Cascade Reactions of Dialkynyl Fischer Carbene Complexes Involving Intramolecular Alkyne Insertions Oriented to the Synthesis of Functionalized Polycycles

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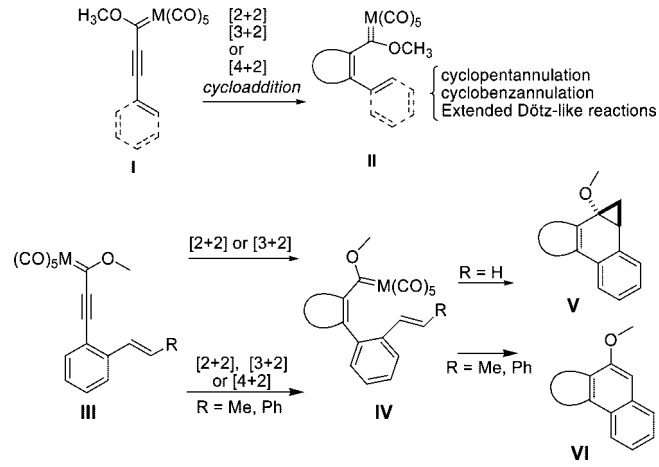
The cascade reactions of alkynylchromium Fischer carbene complexes featuring an additional pendant triple bond are presented. The processes are triggered by [2 + 2], [3 + 2], and [4 + 2] cycloadditions. Depending on the substitution of the appended triple bond, and the nature of the triggering cycloaddition reaction, different polycyclic compounds can be obtained. Predictable results are obtained in most of the cases when the Fischer carbene complex bears a TMS-substituted alkyne. In these cases, naphtalene derivatives substituted with a TMS-ketene are obtained in sequences that involve alkyne exo insertion followed by CO migration. However, the reaction with a carbene complex featuring a terminal alkyne follows an alternative reaction pathway, in which the nucleophilic attack of the triple bond at the carbenic carbon forms a benzo[7]annulene. Mechanistic interpretations based on DFT calculations are provided.

Introduction

Cascade reactions are very attractive processes in synthetic organic chemistry, since they usually provide molecules with a high degree of complexity from readily available starting materials, in a single synthetic operation.[1] In this regard, Fischer carbene complexes are particularly versatile materials for the programming of cascade sequences leading to carbocycles through a variety of mechanistic pathways.[2] Among them, the well-known Dötz benzannulation can be regarded as the most synthetically useful transformation involving a cascade of elementary reactions starting from a Fischer carbene complex.[3]

A representative type of Fischer carbene complexes suitable for the design of reaction cascades are alkynyl Fischer carbene complexes **I** (Scheme 1). In these complexes, the linear arrangement of the triple bond can be broken by a cycloaddition reaction, giving rise to the alkenyl Fischer carbene **II**, in which the carbene moiety is brought closer to a reactive functionality, enabling a subsequent intramolecular reaction. We have studied extensively this strategy and observed that, depending on the type of cycloaddition and the structure of the initial alkynyl Fischer carbene, the alkenyl Fischer carbene **II** may follow different reaction pathways involving cyclopentannulations,[4] benzannulations,[5] and even extended Dötz-like cyclizations.[6]

Scheme 1. Cascade Reactions of Alkynyl Fischer Carbene Complexes



In this context, we have recently reported the cascade reactions of alkynyl Fischer carbene complexes **III**, featuring a pendant double bond (Scheme 1).[7] These complexes upon cycloaddition give rise to alkenyl Fischer carbenes **IV**, which evolve to

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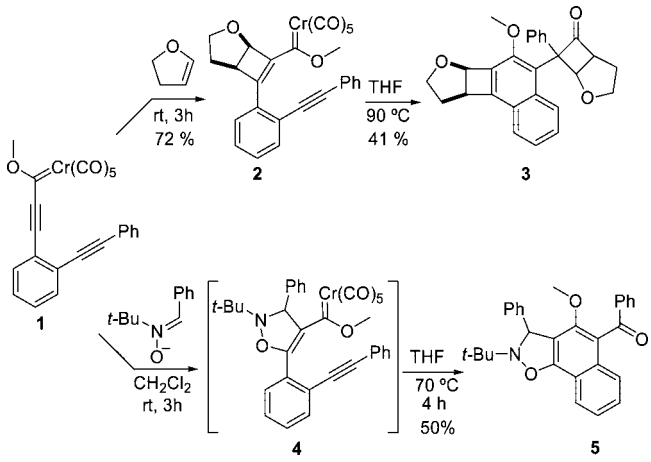
Scheme 2. Cascade Reactions with the Phenyl-Substituted Fischer Carbene Complex 1



produce homonaphthalenes **V** or naphthalenes **VI**, through intramolecular cyclopropanation or metathesis reactions, respectively, depending on the substitution of the double bond.

