# First Stepwise Dötz Reaction: Isolation and Characterization of a Chelated Metallatriene Intermediate. Influence of Its Pattern of Substitution in Product Partition

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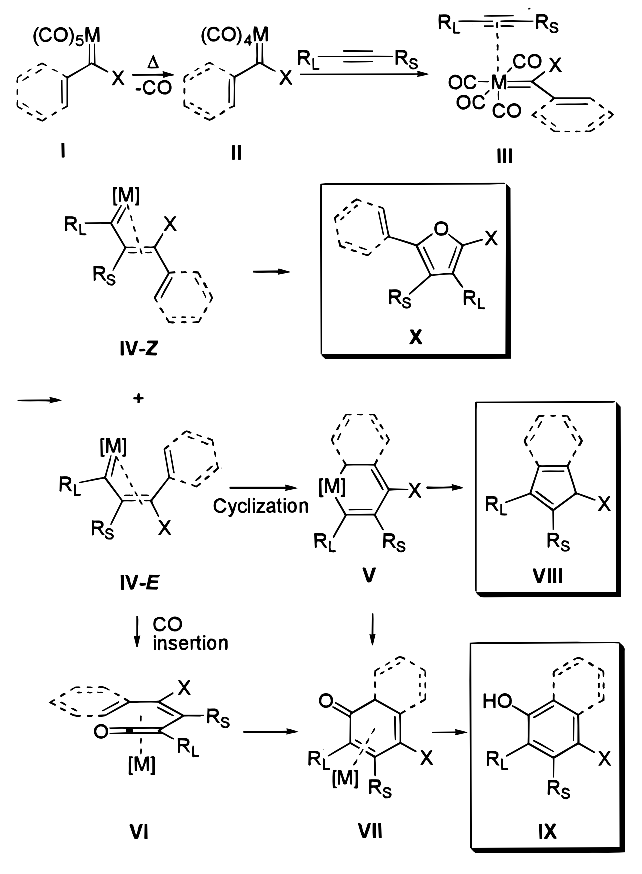
**Abstract:** A series of chelated tetracarbonyl aminovinyl carbene complexes **5** are prepared by high-yielding decarbonylation reaction. $\gamma$-Alkyl-substituted complexes **5a−d** are stable in solid form while $\gamma$-aryl-substituted analogues **5e−g** are stable only in solution. NMR studies determined that complexes **5** undergo a dynamic process in solution, in which the unsaturated $\eta^1$ species are present in low concentration. Reaction of complexes **5** with electron-deficient alkynes under controlled conditions afforded the 1,4,5-$\eta^3$-dienylcarbene complexes **9** arising from the insertion of the alkyne in the metal−carbon bond. The stability and behavior of these complexes were studied and found to be related to their electronic structure and pattern of substitution. Thermal decomposition of carbenes **9** produced either cyclopentadienes **13** or phenol derivatives **15**, the major products in the Dötz reaction, thus demonstrating that they can be the actual intermediates in this reaction. The overall process can be considered a Dötz reaction carried out in three separate steps at low temperature.

## Introduction

Despite the synthetic value of the benzannulation reaction of Fischer carbene complexes and alkynes,[1] the details of its mechanism remain to be ascertained.[2] Great efforts are being made to establish the role of each proposed intermediate in the outcome of the reaction. In particular, knowledge of the effect of the structure and stereoelectronic properties of the intermediates in the product distribution would improve significantly the ability to tune the reaction to a particular final product.

The widely accepted mechanism for the reaction is depicted in Scheme 1. The process is initiated by the dissociation of a CO ligand from complex **I** to produce the coordinatively unsaturated carbene complex **II**.[3] Intermediate **II** is trapped by the alkyne present in the medium, which binds the metal in such a way that the bulkier substituent $R_L$ is placed parallel to the trans CO to avoid unfavorable steric interactions with the

**Scheme 1**



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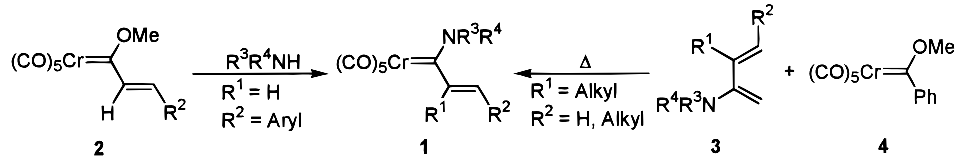
10.1021/ja991865j CCC: $19.00

**Scheme 2**



carbene ligand in complex **III**.[4] This coordination geometry will be ultimately responsible for the regiochemistry observed in the final products. The next step is the insertion of the alkyne into the metal−carbon double bond to afford metallatrienes **IV**. This step can lead to two different isomers of the $\eta^3$-metallatrienes, of which only the *E* isomer should be able to undergo cyclization with the terminal double bond, giving rise to the cyclopentadiene (indene) **VIII** and phenol (naphthol) **IX**.[5] On the other hand, the *Z* derivative is the one responsible for the formation of furan **X**.[6]

Isolating the intermediates and studying their structure and submission to the next mechanistic step in a reaction are, theoretically, the best means of understanding them. However, since the CO dissociation step in the benzannulation reaction is rate limiting, the detection of subsequent intermediates has been cumbersome. Thus, only cleverly designed stereochemically or functionally restricted analogues have been isolated and used to estimate the structural characteristics of the actual intermediates.[7−10] To the best of our knowledge, only one intermediate capable of undergoing the subsequent step has been isolated and characterized, namely the last one, the metal-complexed cyclohexadienone **VII**.[2d]

As stated above, the stereoelectronic properties of the intermediates, especially of those situated in the branching of the reaction pathway, are crucial for the product partition. Unfortunately, little is known about these intermediates. Theoretical calculations on models for several of the intermediates have shed some light on the energetics of the mechanism.[11−13] Also, rigorous evaluation of the proportions of the final products (including minor ones) and correlation with the electronic and steric properties of the starting materials have allowed us to infer the properties of the intermediates.[2d,e]

Despite this, there are still some unanswered questions, especially concerning the reaction of alkenylcarbene complexes. For instance, there is no clear reason why reactions of arylcarbene complexes with alkynes give so many different products and are so sensitive to changes in solvents and concentration while reactions of alkenyl carbenes only give six-membered rings with very few side products and are almost unaffected by changes in reaction conditions.[2d] Also, the electronic effects that have been proposed to explain the exclusive formation of indene derivatives for arylamino carbenes do not seem to work in the case of alkenylamino carbenes, since the reactions of this type of carbenes with alkynes give mainly aminophenols instead of aminocyclopentadienes.[14]

**Table 1.** Pentacarbonyl Aminovinyl Carbene Complexes Prepared

| compd | R$^1$ | R$^2$ | R$^3$ | R$^4$ | method | yield (%) |
|---|---|---|---|---|---|---|
| **1a** | $CH_2CH_2CH_2$ | | $CH_2CH_2OCH_2CH_2$ | | metathesis | 69[a] |
| **1b** | $O(CH_2)_2CH_2$ | | $CH_2CH_2OCH_2CH_2$ | | metathesis | 41 |
| **1c** | $CH_3$ | H | $CH_2CH_2OCH_2CH_2$ | | metathesis | 55 |
| **1d** | $CH_3$ | $CH_2OCH_3$ | $CH_2CH_2OCH_2CH_2$ | | metathesis | 75 |
| **1e** | H | Ph | $CH_2CH_2OCH_2CH_2$ | | aminolysis | 99 |
| **1f** | H | 2-furyl | $CH_2CH_2OCH_2CH_2$ | | aminolysis | 99 |
| **1g** | H | 2-furyl | Me | Me | aminolysis | 99 |
| **1h** | H | 2-furyl | Me | H | aminolysis | 99 |
| **1i** | H | 2-furyl | H | H | aminolysis | 99 |

[a] See ref 17.

In the present contribution we report the first example of a stepwise Dötz reaction, in which the decarbonylation step is carried out in the absence of alkyne. This has permitted us to isolate complexes analogous to **II**. We describe the insertion of alkynes in these compounds at low temperature, which led to the isolation and characterization of the metallatriene intermediates of the Dötz reaction **IV**. Finally, we study the thermal evolution of these intermediates and the effect of their pattern of substitution in the distribution between cyclopentadiene and the phenol derivatives.[15]

## Results

Aminocarbenes **1** (Scheme 2, Table 1) were prepared by two standard methods. Aminolysis of alkoxycarbenes **2** was performed on $\beta$-aryl-substituted complexes, giving rise to the aminocarbene derivatives in almost quantitative yields. However, in the reaction of the alkyl analogues with amines, variable amounts of complexes $(CO)_5(R_2NH)Cr$ are formed as side products, depending on the substituents of the amine and the carbene complex.[16] Therefore, complexes **1**, bearing an alkyl or hydrogen substituent in the $\beta$-position were synthesized by metathesis of 2-aminodienes **3** and pentacarbonylmethoxy(phenyl)carbene chromium **4**.[17] In some cases, variable amounts

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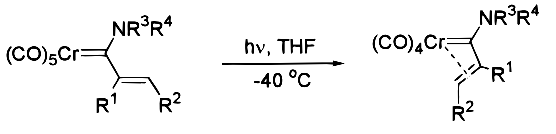
**Scheme 3**



**1** **5**

**Table 2.** Complexes **5** Prepared

| compd | $R^1$ | $R^2$ | yield$^a$ (%) |
|---|---|---|---|
| **5a** | $CH_2CH_2CH_2$ | | 94 (90) |
| **5b** | $O(CH_2)_2CH_2$ | | 84 |
| **5c** | $CH_3$ | H | 90 (77) |
| **5d** | $CH_3$ | $CH_2OCH_3$ | 88 (80) |

$^a$ Yields given in parentheses correspond to the thermal reaction.

of tetracarbonyl carbene complexes **5** (Scheme 3) are formed as side products in the metathesis reaction, but these compounds can be transformed quantitatively into their pentacarbonyl analogues **1** by simply bubbling CO through the crude reaction solutions. This fact suggested that the tetracarbonyl complexes **5** could be formed from **1** under thermal conditions.

Complexes **5a**, **5c**, and **5d** (Scheme 3, Table 2) were prepared by heating solutions of the pure pentacarbonyl complexes **1** in THF (complex **5a**) or toluene (complexes **5c** and **5d**) at reflux temperature. However, to avoid the long periods of time required to complete the reaction, that lead to partial decomposition of the starting and final complexes, we tried to carry out this reaction photochemically. Thus, when irradiated at −40 °C, a carbonyl ligand dissociates from the aminovinyl carbene complex to afford the stable tetracarbonyl species **5**.[18] The best conditions found for this transformation were the irradiation of a THF solution of the carbene complex in a Pyrex Schlenk tube at −40 °C while a constant flow of $N_2$ was bubbled through the reaction in order to remove the released CO. Complexes **5a**−**d** are stable in solid form under inert atmosphere and can be stored at −20 °C for several months.

