclization from an intermediate with a dendralene structure in an analogous way as **14** (see Scheme 5).

We previously described<sup>36</sup> these kinds of photoreactions, which are very dependent on the substrate. Both **14** and **15** are formed through the same reaction path. However, whereas **15'** reacts further under the reaction conditions to yield isoquinoline **15**, compound **14** does not

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## SCHEME 6. Formation of Indene 17



cyclize. Consequently, once isolated, we found **14** to be photoreactive but only detected decomposition after 5 h. Thus, the key feature in the formation of **14** and **15** is the presence in the carbenic substituent of hydrogen atoms that can be abstracted. Compounds **14** and **15'** are formed following the same path described in the previous section. Subsequent photoreaction of **15'** yields the isoquinoline compound **15**. The low yields for **14** and **15** can be attributed to the occurrence of these two consecutive photoreactions. An increase in the chemical yield would be expected under controlled reaction conditions. However, the photochemical studies required are beyond the scope of the present paper and are currently being carried out. It should also be noted that in this case both alkyl and aryl substituents in the alkyne yield the same dendralene-type structure. This fact must be caused by the presence of the methoxy group and its effect on the stability or structure of the intermediates along the reaction path (see Scheme 3).

When the formation of dendralene-type products is blocked by the absence of available hydrogen atoms in the carbenic carbon, one would expect the reaction to yield *2H*-pyrrole derivatives (i.e., path B in Scheme 3 is blocked; only path A is available). In fact, this happens in the reaction of **13** with ethyl ethynyl ether, where *2H*-pyrrole **16** is formed. Nevertheless, a different reaction path appears in the reaction of **13** with toluene. In this particular case, dendralene formation through hydrogen abstraction is also blocked and cyclization occurs. However, unlike compound **16**, where the final product is formed through the path described above (path A, Scheme 3), indene **17** is produced after ring expansion involving the aromatic ring and not the imine moiety (see Scheme 6). Such reactivity has not been found previously for iminecarbene complexes but is a typical reaction outcome for the annulation of aminocarbene complexes in the presence of alkynes (i.e., Dötz reaction).<sup>4</sup>

Once again, small modifications in both carbene and alkyne substituents can open up different reaction paths. To rationalize the experimental results, we computed the effect of the modifications introduced on the intermediates in paths A and B. First, we studied the effect of a methoxy group in the imine moiety, which causes dendralene formation regardless of the alkyne substituents. Second, once this path is blocked by using a phenyl ring,

TABLE 4. Energies of Calculated Structures for Compounds **18** and **19** Relative to the Corresponding Metallacycle

compound	pyrrole formation	dendralene formation
(0.0) <b>18</b>	(13.8) <b>TS-18a</b>	(13.4) <b>TS-18b</b>
(0.0) <b>19</b>	(17.5) <b>TS-19a</b>	(26.0) <b>TS-19b</b>