As a continuation of this work, we decided to investigate a similar process, but incorporating a pendant triple bond, which we expected might participate in different types of cascade processes. We have observed that the main reaction pathway observed for these systems involves an intramolecular exo insertion of the triple bond, which leads to polycyclic structures in a very simple manner. The most relevant results of this study are presented herein.

Results and Discussion

The study was initiated with the dialkyne Fischer carbene complex **1**, which features a pendant triple bond in a suitable position to participate in an intramolecular cascade process upon cycloaddition. This complex is readily available from 1,2-dibromobenzene through conventional transformations (see the Supporting Information for details).

Treatment of complex **1** at room temperature with 2,3-dihydrofuran afforded the new complex **2**, resulting from the [2 + 2] cycloaddition[5a,8] of 2,3-dihydrofuran with the electron-poor triple bond, which turned out to be stable at room temperature. Nevertheless, when the reaction mixture was heated to 90 °C in THF, the polycyclic compound **3** was isolated in moderate yield (Scheme 2). Inspection of the structure of **3** reveals that it contains the organic skeleton of carbene complex **1**, two dihydrofuran subunits, and an additional CO from the metal coordination sphere. Then, we attempted to initiate the cascade process with a [3 + 2] cycloaddition.[9] Thus, reaction of an excess of a nitrone with Fischer carbene **1** at room temperature until complete disappearance of complex **1**, followed by reflux in THF, provided naphthoisoxazole **5** (Scheme 2).

In both cases, a benzannulation to form a naphthalene system occurred; however, a significant difference between compounds **3** and **5** can be found. In compound **3**, a CO ligand and two units of dihydrofuran have been incorporated, while no CO incorporation and only one molecule of nitrone can be distinguished in **5**. Nevertheless, a common mechanistic explanation for the formation of compounds **3** and **5** can be postulated (Scheme 3).

Both polycycles **3** and **5** could be formed by evolution of the intermediate **III**. The cycloaddition reaction on the electron-poor triple bond affords complex **I**, which can dissociate a CO ligand upon heating to give complex **II**. Carbene complex **III** can be formed from the tetracarbonylchromium complex **II** through an intramolecular exo alkyne insertion.[10,11] Then, the tetracarbonyl complex **III** can undergo the insertion of a CO ligand from the metal coordination sphere to give ketene **IV**, which in the presence of an excess of 2,3-dihydrofuran experiences a second [2 + 2] cycloaddition to furnish the polycyclic compound **3**. Alternatively, in the presence of an excess of a nitrone, carbene complex **III** undergoes oxidation, giving rise to the corresponding ketone **5**.

Considering this mechanistic picture, we decided to attempt the isolation of the ketene intermediate, which would render more interesting products from a synthetic point of view. With this aim, we decided to employ a TMS-substituted alkyne,[12] since the enhanced stability of TMS-substituted ketenes is well-known.[13]

Therefore, the Fischer carbene complex **6** was prepared. Delightfully, when the carbene complex **6** was reacted with dihydrofuran under the same reaction conditions previously described for **1**, the silylketene containing naphthalene **7** was isolated in an acceptable yield.[14] It is worth noting that the second [2 + 2] cycloaddition was not observed this time, in spite of the large excess of 2,3-dihydrofuran employed. Interestingly, the reaction triggered by the nitrone also led to a silylketene, the naphthoisoxazole **8**. Clearly, the presence of the TMS group prevented the oxidation of the intermediate tetracarbonyl chromium carbene by the excess nitrone, making possible the subsequent CO insertion step (Scheme 4).

Finally, the cascade process can be also promoted by a [4 + 2] cycloaddition[15] (Scheme 5). Reaction with cyclopentadiene, under the same conditions employed in the examples above, led to the silylketene **9** in moderate yield. The process was also attempted with Danishefsky's diene. Similar to the procedures in the previous examples, the chromium carbene complex **6** was treated with an excess of Danishefsky's diene (an excess of diene is necessary to drive the cycloaddition reaction to complexion) and, after 2 h at room temperature, heated in THF at 80 °C in a sealed tube. Again, the cascade cyclization occurred; however,