The structure of complexes **5** was postulated on the basis of their NMR spectra. Especially relevant are their signals corresponding to the double bond, which are shielded as a consequence of the metal complexation ($\delta = 85.7$ for the CH and 86.9 for the quaternary carbon of complex **5a**). The X-ray structure[17] of complex **5a** shows clearly the interaction of the double bond with the metal in a fashion similar to that reported previously for $\eta^3$-vinyl carbenes ($\eta^3$-allylidenes).[19] As far as we know, no examples of $\eta^3$-vinyl carbenes have been reported in the literature for $d^6$ group VI metals.[20]

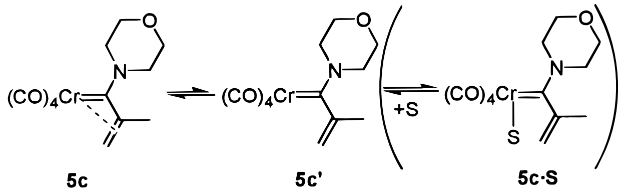
The behavior of **1e**−**g** with respect to CO dissociation is similar to that of **1a**−**d**. Irradiation of their THF solutions at −40 °C produced the corresponding tetracarbonyl complexes **5e**−**g**. However, the isolation of complexes **5e**−**g** was elusive due to product decomposition in the solid form. To ascertain the formation of complexes **5e**−**g**, a solution of **1e** in $CD_2Cl_2$ was irradiated at −40 °C under static vacuum. The NMR analysis of this sample showed signals assignable to **5e** along with those corresponding to the starting material. Thus, compounds **5e**−**g** were generated and used in subsequent reactions without isolation.

Irradiation of complexes **1h** and **1i** bearing one or two N−H bonds, respectively, did not provide the expected tetracarbonyl $\eta^3$-vinyl carbene derivatives. This behavior contrasts with that described for the *N*,*N*-dialkyl derivatives and must be ascribed to the presence of the N−H bonds, since this is the only difference in the structures of **1h** and **1i**.[21]

Complexes **5** are, in solution, in equilibrium between the chelated ($\eta^3$-vinyl carbene ligand) and nonchelated ($\eta^1$-vinyl carbene ligand) forms, probably due to the strain created by the small chelation ring. This behavior was inferred from the NMR analysis of complexes **5**. For example, complex **5c** shows no signals in the metal-complexed carbonyl region. If the temperature is raised to 50 °C, a single signal appears at 231.1 ppm. On the other hand, the spectrum at −20 °C showed three signals in the carbonyl region at 224.4, 227.1, and 237.3 (double intensity[22]) ppm. This type of behavior has been described before for chelated tetracarbonyl (acylamino)carbene[23] and trialkylsilyl aminocarbene[24] complexes, but, to the best of our knowledge, it has never been observed before for a C−C double bond chelated Fischer carbene complex. Interestingly, the signals corresponding to the rest of the carbons of the complex remain almost invariable throughout the temperature range. Especially indicative are the signals for the C−C double bond which remain within a range of 1 ppm of 82.5 (CH) and 57.4 ($CH_2$) ppm.

This observation indicates that an equilibrium between the $\eta^3$-vinyl carbene (**5**) and the $\eta^1$-vinyl carbene (**5′**) complexes occurs (Scheme 4). This $\eta^1$-vinyl carbene complex **5′** is pentacoordinated and probably fluxional.[25] A fast interchange of the four carbonyl ligands occurs before the $\eta^1$ complex reverts to the $\eta^3$ isomer. Since no signals assignable to a nonchelated carbene appear, the population of the $\eta^1$ complex **5′** must be necessarily low. This fact implies that the $\eta^3$-vinyl carbene is not only more stable than the $\eta^1$ isomer but also more stable than its solvent (THF)-complexed analogue **5·S**, which is, in principle, readily accessible from it.

**Scheme 4**



**5c** **5c'** **5c·S**

The ready availability of the unsaturated species **5′** at room temperature prompted us to investigate the participation of isolated complexes **5** in the Dötz reaction. To prove that tetracarbonyl complexes **5** are true intermediates, we tested the reaction of **5a** with a series of alkynes. The reaction gave unsatisfactory results in most cases when electron-rich or normal

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[18] The main photoprocess of Fischer carbene complexes is the decarbonylation: (a) Foley, H. C.; Strubinger, L. M.; Targos, T. S.; Geoffrey, G. L. *J. Am. Chem. Soc.* **1983**, *105*, 3064. (b) Bell, S. E. J.; Gordon, K. C.; McGarvey, J. J. *J. Am. Chem. Soc.* **1988**, *110*, 3107. (c) Knorr, J. R.; Brown, F. L. *Organometallics* **1994**, *13*, 2178.

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[20] For leading references on $\eta^3$-vinyl carbenes, see: Mitsudo, T. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1525.

[21] The decarbonylation reaction was also tried with some alkoxyvinyl carbenes, but we found them inert to either photochemical or thermal conditions. Theorethical calculations anticipated the lower stabilization gained by chelation of the vinyl group in alkoxyvinyl carbenes, as compared with the aminovinyl carbenes.[11]

[22] The fact that the two *cis* carbonyl ligand $^{13}C$ NMR chemical shifts are identical is fortuitous, since both carbon atoms have different environments due to the substituents in the double bond. For example, these carbon atoms have different chemical shifts in complex **5a** (see Experimental Section).

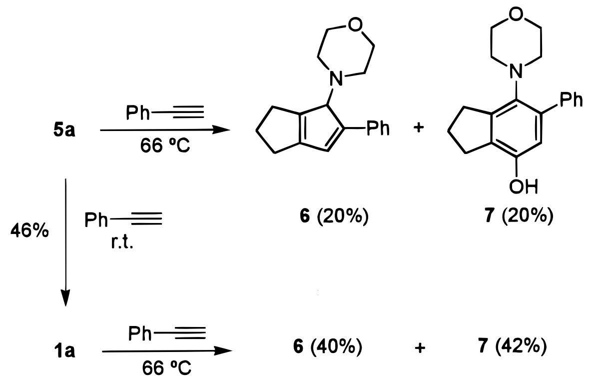
[23] Grotjahn, D. B.; Dötz, K. H. *Synlett* **1991**, 381.

[24] Hepp, W.; Schubert, U. *J. Organomet. Chem.* **1990**, *385*, 221.

[25] Hofmann, P.; Hämmerle, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 908.

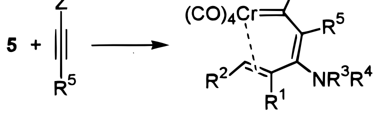
alkynes were employed. Thus, although tetracarbonyl carbene complexes **5** are stable at room temperature in a solution of THF for long periods of time, they react readily with an added acetylene such as phenylacetylene to produce the pentacarbonyl complex **1a** as the only identifiable product, in 46% yield (Scheme 5). When the reaction is carried out at THF reflux temperature with an excess of alkyne, it is possible to isolate **6** and **7** as a 1:1 mixture in a global yield of 40%. In addition, a mass balance in the crude reaction indicated that 4−5 equiv of alkyne was consumed. On the other hand, when the reaction is performed with the pentacarbonyl complex **1a** instead of the tetracarbonyl derivative **5a**, it gives rise to the same mixture of products with 80% global yield. The products isolated in the reaction of phenylacetylene with tetracarbonyl complex **5a** arise from the decomposition of this carbene to furnish the pentacarbonyl complex **1a** in ca. 50%, which further reacts with phenylacetylene to give the same products but in lower yield. A possible interpretation of these results can be as follows: from the reaction of tetracarbonyl carbene with alkyne a tetracarbonyl species **A** arises that is susceptible of releasing 1 equiv of CO in the presence of a high concentration of a CO acceptor (**5a**). From this CO interchange would result 1 equiv of the pentacarbonyl complex **1a** and 1 equiv of a tricarbonyl species capable of polymerizing the alkyne. When all the tetracarbonyl carbene **5a** has been consumed, the normal Dötz process takes place from **1a**. Tetracarbonyl complex **5a** is regenerated from **1a**, as well as the complex **A** arising from its reaction with phenylacetylene. Now the concentration of both intermediates is so low that the CO interchange process is difficult to achieve, and then the complex **A** evolves into the usual Dötz products.

**Scheme 5**



Fortunately, reaction of complexes **5** with electron-deficient alkynes was more fruitful. When carbene complex **5a** (Scheme 6, Table 3) was treated with dimethyl acetylenedicarboxylate (**8**) in $CD_2Cl_2$ at −80 °C, and the reaction mixture was allowed to warm slowly while being monitored by $^{13}C$ NMR analysis, no change in the composition of the mixture was observed until −20 °C. At this temperature the appearance of a new set of signals could be observed corresponding to complex **9a**, along with those of the pentacarbonyl carbene **1a**, which comes from the aforementioned decomposition of **5a**. The total disappearance of the starting materials lasted 22 h, and during this time, no other signals assignable to any intermediate could be observed. At this temperature, complex **9a** is stable, and no decomposition products were observed after 1 week.