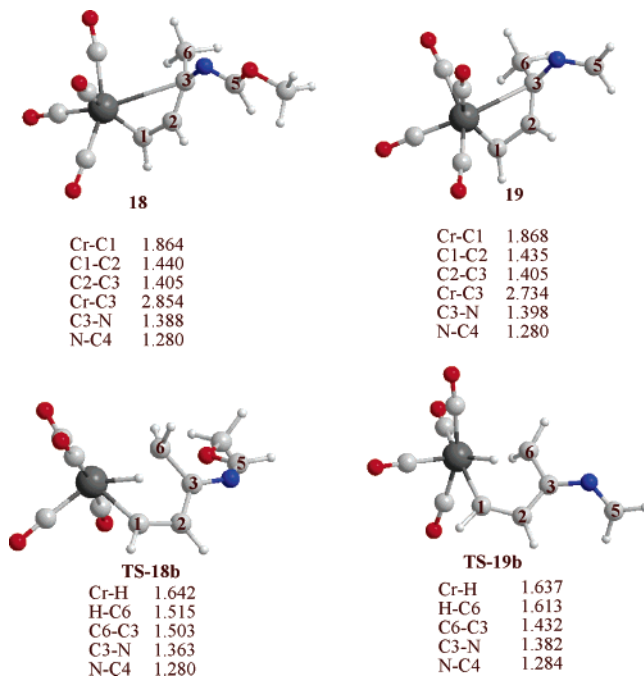
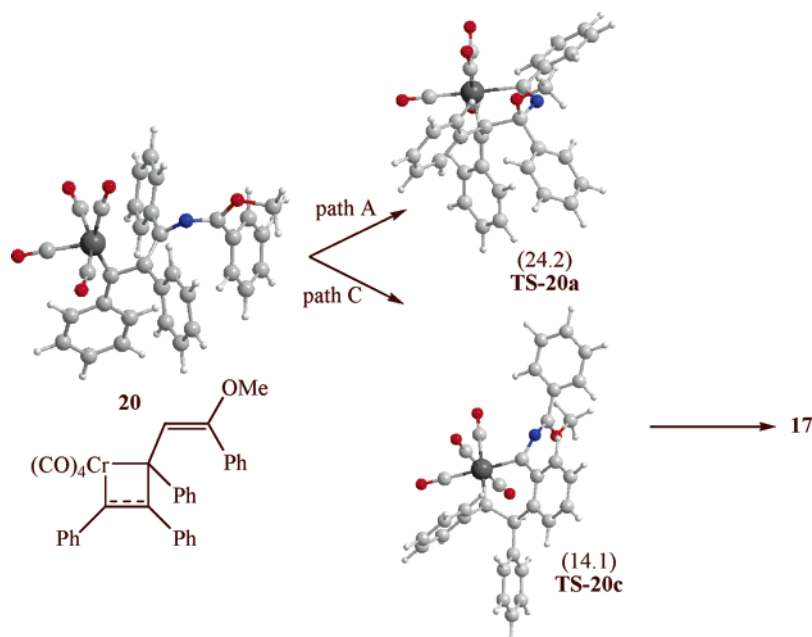


FIGURE 4. Selected geometrical parameters (bond lengths in Å) of intermediates **18** and **19** and the corresponding transition structures to dendralene formation, **TS-18b** and **TS-19b**.

we explored the appearance of a third reaction path leading to indene products (Dötz reaction) and the competition of this route with *2H*-pyrrole formation. The results of the calculated paths A and B (see Scheme 3) for the iminecarbene models **18** and **19** are shown in Table 4.

Comparison between carbene complexes **18** and **19** allows a direct evaluation of the influence of the methoxy substituent located on the iminic carbon. The methoxy group contributes to the stabilization of the transition structures for both paths A and B. For metallacycle **19**, the preferred path leads to pyrrole formation. This preference changes on the introduction of the methoxy group, and dendralene becomes the preferred product. Although the energy difference in **18** is only slight, the destabilization caused in transition structures leading to pyrrole by substitution with groups of higher steric demand has been described above. The structures for the corresponding metallacycle intermediate and transition states are shown in Figure 4. Only slight differences can be seen in all of the parameters apart from the Cr–C3