**Scheme 6**



**9**

**Table 3.** Complexes **9** Prepared

| compd | $R^1$ | $R^2$ | $R^3$ | $R^4$ | $R^5$ | Z | yield (%) |
|---|---|---|---|---|---|---|---|
| **9a** | $CH_2CH_2CH_2$ | | $CH_2CH_2OCH_2CH_2$ | | $CO_2Me$ | $CO_2Me$ | 54 |
| **9b** | $OCH_2CH_2CH_2$ | | $CH_2CH_2OCH_2CH_2$ | | $CO_2Me$ | $CO_2Me$ | 95 |
| **9c** | $CH_3$ | H | $CH_2CH_2OCH_2CH_2$ | | $CO_2Me$ | $CO_2Me$ | 73 |
| **9d** | $CH_3$ | $CH_2OCH_3$ | $CH_2CH_2OCH_2CH_2$ | | $CO_2Me$ | $CO_2Me$ | 69 |
| **9e** | H | Ph | $CH_2CH_2OCH_2CH_2$ | | $CO_2Me$ | $CO_2Me$ | 55[a] |
| **9f** | H | 2-furyl | $CH_2CH_2OCH_2CH_2$ | | $CO_2Me$ | $CO_2Me$ | 50[a] |
| **9g** | H | 2-furyl | Me | Me | $CO_2Me$ | $CO_2Me$ | 35[a] |
| **9h** | H | 2-furyl | Me | H | $CO_2Me$ | $CO_2Me$ | 10[a,b] |
| **9i** | H | 2-furyl | H | H | $CO_2Me$ | $CO_2Me$ | 9[a,c] |
| **9j** | H | Ph | $CH_2CH_2OCH_2CH_2$ | | H | $CO_2Me$ | 48[a] |
| **9k** | H | Ph | $CH_2CH_2OCH_2CH_2$ | | H | $CONMe_2$ | 54[a] |
| **9l** | H | Ph | $CH_2CH_2OCH_2CH_2$ | | H | CN | 22[a] |

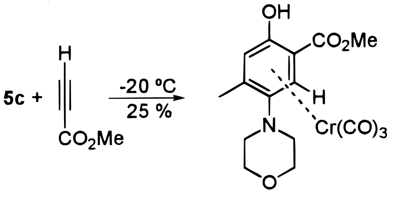
[a] Yield based on complex **1**. [b] With 55% recovery of **1h**. [c] With 80% recovery of **1i**.

The structure of the observed complex **9a** was deduced from its $^{13}C$ NMR analysis, the most significant data being the following. The carbene carbon chemical shift is 245.9 ppm; 10 ppm upfield from that of **5a**, 257.6 ppm. It is known that chemical shifts of carbene atoms correlate well with the electron-donating ability of their substituents; therefore, these high-field chemical shifts contrast with the fact that two electron-withdrawing ester groups are placed in the dienyl system of the complexes. The chemical shifts for two of the carbons belonging to the diene moiety are in the range of a noncoordinated C−C double bond (157.9 and 130.7 ppm) while the other two signals are displaced to high field (93.8 and 102.1 ppm), indicating that this double bond is coordinated to the metal. $^{13}C$-DEPT pulse sequence experiments showed that the terminal double bond is the one actually bonded to the metal. Finally, four signals assignable to the carbonyl carbons are observed at room temperature in the expected chemical shift range, indicative that chelate ring opening, if it happens, is slow in the NMR time scale. This is what could be expected, since ring strain in **9a** is significantly lower than in complexes **5**.

To test the generality of the insertion process, carbene complexes **5a**−**g** were reacted with a series of electron deficient alkynes to yield the complexes **9** (Scheme 6, Table 3) as solids after suitable workup (see Experimental Section). In these reactions, a variable amount of complexes **1** (up to 15%) is always recovered. Although in all cases the reaction was carried out at −20 °C, the procedure was dependent on the stability of the starting carbene complexes **5**. Thus, in the case of complexes **9a**−**d**, the starting materials were the corresponding previously isolated complexes **5a**−**d**. On the other hand, since complexes **5e**−**g** could not be isolated (vide supra), the reactions of these complexes were performed in *one pot* with the crude solutions after the photochemical CO dissociation of carbenes **1e**−**g**. Finally, complexes **9h**−**i** bearing at least one hydrogen at the nitrogen could be prepared by irradiation in situ of a 1:1 mixture of carbenes **1h**−**i** and DMAD under carefully controlled conditions.

The thermal stability of complexes **9** is surprisingly high, taking into account that the carbene carbon is directly attached to an electron-withdrawing group, and must be ascribed to an effective electron donation from the vinylogous amine. In fact, the rotation of the amine about the N−C bond is slow at room temperature, as can be deduced from the inequivalence of the carbons of the amine in $^{13}C$ NMR. This stability is also dependent on the substitution pattern at the metallatriene complex. Thus, complexes **9a−d**, in which $R^2$ is an alkyl group or hydrogen and $R^5$ is an ester (Scheme 6), evolve to the cyclopentannulation products overnight in solution at room temperature while complexes **9e−i** ($R^2$ = Ar, $R^5$ = $CO_2Me$) are stable for days in these conditions. On the other hand, carbenes arising from propiolic acid derivatives **9j−l** ($R^5$ = H; Scheme 6) are also less stable than their DMAD analogue **9e**, and, among them, the stability decreases as the electron-withdrawing capability of the group directly attached to carbene carbon increases. Finally, the unstability of the carbenes **9** reaches its maximum degree when both $R^5$ and $R^2$ are hydrogen. Thus, the reaction of the alkyl-substituted carbene **5c** with methyl propiolate **10** led to a carbene complex that evolves to the $Cr(CO)_3$ complexed phenol **11** (Scheme 7) at the reaction temperature (−20 °C).

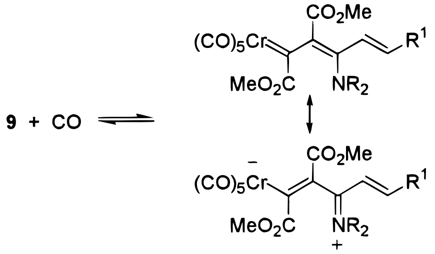
**Scheme 7**



**10** **11**

All attempts to obtain X-ray quality crystal from carbenes **9** were unsuccessful. Therefore, to gain some insight into the structure of these compounds, we prepared the pentacarbonyl derivatives **12** (Scheme 8, Table 4) by reaction of some carbenes **9** with CO. The structure of complexes **12** was postulated on the base of its $^1H$ and $^{13}C$ NMR analysis. The most significant spectroscopic finding for **12g** is the following. The carbene carbon resonance chemical shift, 224.1 ppm, for **12g** is 20 ppm upfield compared with that of its tetracarbonyl analogue **9g**, and the chemical shift for the C5−C6 double bond signals (148.4 and 122.8) is now indicative of an uncoordinated double bond. The pentacarbonyl moiety is reflected by the two signals in the metal−carbonyl region.

**Scheme 8**



**12**

**Table 4.** Complexes **12** Prepared

| carbene | $R^1$ | $NR_2$ | yield (%) |
|---|---|---|---|
| **12e** | Ph | $N(CH_2CH_2)_2O$ | 90 |
| **12f** | Fu | $N(CH_2CH_2)_2O$ | 85 |
| **12g** | Fu | $NMe_2$ | 95 |

The X-ray structure of **12g** (Figure 1, Tables 5−7) reveals some details about the nature of the bond between the chromium and the carbene atom. The complex can be best described as a zwitterion in which the nitrogen-containing conjugated system is positively charged, since the unit Cr−C1−C2−C14 is on a plane almost perpendicular to that formed by N−C3−C4−C5 (dihedral angle C1−C2−C3−N = 99.2°).[26]

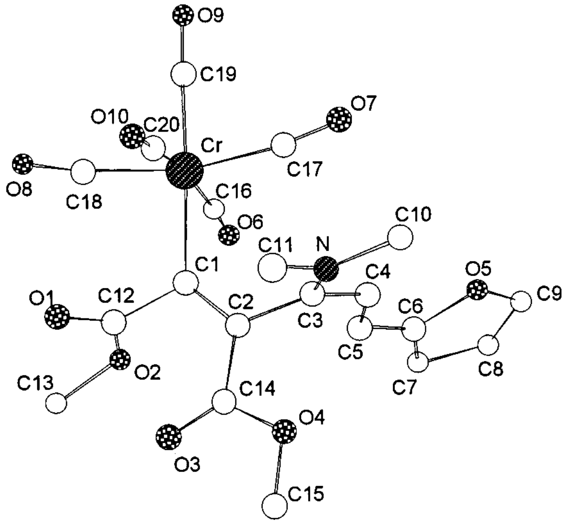


**Figure 1.** Molecular structure of **12g** (hydrogen atoms have been omitted for clarity).

**Table 5.** Selected Bond Distances (Å) for **12g**

| | | | | | |
|---|---|---|---|---|---|
| Cr−C1 | 2.140(3) | C1−C2 | 1.354(5) | C12−O1 | 1.204(5) |
| Cr−C16 | 1.884(5) | C2−C3 | 1.493(5) | C14−O3 | 1.199(4) |
| Cr−C17 | 1.884(4) | C3−C4 | 1.432(5) | C16−O6 | 1.144(6) |
| Cr−C18 | 1.891(4) | C4−C5 | 1.336(5) | C17−O7 | 1.146(5) |
| Cr−C19 | 1.851(5) | C1−C12 | 1.485(4) | C18−O8 | 1.142(5) |
| Cr−C20 | 1.887(5) | C2−C14 | 1.481(4) | C19−O9 | 1.148(5) |
| | | C3−N | 1.304(5) | C20−O10 | 1.137(6) |

**Table 6.** Selected Dihedral Angles (deg) for **12g**

| | | | |
|---|---|---|---|
| Cr−C1−C2−C3 | −5.6.1(5) | Cr−C1−C12−O1 | −79.2(4) |
| C1−C2−C3−C4 | −81.7(4) | C1−C2−C14−O3 | −1.0(6) |
| C2−C3−C4−C5 | −6.5(5) | C1−C2−C3−N | 99.2(4) |
| N−C3−C4−C5 | 173.3(4) | C14−C2−C3−N | −83.1(4) |

**Table 7.** Crystal Data and Structure Refinement for **12g**

| | |
|---|---|
| empirical formula | $C_{20}H_{17}NO_{10}Cr$ |
| formula weight | 483.35 |
| temperature | 293(2) K |
| wavelength | 0.710 73 Å |
| crystal system, space group | triclinic, $P\bar{1}$ |
| unit cell dimensions | $a = 9.1582(18)$ Å; $\alpha = 103.80(2)°$<br>$b = 10.905(2)$ Å; $\beta = 100.23(2)°$<br>$c = 14.564(5)$ Å; $\gamma = 105.08\ (1)°$ |
| volume | 1318.6(6) $Å^3$ |
| *Z*, calculated density | 2, 1.217 $Mg/m^3$ |
| absorption coefficient | 0.590 $mm^{-1}$ |
| *F*(000) | 568 |
| crystal size | 0.26 × 0.20 × 0.17 mm |
| $\theta$ range for data collection | 1.49−24.98° |
| index ranges | $0 \le h \le 10$, $-12 \le k \le 12$,<br>$-17 \le l \le 17$ |
| reflections collected/unique | 4940/4622 [*R*(int) = 0.0185] |
| completeness to $2\theta$ = 24.98° | 100.0% |
| refinement method | full-matrix least-squares on $F^2$ |
| data/restraints/parameters | 4622/0/331 |
| goodness-of-fit on $F^2$ | 1.288 |
| final *R* indices [$I > 2\sigma(I)$] | $R1 = 0.0429$, $wR2 = 0.1102$ |
| *R* indices (all data) | $R1 = 0.0998$, $wR2 = 0.1227$ |
| largest diff. peak and hole | 0.530 and −0.522 e $Å^{-3}$ |

This alkyne insertion reaction has opened an easy route for the preparation of different tetra- and pentacarbonyl carbene complexes with an electron acceptor group directly attached to the carbene atom. There are few reports concerning group VI metal carbenes with this structural characteristic. In fact, to the

**Scheme 9**

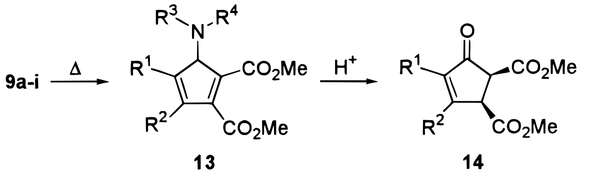


**Table 8.** Cyclopentadienes **13** Prepared

| compd | $R^1$ | $R^2$ | $R^3$ | $R^4$ | yield (%) |
|---|---|---|---|---|---|
| **13a** | $CH_2CH_2CH_2$ | | $CH_2CH_2OCH_2CH_2$ | | 74 |
| **13b** | $OCH_2CH_2CH_2$ | | $CH_2CH_2OCH_2CH_2$ | | 62 |
| **13c** | $CH_3$ | H | $CH_2CH_2OCH_2CH_2$ | | 68 |
| **13d** | $CH_3$ | $CH_2OCH_3$ | $CH_2CH_2OCH_2CH_2$ | | 65[a] |
| **13e** | H | Ph | $CH_2CH_2OCH_2CH_2$ | | 52[b] |
| **13h** | H | 2-furyl | $CH_3$ | H | 44 |
| **13i** | H | 2-furyl | H | H | 35 |

[a] As a 60:40 mixture of regioisomers. [b] As a 71:29 mixture of regioisomers.

**Scheme 10**

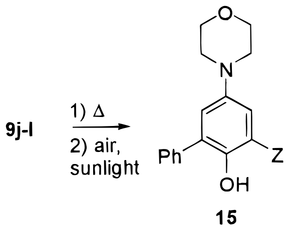


**Table 9.** Phenols **15** Prepared

| carbene | phenol | Z | yield (%) |
|---|---|---|---|
| **9j** | **15j** | $CO_2Me$ | 92 |
| **9k** | **15k** | $CONMe_2$ | 45 |
| **9l** | **15l** | CN | 20 |

extent of our knowledge, only two other approaches to this family of carbenes have been reported.[27,28] These syntheses have the limitation that, along with the electron attractor group, only an amino group directly attached to the carbene atom can be introduced in the structure of the complex. The reactions reported herein allow the introduction, along with the acceptor group, of a dienyl system with very different possible substituents in α, $\gamma$, and $\delta$ positions and several amines in position $\beta$. Furthermore, various acid derivatives can be introduced as electron attractor moieties, thus expanding the range of functional groups that have been attached to a carbene complex. Even more, as far as we know, this is the first synthesis of a stable chelated dienyl carbene complex of chromium.

The structure of complexes **9** differs from that of complexes usually postulated as intermediates in Dötz reaction. In fact, complexes **9** are isomers of **IV** (Scheme 1) in which the metal has migrated from the internal to the terminal double bond in order to be stabilized.[29,30] To establish whether carbenes **9** are, in fact, intermediates of Dötz reaction, we decided to study the thermal behavior of a representative selection of them.

We started with complexes **9** prepared from DMAD insertion, which undergo the cyclopentannulation process to afford carbocycles **13** (Scheme 9, Table 8). Decomposition of carbenes **9a**−**d** takes place at 25 °C while reaction of **9e**, **9h**, and **9i** is more sluggish and it is necessary to warm their THF solutions to 60 °C to bring the reaction to completion in reasonable time. Compounds **13** were obtained in some cases as an inseparable mixture of isomers in which the double bonds are shifted through the ring. To ascertain the identity of the cyclopentadienes, **13c** and **13e** were hydrolyzed to afford cyclopentenones **14c** and **14e** as single stereoisomers. The stereochemistry of **14** was postulated by NOE experiments performed on the diethyl derivative **14e′**, since the signal for one of the hydrogens of the cycle in **14e** is obscured by those of the ester methoxy groups.

The reactions of Fischer aminovinyl carbene complexes and alkynes have been reported to produce phenol derivatives as the major product under thermal conditions,[14] and, to the best of our knowledge, there is only one example of cyclopentannulation reaction of Fischer aminovinyl carbenes and alkynes.[14a] Although quite a large number of pentacarbonyl dienyl carbene complexes are known to give rise to cyclopentadienes,[31] as far as we know, no example has been reported previously with chelated tetracarbonyl analogous.

A similar treatment was carried out with complexes arising from propiolic acid derivatives, and surprisingly a completely different behavior was found. As is shown in Scheme 10, complexes **9j**−**l** undergo CO insertion prior to cyclization to give phenols **15** in a completely selective fashion, without detectable traces of corresponding cyclopentadiene (Table 9).[32] A possible explanation for the selectivity of this reaction will be given in the Discussion.

These results show that metallatrienes **9j**−**l** can be considered as real intermediates in the Dötz benzannulation process. Although a few examples of complexes similar to the intermediate **IV** (Scheme 1) have been described,[19,33] as far as we know there is no previous report of the thermal conversion of a well-characterized $\eta^3$-dienyl carbene or $\eta^3$-vinyl carbene into a phenol.[34] This conversion has been proposed to occur via a complexed dienylketene **VI** (Scheme 1)[1a] or a metallacycloheptadienone,[5] or directly.[13b,c] To discriminate among these options, we monitorized the decomposition of **9j** by NMR. The reaction took place smoothly in 9 h at room temperature, but no intermediate was observed. The only observable products were the starting carbene **9j**, the phenol **15j**, and its $(CO)_3Cr$ complex. We cannot conclude anything from this result, except that if the reaction proceeds via any intermediate, it is transformed faster than produced.

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(26) The nature of the bonding between the metal and the carbene carbon can be seen as intermediate between that of a typical carbene and that of a $Csp^2$-bonded alkyl pentacarbonyl chromate. As a consequence, Cr−carbene and Cr−CO bond distances for **12g**, and the Cr−*C* $^{13}C$ NMR chemical shift (224 ppm), are intermediate between those of standard Fischer aminovinyl carbene complexes and those reported for $\beta$-phosphoniumalkyl- and α-imoniumalkylpentacarbonylchromates. (a) Aumann, R.; Jasper, B.; Läge, M.; Krebs, B. *Chem. Ber*. **1994**, *127*, 2475. (b) Barluenga, J.; Tomás, M.; Rubio, E.; López-Pelegrín, J. A.; García-Granda, S.; Pertierra, P. *J. Am. Chem. Soc*. **1996**, *118*, 695.

(27) Dvorák, D.; Ludwig, M. *Organometallics* **1998**, *17*, 3627.

(28) (a) Aumann, R.; Fischer, E. O. *Angew. Chem., Int. Ed. Engl*. **1967**, *6*, 879. (b) Aumann, R.; Fischer, E. O. *Chem. Ber*. **1968**, *101*, 954.

(29) This stabilization has been previously postulated: Harvey, D. F.; Grenzer, E. M.; Gantzel, P. K. *J. Am. Chem. Soc*. **1994**, *116*, 6719.

(30) We are aware that, although the most stable form of tetracarbonyl dienylcarbene complexes is **9** and not **IV**, it is this one which should be formed initially from insertion of acetylene, and, if an equilibrium between both isomers occurs, complexes **IV** might be also the reactive species.

(31) Aumann, R.; Nienaber, H. *Adv. Organomet. Chem*. **1997**, *41*, 163.

(32) $(CO)_3Cr$ adducts of the hydroxyl free phenol can be obtained with the suitable workup of the reaction, by oxygen-free chromatography or crystallization from the reaction crude material. Nevertheless, better yields are obtained by oxidative cleavage of the chromium−arene bond in mild conditions (air and sunlight) followed by silica gel chromatography to yield the metal-free phenol.

(33) (a) Mitsudo, T.; Fujita, K.; Nagano, S.; Suzuki, T.; Watanabe, Y.; Masuda, H. *Organometallics* **1995**, *14*, 4228. (b) Park, J.; Kim, J. *Organometallics* **1995**, *14*, 4341.

(34) The thermal cyclization of an $\eta^1$-dienylcarbene to a phenol has been observed: Barluenga, J.; Aznar, F.; Palomero, M. A.; Barluenga, S. *Org. Lett*. **1999**, *1*, 541.

**Scheme 11**

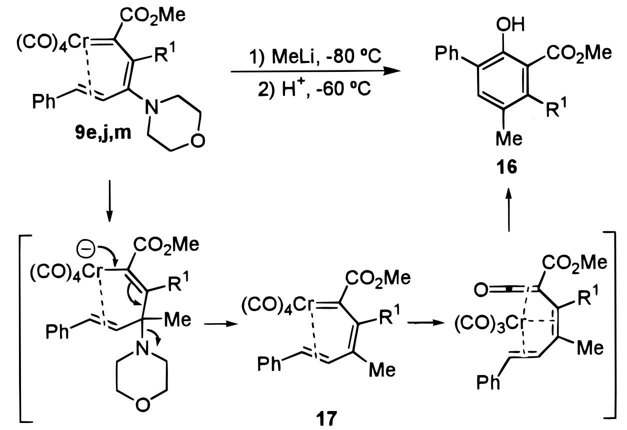

**Table 10.** Phenols **16** Prepared

| carbene | R$^1$ | phenol | yield (%) |
|---|---|---|---|
| **9e** | $CO_2Me$ | **16e** | 71 |
| **9j** | H | **16j** | 32 |

On the other hand, it is well known that acceptor-substituted carbene complexes of late transition metals have been proposed for a long time as very unstable intermediates in the reaction of organic ylides with electrophilic coordinatively unsaturated late transition metals.[35] Therefore, as we have mentioned before, it is reasonable to think that the high stability of complexes **9** has to be ascribed to the electron donor effect of the amine. We envisioned that it could be interesting to try to modify the nature of the metallatriene complex by exchanging the amine group for another without electron-donating ability, such as an alkyl group. Thus, complexes **9e** and **9j** were treated with methyllithium at −80 °C to give phenols **16** (Scheme 11, Table 10) almost instantaneously. This result can be rationalized by an initial attack of the methyllithium at the $\beta$ position, followed by amine extrusion, which furnishes the nonstabilized carbene **17**. This carbene lacks the stabilization of the amine and undergoes cyclization quickly at low temperature to afford the phenol **16** in a fashion similar to the last steps of Dötz reaction (see Discussion). As a whole, this reaction can be seen as the equivalent of a Dötz reaction with a nonstabilized vinyl carbene complex.