## SCHEME 7. Two Paths Starting from Compound 20



distance. The longer Cr–C3 distance in **18** suggests a higher degree of alkyne insertion, and this could be related to the higher energy of the transition state leading to pyrrole formation (**TS-18a**). On the other hand, more marked changes occur in path B (dendralene formation). In this case, the hydrogen atom has to migrate from methyl group C6 to C1. In **TS-19b**, the hydrogen atom is clearly farther from the metal center and the C atoms (H–C6 1.613 Å, Cr–H 1.637 Å, H–C1 1.589 Å). However, the presence of a methoxy substituent can stabilize the transition state by electron density donation, which is reflected in the distances involved (H–C6 1.515 Å, Cr–H 1.642 Å, H–C1 1.423 Å). This stabilization gives rise to the lower energy of the transition state leading to the cross-conjugated product in the case of **18**. The effect of the methoxy group must be general for any carbene complex. Moreover, the computed complexes have hydrogen atoms as substituents, whereas the experimentally available complexes contain larger substituents that, as seen before, cause a higher preference for dendralene formation. Thus, path B is the preferred route for methoxy-substituted carbene complexes, leading to the formation of **14** and **15** being more favorable than the corresponding pyrrole derivatives. However, when this path is blocked (i.e., when aryl groups are used instead of alkyl groups as the carbenic carbon substituent), two different possibilities still remain: path A leading to pyrrole formation (compound **16**) or Dötz annulation to yield indene formation (compound **17**). Whereas aminocarbene complexes usually afford indene products,<sup>4</sup> the typical product for iminecarbene complexes has the pyrrole structure.<sup>12</sup> The reaction paths leading to these two types of product have been studied previously at the theoretical level.<sup>16,37</sup> We therefore focused only on the effect of the substituents in determining the fate of the metallacycle intermediate.

We computed both paths for **20**, which subsequently yields **17**. Dendralene formation is blocked in this

compound, and only pyrrole or indene derivatives are available. Results of the calculations for the key intermediates along both paths are shown in Scheme 7.

As can be seen, the two paths are very different in energy, and in agreement with the experimental data, path C is more favorable. However, the possibility of some contribution from path A cannot be ruled out in general terms. The stabilizing effect of the methoxy group through electron density donation seems to be responsible for this preference, but this subtle equilibrium can be altered by any modification in any position of the molecule. As we have seen in the case of compound **16** (Scheme 4), a change in the alkyne substituents led to pyrrole formation. Likewise, replacement of the methoxy substituent in the iminic carbon by a phenyl or alkyl group is detrimental to path C.<sup>16</sup> Formation of any of the possible structures is feasible in the photoreaction of iminecarbene complexes with alkynes. However, we can control and therefore predict the outcome of the reaction by tuning the behavior of the key metallacycle through the introduction of different substituents in both the alkyne and carbene moiety.

## Conclusions

We have investigated the photochemically induced reaction of a range of iminecarbene complexes with alkynes. The outcome of these reactions is different depending on the substituents present in both the alkyne and carbene complex. Up to four different types of final products were found, although in all cases studied only one type of product is finally isolated. We have used theoretical calculations to explore the available reaction paths. *2H*-Pyrrole derivatives are generally obtained with aryl-substituted alkynes. Cross-conjugated azatrienes were found when dialkyl alkynes were used and suitable H atoms are present in the carbene complex moiety. The formation of this kind of compound occurs through an intramolecular hydrogen abstraction from an alkyl group. Subsequent photoreaction of these compounds yields

(37) Torrent, M.; Duran, M.; Solà, M. *J. Am. Chem. Soc.* **1999**, *121*, 1309.



isoquinoline derivatives. In cases where alkyl groups are not available, 2*H*-pyrrole or indene derivatives can be formed. Indene products are produced through the Dötz annulation, which has not been previously reported for iminecarbene complexes.

### Experimental Section

**General Procedure for Irradiation.** The carbene complex (0.25 mmol) was dissolved in 50 mL of deoxygenated hexane. Five equivalents of alkyne were added, and the mixture was irradiated at room temperature under an Ar atmosphere, through Pyrex glass with a 125-W medium-pressure mercury lamp, until the carbene was consumed (TLC, hexane/CH<sub>2</sub>Cl<sub>2</sub> 1:1). The solvent was removed using a rotary evaporator and the crude product was filtered through Celite to remove

chromium residues. The product was purified by column chromatography (silica gel, hexane/Et<sub>2</sub>O).

**Acknowledgment.** We thank the Spanish MEC (BQU2001-1625), the Universidad de La Rioja (API-04/06) and the Comunidad Autónoma de La Rioja (ACPI-2003/08) for financial support. D.S. is financed by the Ramón y Cajal program from the MEC. M.C. thanks the Spanish MEC for her fellowship.

**Supporting Information Available:** Spectroscopic data for new compounds and Cartesian coordinates for the geometries discussed in the text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JO050676I