## Discussion

It is generally accepted that the first and rate-determining step of Dötz reactions is the thermal decarbonylation of the starting pentacarbonyl carbene **I** to yield the tetracarbonyl carbene complex **II**, which is coordinatively unsaturated (Scheme 12). This intermediate can be stabilized by intramolecular coordination of the double bond,[36] leading to a $\eta^3$-allylidene complex **II′**. From the NMR data of isolated carbenes of the type **II′** (complexes **5a**−**e**) it is reasonable to conclude that there is an equilibrium between species **II** and **II′** in solution, which is fast but more attracted to the more stable chelate form, although it has never been observed.[37] This mode of stabilization can be achieved with reasonable ease by alkenyl carbene complexes, but not by aryl ones, since it implies an $\eta^2$-coordination. It is at this early stage where the pathways of reactions of alkenyl and aryl complexes first differ.

The next step would consist of the coordination of the acetylene to yield complex **III**, followed by insertion in the metal−carbene bond giving rise to a new $\eta^3$-allylidene complex **IV**, in which the newly formed double bond can be *Z* or *E*, depending on the stereochemistry of the process. Theoretical calculations concerning this step conclude that this insertion is an exothermic process with a very low energetic barrier, if any at all. Wulff and colleagues have proposed recently that it is at this stage where the partitioning between cyclopentadienes **VIII** and phenols **IX**, on one side, and furans and bicyclic lactones, on the other side, occurs.[2a] They stated that the product distribution is determined by the equilibrium between both isomers of $\eta^3$-allylidene, which can interchange in the reaction conditions. In the work described herein, only products arising from the *E* isomer of complexes **IV** have been observed, but, since the insertion process takes place at low temperature, we cannot conclude whether this is the kinetic product or the only one possible from the starting materials.

Species of type **IV-*E*** arising from alkenyl carbene complexes can be stabilized by isomerization to the 1,4,5-$\eta^3$-pentadienylidene form **XI**. This stabilization occurs by releasing the strain of the small chelation ring and also by liberating the internal double bond that allows the conjugation of the lone pairs of the heteroatom with the carbene moiety.[38] It is important to notice that this kind of complexation might not be favorable in intermediates arising from aryl carbenes, as an $\eta^2$-coordination of the aryl moiety should be necessary.

Assuming that the energetic barrier between **III** and **IV** is almost null,[12] the one between **IV** and **XI** must be at least lower than the barrier of alkyne coordination to the metal, since experiments monitored by NMR spectroscopy did not show accumulation of **IV** in the reaction mixture. Only a smooth conversion of the signals of complex **5a** in the signals of complex **9a** could be observed upon addition of DMAD at low temperature.

Although an X-ray structure of none of the complexes **9** could not be obtained, we propose the structure **XI** depicted in Scheme 12 according to the MNR data. In this structure there is a very important donation from the nitrogen lone pairs to the chromium atom.[39] The terminal double bond must adopt a planar disposition toward the chromium atom in order to chelate the metal efficiently. This disposition cannot be achieved without a significant twisting of the metallatriene unit, which is no longer conjugated. This folding occurs around the C3−C4 single bond between the terminal double bond and the rest of the $\pi$ system, which would be on a plane. This disposition is essentially the same as that which has been obtained by DFT calculations on a similar system.[13c]

A slightly different structure can be proposed for those carbenes **XI**, where R$^1$ is an ester group. In this case, the negative charge supported by the metal in the zwitterionic form can be stabilized by retrodonation to the ester group, and conjugation between the chromium and the imonium moiety is no longer necessary. Now, a conjugation is possible between the imonium and the terminal double bond maintaining the chelation stabilization. This can happen assuming a rotation around the bond between C2 and C3 instead of that between C3 and C4. This structure is depicted in Scheme 12 as **XI′**. The strength of the coordination of the double bond to the metal is now increased since (a) the structural arrangement is geometrically more accurate and (b) the double bond is more

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(35) Dörwald, F. Z. *Metal Carbenes in Organic Synthesis*; Wiley-VCH: Weinheim, 1999.

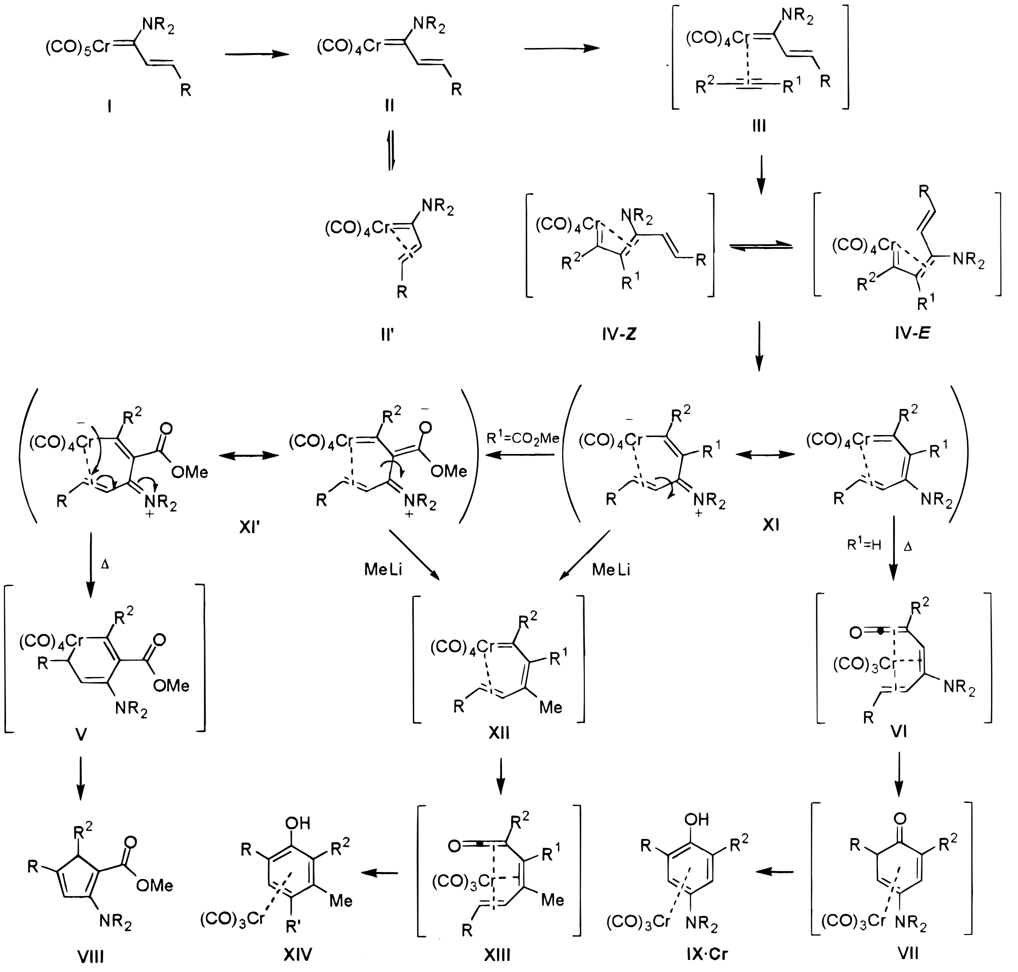
(36) Theoretical calculations show that this coordination is stabilizing.[11]

(37) This kind of equilibrium might occur not only with aminoalkenyl carbenes but also with alkoxyalkenyl carbenes.[11]

(38) This stabilization has been calculated to be 23 kcal/mol for tetracarbonyl(3-hydroxypenta-2,4-dienylidene)chromium(0).[13c]

(39) This effect would explain the unexpected value for the $^{13}C$ chemical shift of the carbene carbon in these species (e.g., 246 ppm for **9a**).

**Scheme 12**



electron deficient, thus leading to a greater contribution of d-$\pi^*$ back-bonding. This structure has been proposed since it is essentially the same as that which has been observed in the X-ray structure of the related pentacarbonyl complex **12g**, except for the complexation of the terminal double bond. In this structure, we reproduce the zwitterionic character, the conjugation of the chromium with the ester instead of the imonium moiety, and the conjugation of this imonium with the double bond. From the greater thermal stability of the complexes bearing an ester in position 2, as compared to those that lack it (**9e** compared with **9j**) we can conclude that the overall effect is stabilizing.

By assuming these different structures for **XI** and **XI′**, the different outcome of the thermal progress of both structures can be rationalized as follows: in the latter (**XI′**), an intramolecular nucleophilic attack from the negatively charged chromium on the vinyl imonium moiety could be more advantageous.[40,41] This attack yields the metallacyclohexadiene **V** which would undergo reductive elimination to furnish the five-membered ring product **VIII** exclusively. On the other hand, the conformer **XI** is less likely to suffer this kind of attack, since the double bond is not conjugated with the imonium cation. Thermal evolution of these intermediates would involve a CO insertion process giving rise to phenol **IX**, which is the main product of the Dötz reaction of alkenyl amino carbenes.

It is worth noting that the allochemical effect proposed by Wulff and colleagues as necessary for the CO insertion to take place in aryl carbene complexes reactions[2e] cannot be claimed in this case since the cyclization step is carried out starting from isolated carbenes **XI**, in the absence of additional alkyne. It is known that the reactions of alkenyl carbene complexes are little or not affected by changes in the concentration of alkyne.[2d] This lack of influence can be explained by a mechanism in which CO insertion is concomitant with the complexation of the Cr(CO)$_3$ moiety to all three double bonds of the dienylketene **VI** just formed. The chromium maintains an 18-electron configuration throughout all the CO insertion process.[42] The evolution of this dienylketene through the usually proposed electrocyclic closure leads to Cr(CO)$_3$-complexed cyclohexadienone **VII** and then to the complexed phenol **IX**.

Finally, the electronic nature of the differentiation between pathways leading to five- and six-membered ring products can be supported by the reaction of complexes **XI** (and **XI′**) with carbon nucleophiles. This reaction gives phenols in which the amine group has been substituted for the nucleophile. In the proposed mechanism for this reaction, we assume that this substitution takes place as the first step, by nucleophilic attack on the imonium cation of **XI**, followed by amine extrusion, leading to formation of metallatriene **XII**. This complex is very similar to **XI** except for the fact that no stabilization can be achieved by electron donation toward the metal. Charge separation is not produced, and a nucleophilic attack of the

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[40] A similar attack has been proposed for the [4 + 1] reaction of chromium phenylmethoxycarbene with 2-methyl-1,3-dimorpholino-1,3-butadiene. Barluenga, J.; Aznar, F.; Fernández, M. *Chem. Eur. J.* **1997**, *3*, 1629.

[41] The formation of **VIII** from **XI′** could also take place through a Nazarov-type reaction. Yamashita, A. *Tetrahedron Lett.* **1986**, *27*, 5915.

[42] An alternative mechanism that accounts for the direct formation of **VII** from **XI** without the intervention of an additional molecule of alkyne in reactions of alkenyl carbenes has been proposed.[13c]

chromium to the complexed double bond is not favorable. The most favorable reaction pathway would be the insertion of CO that leads, following a mechanism analogous to the one explained above, to the final product, the phenol **XIV**, as a $(CO)_3Cr$ complex. This reaction is very fast even at low temperature, suggesting that the CO insertion process has a low energetic barrier as well.

## Conclusions

We report herein a comprehensive study of the thermal and photochemical decarbonylation of alkenyl amino carbene complexes. This reaction is quite general and furnishes a new type of carbenes **5** that are valuable as low-temperature generators of 16-electron tetracarbonyl chromium carbene complexes. The synthesis and isolation of these complexes have allowed us to carry out the reaction with alkynes at low temperature and to isolate and characterize the carbene complexes **9**. Since some of these carbene complexes lead to phenols upon warming, both complexes **5** and **9** can be considered as Dötz benzannulation reaction intermediates. The overall process can be seen as a Dötz reaction carried out in three separate steps at low temperature. As far as we know, this is the first example of such a stepwise Dötz reaction. On the other hand, the insertion of alkynes into complexes **5** can be considered as a general method for the synthesis of electron-withdrawing substituted carbene complexes, either as $\eta^1$-pentacarbonyl or as $\eta^3$-tetracarbonyl. As far as we know, this is the first synthesis of such a chelated dienyl carbene complex. The reaction of complexes **5** with DMAD is also the first general reaction of cyclopentannulation of alkenylcarbene complexes with alkynes.

Finally, we have carried out a three-component Dötz reaction in which we have substituted the carbene donor group for a carbonated nucleophile.

## Experimental Section

All reactions were carried out under nitrogen atmosphere. Tetrahydrofuran (THF), toluene, and ether were dried by distillation from sodium/benzophenone. Melting points are uncorrected. Chromatographic purifications were performed on silica gel (230−400 mesh) by flash technique. Analytical TLC plates (covered with silica gel 60 $F_{254}$) were viewed by UV light or developed by heating after treatment with an acidic solution of Ce(IV) and Mo(VI). $^1H$ and $^{13}C$ NMR spectra were recorded on a Bruker AC-200 or AC-300 spectrometer. Chemical shifts refer to TMS in $^1H$ experiments and to deuterated solvent in $^{13}C$ experiments. IR analyses were performed on a Mattson 3000 FTIR spectrometer. HRMS spectra were recorded on a Finnigan-Mat 95. Elemental analyses were obtained on a Perkin-Elmer 240-B analyzer.

Photochemical reactions were carried out in Schlenk tubes (Pyrex) equipped with external jackets for continuos coolant flow (2-propanol) and placed 2 cm away from a 400-W medium-pressure mercury lamp. The solutions were deoxygenated by nitrogen bubbling for 15 min prior to irradiation. In the cases in which a loss of CO is expected, bubbling was maintained during irradiation. The reactions were monitored by TLC or IR techniques until disappearance of the starting materials.

**General Procedure for the Preparation of $\eta^3$-Aminovinyl Carbene Complexes 5.** A 0.05 M solution of aminovinyl carbene complex **1** in degassed THF was irradiated at temperatures between −45 and −35 °C. The reaction was monitored by IR analyses until disappearance of the absorption signals corresponding to the starting complex. For complexes **5a**−**d**, the solution was then filtered through a pad of Celite, and the solvents were evaporated under vacuum. The residue was crystallized in deoxygenated hexane−dichloromethane. Complexes **5e**−**g** were not isolated but were used in situ in the next reaction.

**Tetracarbonyl[$\eta^3$-(1-cyclopentenyl)morpholinomethylene]chromium(0) (5a).** A 0.71 g (2 mmol) amount of **1a** was irradiated for 4 h to yield, after crystallization, 0.62 g (1.86 mmol, 94%) of **5a**. Mp: 137−139 °C (red prisms). $R_f = 0.19$ (hexane:ethyl acetate 3:1). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta = 4.67$ (t, 1H, $J = 3.3$ Hz, ${=}CH$), 4.01−3.63 (m, 8H, $N(CH_2CH_2)_2O$), 2.67−2.51 (m, 1H), 2.35−2.20 (m, 2H), 1.96 (dd, 1H, $J = 7.8$, 14.0 Hz), 1.88−1.71 (m, 1H), 1.64−1.35 (m, 1H). $^{13}C$ NMR (75.5 MHz, −40 °C, $CD_2Cl_2$): $\delta = 257.6$ ($C{=}Cr$), 235.8 (CO), 234.9 (CO), 224.2 (CO), 222.0 (CO), 86.6 (${=}C$), 85.0 (${=}CH$), 67.5 ($NCH_2CH_2O$), 67.1 ($NCH_2CH_2O$), 58.5 ($NCH_2CH_2O$), 57.0 ($NCH_2CH_2O$), 35.4 (${=}CCH_2$), 31.1 ($CH_2CH_2CH_2$), 20.5 ($CH_2CH_2CH_2$). Anal. Calcd for $C_{14}H_{15}NO_5Cr$: C, 54.36; H, 4.85; N, 4.53. Found: C, 54.58; H, 4.64; N, 4.25.

**Tetracarbonyl($\eta^3$-1-morpholino-3-phenyl-2-propenylidene)chromium(0) (5e).** A solution of 20 mg of **1e** in 1 mL of $CD_2Cl_2$ was irradiated in a NMR tube under static vacuum for 6 h. Each hour, the sample was degassed (two freeze−pump−thaw cycles) in order to remove the released CO. $^1H$ and $^{13}C$ NMR analyses showed a 40:60 mixture of **1e** and another compound that was identified as **5e**. $^1H$ NMR (300 MHz, $CD_2Cl_2$): $\delta = 7.50-7.20$ (m, 5H, Ph), 5.01 (d, 1H, $J = 12$ Hz, ${=}CH$), 4.93 (d, 1H, $J = 12$ Hz, ${=}CH$), 4.00−3.60 (m, 8H, $N(CH_2CH_2)_2O$). $^{13}C$ NMR (75.5 MHz, $CD_2Cl_2$): $\delta = 257.8$ ($C{=}Cr$), 229.6 (broad, 4×CO), 138.3 (*C ipso*), 129.3 (2×CH, Ph), 127.9 (CH, *p*-Ph), 127.6 (2×CH, Ph), 75.0 (${=}CH$), 68.1 ($NCH_2CH_2O$), 67.8 ($NCH_2CH_2O$), 64.9 (${=}CH$), 61.2 ($NCH_2CH_2O$), 57.8 ($NCH_2CH_2O$).

**Reaction of Carbene Complex 1a with Phenylacetylene.** A solution of 0.18 g (0.5 mmol) of **1a** and 0.10 g (1 mmol) of phenylacetylene in 10 mL of THF was refluxed for 1 h. The solvents were removed under reduced pressure, and the residue was chromatographed using hexane:ethyl acetate 1:1 as eluent. Two products were obtained: 0.08 g (0.20 mmol, 40%) of tricarbonyl ($\eta^5$-1,4,5,6-tetrahydro-1-morpholino-3-phenylpentalene)chromium(0) (**6**) and 0.09 g (0.21 mmol, 42%) of tricarbonyl ($\eta^6$-2,3-dihydro-4-hydroxy-7-morpholino-5-phenylindene)chromium(0) (**7**). Spectral data for **6**. $R_f = 0.33$ (hexane:ethyl acetate 3:1). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta = 7.50-6.91$ (m, 5H, Ph), 5.69−5.40 (m, 2H), 3.80−3.55 (m, 4H, $N(CH_2CH_2)_2O$), 3.00−1.40 (m, 10H, $N(CH_2CH_2)_2O$, $CH_2-CH_2-CH_2$). $^{13}C$ NMR (75.5 MHz, $CDCl_3$): $\delta = 238.9$ (3×CO), 133.6 (C, aryl), 128.3 (2×CH, Ph), 127.5 (CH, *p*-Ph), 126.7 (2×CH, Ph), 106.1 (${=}C$), 102.5 (${=}C$), 100.3 (${=}CH$), 87.7 (${=}C$), 84.0 (CH), 66.1 ($N(CH_2CH_2)_2O$), 50.1 ($N(CH_2CH_2)_2O$), 25.6 ($CH_2$), 24.2 ($CH_2$), 22.2 ($CH_2$). Anal. Calcd for $C_{21}H_{21}NO_4Cr$: C, 62.53; H, 5.25; N, 3.47. Found: C, 62.81; H, 5.52; N, 3.67. Spectral data for **7**: $R_f = 0.14$ (hexane:ethyl acetate 3:1). $^1H$ NMR (300 MHz, THF-$d_8$): $\delta = 7.55-7.05$ (m, 5H, Ph), 5.37 (s, 1H, aryl), 3.70−3.30 (m, 4H, $N(CH_2CH_2)_2O$), 3.00−2.50 (m, 4H, $N(CH_2CH_2)_2O$), 2.20−1.80 (m, 2H, $CH_2-CH_2-CH_2$), 1.75−1.45 (m, 4H, $CH_2-CH_2-CH_2$). $^{13}C$ NMR (75.5 MHz, THF-$d_8$): $\delta = 237.2$ (3×CO), 137.5 (C, aryl), 131.6 (2×CH, Ph), 130.3 (CH, *p*-Ph), 130.2 (2×CH, Ph), 123.7 (C, aryl), 120.3 (C, aryl), 115.7 (C, aryl), 104.9 (C, aryl), 100.9 (C, aryl), 90.0 (CH, aryl), 68.9 ($N(CH_2CH_2)_2O$), 54.2 ($N(CH_2CH_2)_2O$), 33.2 ($CH_2$), 31.8 ($CH_2$), 27.7 ($CH_2$). Anal. Calcd for $C_{22}H_{21}NO_5Cr$: C, 61.25; H, 4.91; N, 3.25. Found: C, 61.47; H, 5.21; N, 3.48.

**Reaction of Carbene Complex 5a with Phenylacetylene.** A solution of 0.17 g (0.5 mmol) of **5a** in 20 mL of $CH_2Cl_2$ was treated with 0.10 g (1 mmol) of phenylacetylene at room temperature. The reaction was monitored by TLC. When the starting material was consumed (6 h) the solvents were removed under reduced pressure, and the residue was chromatographed to yield 0.08 g (0.23 mmol, 46%) of **1a** as the only identifiable product. When this reaction was carried out in refluxing THF temperature, the disappearance of the carbene took 1 h, and the products isolated after column chromatography were **6** (0.04 g, 0.1 mmol, 20%) and **7** (0.04 g, 0.1 mmol, 20%).

**General Procedure for the Preparation of 1,4,5-$\eta^3$-Methoxycarbonyldienylcarbene Complexes 9.** A 0.1 M solution of carbenes **5a**−**d** in $CH_2Cl_2$ was treated with 1 equiv of DMAD at −20 °C for 24 h, and then a 2-fold volume of hexane was added. The reaction was cooled to −40 °C, and a dark brownish solid precipitated after 1 day. The solution was decanted under $N_2$ at −20 °C and the resultant solid washed with hexane to give **9a**−**d.** These solids are thermally unstable, and satisfactory elemental analyses could not been obtained in one case. Complexes **9e**−**g** and **9j**−**l** were prepared by irradiation of a 0.05 M solution of aminovinyl carbene complex **1e**−**g** in degassed THF at temperatures between −45 and −35 °C. The reaction was monitored by IR analyses until disappearance of the absorption signals corresponding to the starting complex. DMAD (1 equiv) was added at −40 °C, and the reaction was warmed and allowed to react overnight. Complexes **9h**−**i** were prepared by irradiation of solutions of **1h**−**i** in the presence of DMAD in THF. In both cases, the solutions were evaporated under vacuum, and the residue was chromatographed using hexane:ethyl acetate 1:1 as eluent.

**Tetracarbonyl[1,4,5-$\eta^3$-(1-cyclopentenyl)-1,2-dimethoxycarbonyl-3-morpholinopropenylidene]chromium(0) (9a).** **5a** (0.33 g, 1.0 mmol) was reacted with 0.14 g (1.0 mmol) of DMAD in 10 mL of $CH_2Cl_2$ to afford 0.25 g (0.54 mmol, 54%) of **9a** as a brown powder. $R_f = 0.11$ (hexane:ethyl acetate 1:1). $^1$H NMR (300 MHz, $CD_2Cl_2$): $\delta = 4.81$ (s, 1H, C═C*H*), 3.90 (s, 3H, $CO_2CH_3$), 3.72−4.20 (m, 8H, $N(CH_2CH_2)_2O$), 3.66 (s, 3H, $CO_2CH_3$), 2.36−2.92 (m, 4H, $CH_2CH_2CH_2$), 1.61−1.94 (m, 2H, $CH_2CH_2CH_2$), $^{13}$C NMR (50.3 MHz, $CDCl_3$): $\delta = 245.9$ (*C*═Cr), 231.1 (*C*O), 230.0 (*C*O), 220.9 (*C*O), 220.2 (*C*O), 178.1 ($CO_2$-$CH_3$), 167.5 ($CO_2CH_3$), 157.9 (═*C*), 130.7 (═*C*), 102.1 (═*C*), 93.8 (═*C*H),), 67.1 ($NCH_2CH_2O$), 66.8 ($NCH_2CH_2O$), 54.2 ($NCH_2CH_2O$), 53.8 ($NCH_2CH_2O$), 52.3 ($CO_2CH_3$), 51.4 ($CO_2CH_3$), 36.7 ($CH_2C$═), 34.0 ($CH_2C$═), 20.7 ($CH_2CH_2CH_2$). Anal. Calcd for $C_{20}H_{21}NO_9Cr$: C, 50.96; H, 4.49; N, 2.97. Found: C, 50.80; H, 4.37; N, 2.63.

**Tetracarbonyl(1,4,5-$\eta^3$-1,2-dimethoxycarbonyl-3-morpholino-5-phenyl-2,4-pentadien-1-ylidene)chromium(0) (9e).** **1e** (1.00 g, 2.5 mmol) was irradiated in 150 mL of degassed THF at −40 °C until IR analysis showed no absorption signals of the starting carbene. Then, 0.36 g (2.5 mmol) of DMAD was added, and the reaction mixture was allowed to react overnight to afford, after chromatography, 0.75 g (1.4 mmol, 55%) of **9e**. Mp: 139−141 (dark green prisms). $R_f = 0.14$ (hexane:ethyl acetate 1:1). $^1$H NMR (200 MHz, $CDCl_3$): $\delta = 7.59$−7.07 (m, 5H, Ph), 4.86 (d, 1H, $J = 11.5$ Hz, ═C*H*), 4.73 (d, 1H, $J = 11.5$ Hz, ═C*H*), 4.51−3.90 (m, 8H, $N(CH_2CH_2)_2O$), 3.82 (s, 3H, $CO_2CH_3$), 3.65 (s, 3H, $CO_2CH_3$). $^{13}$C NMR (50.3 MHz, $CDCl_3$): $\delta =$ 252.5 (*C*═Cr), 235.0 (*C*O), 228.8 (*C*O), 226.7 (*C*O), 222.9 (*C*O), 178.1 ($CO_2CH_3$), 177.3 ($CO_2CH_3$), 157.6 (═*C*), 138.3 (*C ipso*), 128.5 (2×*C*H, Ph), 128.2 (*C*H, *p*-Ph), 126.2 (2×*C*H, Ph), 122.68 (═*C*), 89.8 (═*C*H), 68.2 (═*C*H), 66.4 (2×$NCH_2CH_2O$), 53.9 ($NCH_2CH_2O$), 51.8 ($CO_2CH_3$), 51.4 ($NCH_2CH_2O$), 50.9 ($CO_2CH_3$). Anal. Calcd for $C_{23}H_{21}NO_9Cr$: C, 54.44; H, 4.17; N, 2.76. Found: C, 54.43; H, 4.22; N, 2.78.

**Tetracarbonyl(1,4,5-$\eta^3$-5-furyl-1,2-dimethoxycarbonyl-3-methylamino-2,4-pentadien-1-ylidene)chromium(0) (9h).** **1h** (0.65 g, 2.0 mmol) and DMAD (0.28 g, 2 mmol) were irradiated in 150 mL of deoxygenated $Et_2O$ at −40 °C for 6 h. The reaction crude material was chromatographed to afford 0.09 g of **9h** (0.2 mmol, 10%) and 0.04 g of **13h** (0.2 mmol, 10%). In addition, 0.36 g (1.1 mmol, 55%) of **1h** was recovered unreacted. Longer reaction time did not increase the chemical yield of **9h**. Mp: 147−150 °C. $R_f = 0.52$ (dichloromethane:ethyl acetate 8:1). $^1$H NMR (300 MHz, $CDCl_3$): $\delta = 10.74$ (br s, 1H, N*H*), 7.23 (s, 1H, 5-Fu), 6.39 (d, 1H, $J = 3.4$ Hz, 4-Fu), 6.32 (d, 1H, $J = 1.5$ Hz, 3-Fu), 4.93 (d, 1H, $J = 10.5$ Hz, ═C*H*), 4.78 (d, 1H, $J = 10.5$ Hz, ═C*H*), 3.78 (s, 3H, $CO_2CH_3$), 3.64 (s, 3H, $CO_2CH_3$), 3.57 (d, 3H, $J = 4.8$ Hz, $NCH_3$). $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta = 271.3$ (*C*═Cr), 234.5 (*C*O), 227.0 (*C*O), 226.2 (*C*O), 223.3 (*C*O), 186.9 ($CO_2CH_3$), 177.3 ($CO_2CH_3$), 161.1 (═*C*), 153.7 (*C*, 2-Fu), 141.8 (*C*H, 5-Fu), 123.3 (═*C*), 111.9 (*C*H, 4-Fu), 107.4 (*C*H, 3-Fu), 77.4 (═*C*H), 63.5 (═*C*H), 52.0 ($CO_2CH_3$), 50.9 ($CO_2CH_3$), 32.4 ($NCH_3$). Anal. Calcd for $C_{18}H_{15}NO_9Cr$: C, 48.99; H, 3.43; N, 3.17. Found: C, 49.18; H, 3.63; N, 3.28.

**General Procedure for the Preparation of $\eta^1$-Methoxycarbonyldienylcarbene Complexes 12e−g.** A 0.1 M solution of carbene complexes **9e**−**g** was pressurized under 4 bar of CO for 2 days. The solvent was then evaporated under vacuum and the crude mixture chromatographed (silica gel, hexane:ethyl acetate 1:1).

**Pentacarbonyl[3-(dimethylamino)-5-furyl-1,2-dimethoxycarbonyl-2,4-pentadien-1-ylidene]chromium(0) (12 g).** Reaction of 0.10 g (0.22 mmol) of **9g** afforded 0.10 g (0.21 mmol, 95%) of **12g**. Mp: 128−130 °C (black prisms). $R_f = 0.05$ (hexane:ethyl acetate 1:1). $^1$H NMR (300 MHz, $CDCl_3$): $\delta = 7.67$ (s, 1H, 5-Fu), 7.60 (d, 1H, $J = 15$ Hz, ═C*H*), 7.09 (d, 1H, $J = 15$ Hz, ═C*H*), 6.96 (s, 1H, 4-Fu), 6.59 (s, 1H, 3-Fu), 3.83 (s, 3H, $CO_2CH_3$), 3.67 (s, 3H, $CO_2CH_3$), 3.61 (s, 6*H*, $N(CH_3)_2$). $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta = 224.1$ (*C*═Cr), 219.8 (*C*O *trans*), 218.4 (4×*C*O *cis*), 179.1 ($CO_2CH_3$), 178.0 ($CO_2CH_3$), 157.7 (═*C*), 150.5 (*C*, 2-Fu), 148.4 (═*C*H), 141.4 (*C*H, 5-Fu), 124.2 (═*C*), 122.8 (═*C*H), 114.6 (*C*H, 3-Fu), 114.1 (*C*H, 4-Fu), 51.9 ($CO_2CH_3$), 50.4 ($CO_2CH_3$), 44.9 ($NCH_3$), 41.8 ($NCH_3$). Anal. Calcd for $C_{20}H_{17}NO_{10}Cr$: C, 49.70; H, 3.54; N, 2.90. Found: C, 49.71; H, 3.64; N, 2.95.

**Crystallographic Structural Determination.** Data collection, crystal, and refinement parameters for **12g** are collected in Table 7. The unit cell parameters were obtained from the least-squares fit of 25 reflections. On all reflections, profile analysis was performed.[43] Lorentz and polarization corrections were applied, and the data were reduced to $F^2$ values using THE REFLEX.[44] The structures were solved by Patterson methods using the program DIRDIF.[45] Refinement on $F^2$ was done using SHELXL 97.[46] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were calculated geometrically through HFIX and refined riding with common isotropic thermal parameters. Atomic scattering factors were taken from *International Tables for X-Ray Crystallography*.[47] Geometrical calculations were made with PARST. All calculations were made at the University of Oviedo on the Scientific Computer Center and X-Ray Group DEC/AXP Computers.

**1-(1,4,5,6-Tetrahydro-2,3-dimethoxycarbonyl-1-pentalenyl)morpholine (13a).** A solution of 0.42 g (0.89 mmol) of **13a** in 10 mL of $CH_2Cl_2$ was allowed to stand at room temperature for 8 h. The reaction mixture was concentrated and the crude material chromatographed to yield 0.20 g (0.66 mmol, 74%) of **13a** as a yellow oil. $R_f = 0.40$ (hexane:ethyl acetate 1:1). $^1$H NMR (300 MHz, $CDCl_3$): $\delta = 4.56$ (s, 1H, NC*H*), 3.76−3.54 (m, 4H, $N(CH_2CH_2)_2O$), 3.65 (s, 3H, $CO_2CH_3$), 3.61 (s, 3H, $CO_2CH_3$), 3.38−3.13 (m, 4H, $N(CH_2CH_2)_2O$), 2.69−2.45 (m, 4H, $CH_2CH_2CH_2$), 2.29−2.02 (m, 2H, $CH_2CH_2CH_2$). $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta = 175.4$ ($CO_2$Me), 170.4 ($CO_2$Me), 164.0 (═*C*), 149.9 (═*C*), 123.6 (═*C*), 108.6 (═*C*), 66.4 ($N(CH_2CH_2)_2O$), 60.5 (*C*H), 52.4 ($CO_2CH_3$), 50.6 ($CO_2CH_3$), 49.2 ($N(CH_2CH_2)_2O$), 29.8 ($CH_2$), 27.7 ($CH_2$), 26.5 ($CH_2$). Anal. Calcd for $C_{16}H_{21}NO_5$: C, 62.53; H, 6.89; N, 4.56. Found: C, 62.60; H, 6.99; N, 4.61.

**Methyl 2-Hydroxy-5-morpholino-3-phenylbenzoate (15j).** **9j** (0.45 g, 1 mmol) was dissolved in 20 mL of THF and allowed to stand at room temperature for 9 h and then exposed to air and sunlight for several hours to afford, after chromatography, 0.29 g (0.92 mmol, 92%) of **15j**. $R_f = 0.35$ (hexane:ethyl acetate 1:1). $^1$H NMR (200 MHz, $CDCl_3$): $\delta = 10.92$ (s, 1H, O*H*), 7.64−7.35 (m, 6H, aryl), 7.23 (d, 1H, $J = 3.2$ Hz, aryl), 3.98 (s, 3H, $CO_2CH_3$), 3.89 (t, 4H, $J = 4.6$ Hz, $N(CH_2CH_2)_2O$), 3.11 (t, 4H, $J = 4.6$ Hz, $N(CH_2CH_2)_2O$). $^{13}$C NMR (50.3 MHz, $CDCl_3$): $\delta = 170.8$ ($CO_2CH_3$), 153.5 (*C*, aryl), 143.7 (*C*, aryl), 137.3 (*C*, aryl), 131.1 (*C ipso*), 129.2 (2×*C*H, Ph), 128.1 (2×*C*H, Ph), 127.4 (*C*H, *p*-Ph), 127.1 (*C*H, aryl), 115.5 (*C*H, aryl), 112.3 (*C*, aryl), 66.9 ($N(CH_2CH_2)_2O$), 52.4 ($CO_2CH_3$), 50.7 ($N(CH_2CH_2)_2O$). Anal. Calcd for $C_{18}H_{19}NO_4$: C, 68.99; H, 6.11; N, 4.47. Found: C, 69.21; H, 6.25; N, 4.62. Chromium tricarbonyl-complexed methyl 2-hydroxy-5-morpholino-3-phenylbenzoate **15j·(CO)$_3$Cr** is obtained in lower yields by chromatography without exposition to sunlight. In these conditions, 0.36 g (0.80 mmol, 80%) of **15j·(CO)$_3$Cr** (red prisms) was obtained. Mp: 152−154 °C. $R_f = 0.42$ (hexane:ethyl acetate 1:1). $^1$H NMR (300 MHz, $CDCl_3$): $\delta = 10.59$ (s, 1H, O*H*), 7.65−7.60 (m, 2H, Ph), 7.45−7.35 (m, 3H, Ph), 5.82 (d, 1H, $J = 2.0$ Hz, aryl), 5.78 (d, 1H, $J = 2.0$ Hz, aryl), 4.00 (s, 3H, $OCH_3$), 3.83 (m, 4H, $N(CH_2CH_2)_2O$), 2.92 (m, 4H, $N(CH_2CH_2)_2O$). $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta = 232.8$ (3×*C*O), 171.5 ($CO_2CH_3$), 140.0 (*C*, aryl), 133.7 (*C*, aryl), 130.2 (2×*C*H, Ph), 128.6 (*C*H, *p*-Ph), 128.3 (2×*C*H, Ph), 120.0 (*C*, aryl), 97.3 (*C*, aryl), 86.9 (*C*H, aryl), 78.8 (*C*H, aryl), 70.8 (*C*, aryl), 66.0 ($N(CH_2CH_2)_2O$), 53.4 ($CO_2CH_3$), 48.9 ($N(CH_2CH_2)_2O$). Anal. Calcd

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(47) *International Tables for X-Ray Crystallography*; Birmingham Kynoch Press: Birmingham, UK, 1974 (present distributor, Kluwer Academic Publishers: Dordrecht); Vol. IV.

for $C_{21}H_{19}NO_7Cr$: C, 56.13; H, 4.26; N, 3.12. Found: C, 56.35; H, 4.10; N, 2.96.

**Dimethyl 3-Hydroxy-6-methyl-4-phenylphthalate (16e).** A solution of 1 mmol of methyllithium in 10 mL of diethyl ether was added dropwise to a solution of 0.51 g (1 mmol) of **9e** in 20 mL of THF at −78 °C. The reaction mixture was then warmed to −60 °C, and a mixture of 3 mL of saturated aqueous $NH_4Cl$ and 10 mL of THF was added at this temperature. The reaction mixture was exposed to air and sunlight for several hours. $Et_2O$ (20 mL) was added, and the mixture was washed with 0.1 N HCl (2 × 20 mL) and brine (20 mL), dried over $Na_2SO_4$, and filtrated through Celite. The volatiles were removed in vacuo, and the residue was chromatographed to furnish 0.21 g (0.71 mmol, 71%) of **16e**. $R_f = 0.11$ (hexane:ethyl acetate 3:1). $^1H$ NMR (200 MHz, $CDCl_3$): $\delta = 11.31$ (s, 1H, O*H*), 7.62−7.40 (m, 5H, Ph), 7.38 (s, 1H, aryl), 3.97 (s, 3H, $CO_2CH_3$), 3.94 (s, 3H, $CO_2CH_3$), 2.30 (s, 3H, $CH_3$). $^{13}C$ NMR (50.3 MHz, $CDCl_3$): $\delta = 169.7$ ($CO_2CH_3$), 169.3 ($CO_2CH_3$), 157.0 (*C*, aryl), 138.0 (*C*H, aryl), 136.4 (*C*, aryl), 133.6 (*C*, aryl), 131.6 (*C*, aryl), 129.2 (2×*C*H, Ph), 128.1 (2×*C*H, Ph), 127.6 (*C*H, Ph), 125.4 (*C*, aryl), 109.1 (*C*, aryl), 53.0 ($CO_2CH_3$), 52.3 ($CO_2CH_3$), 18.4 ($CH_3$). Anal. Calcd for $C_{17}H_{16}O_5$: C, 67.99; H, 5.37. Found: C, 68.34; H, 5.58. In a separate run, chromium tricarbonyl-complexed dimethyl 3-hydroxy-6-methyl-4-phenylphthalate **16e·Cr(CO)$_3$** was obtained in lower yields by the same aqueous workup and chromatography without exposition to sunlight. In these conditions, 0.25 g (0.57 mmol, 57%) of **16e·Cr(CO)$_3$** (red prisms) was obtained. $R_f = 0.48$ (hexane:ethyl acetate 1:1). $^1H$ NMR (200 MHz, $CDCl_3$): $\delta = 10.91$ (s, 1H, O*H*), 7.65−7.55 (m, 2H, Ph), 7.50−7.40 (m, 3H, Ph), 5.94 (s, 1H, aryl), 4.03 (s, 3H, $CO_2CH_3$), 3.99 (s, 3H, $CO_2CH_3$), 2.15 (s, 3H, $CH_3$). $^{13}C$ NMR (50.3 MHz, $CDCl_3$): $\delta = 230.4$ (3×*C*O), 170.7 ($CO_2CH_3$), 166.3 ($CO_2CH_3$), 140.4 (*C*, aryl), 132.8 (*C*, aryl), 130.1 (2×*C*H, Ph), 128.7 (*C*H, Ph), 128.2 (2×*C*H, Ph), 105.9 (*C* aryl), 98.4 (*C*H, aryl), 98.0 (*C*, aryl), 96.5 (*C*, aryl), 68.6 (*C*, aryl), 53.8 ($CO_2CH_3$), 53.4 ($CO_2CH_3$), 17.8 ($CH_3$). Anal. Calcd for $C_{20}H_{16}O_8Cr$: C, 55.05; H, 3.70. Found: C, 54.91; H, 3.59.

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**Supporting Information Available:** Experimental procedures and analytical data for all new compounds and X-ray crystallographic data for **12g**, including tables of atomic coordinates, bond lengths, bond angles, and anisotropic displacement coefficients (PDF). An X-ray crystallographic file, in CIF format, is also available. This material is available free of charge via the Internet at http://pubs.acs.org.

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