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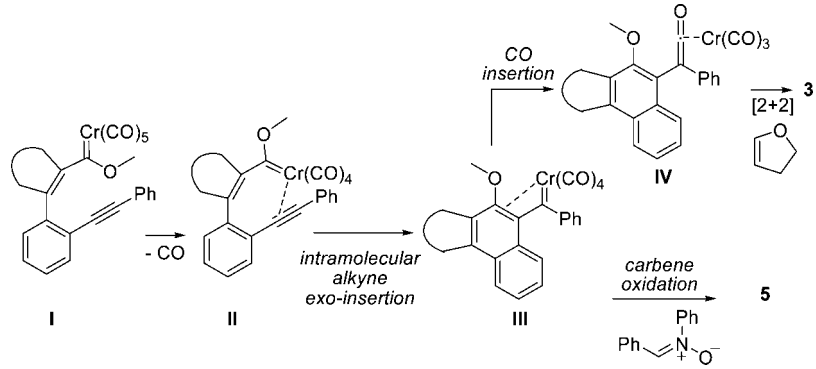
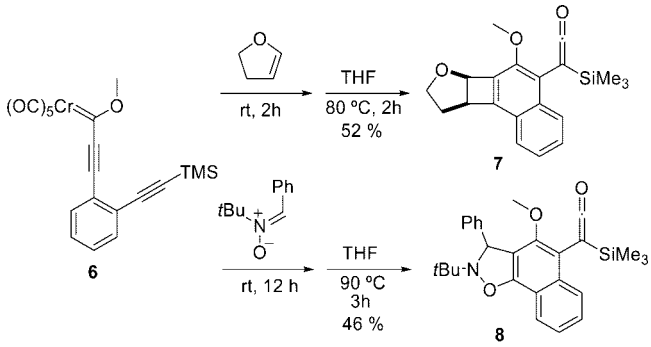
(14) Silylketenes have been previously prepared by intramolecular reactions of aminocarbenes: Grotjahn, D. B.; Dötz, K. H. *Synlett* **1991**, 381–390.

(15) (a) Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 6726–6727. (b) Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1984**, *106*, 7565–7567. (c) Wulff, W. D.; Bauta, W. E.; Kaesler, R. W.; Lankford, P. J.; Miller, R. A.; Murray, C. K.; Yang, D. C. *J. Am. Chem. Soc.* **1990**, *112*, 3642–3659.

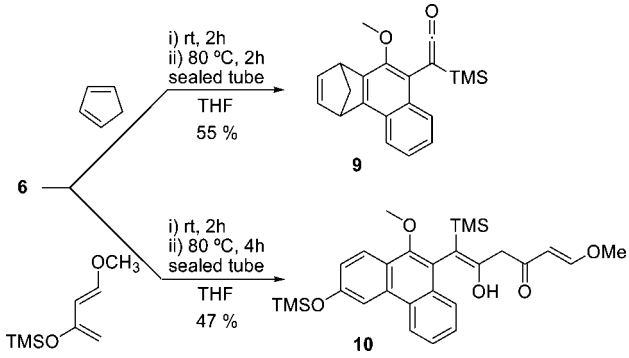
Scheme 3. Mechanistic Working Proposal for the Formation of Compounds 3 and 5



Scheme 4. Synthesis of Silylketenes 7 and 8 by Reaction of the TMS-Substituted Fischer Carbene Complex 6



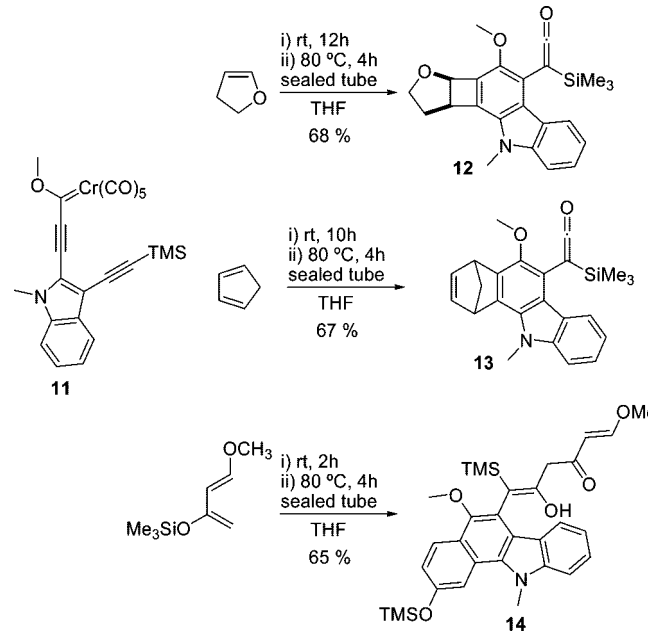
Scheme 5. Cascade Reactions of Fischer Carbene Complex 6 Triggered by [4 + 2] Cycloadditions



in this instance the silylketene could not be isolated and reacted with a second molecule of diene to provide the phenanthrene derivative **10**.

To investigate the scope of this cyclization in the synthesis of complex polycyclic molecules, we decided to modify the structure of the initial dialkynyl Fischer carbene complex. Thus, the five-membered ring of the indole was investigated as a new platform to attach the two triple bonds of the dialkynylchromium carbene complex. The required complex **11** was readily synthesized from 1-methyl-1*H*-indole-2-carboxaldehyde through conventional transformations (see the Supporting Information for details). It is worth noting that the reactions employing the indolic Fischer carbene **11** gave results similar to those for the benzene-based system (Scheme 6). Thus, the reaction initiated by the [2 + 2] cycloaddition with 2,3-dihydrofuran gave the carbazole derivative **12**, featuring the silylketene, and its structure was confirmed by X-ray diffraction analysis.[16] Similarly, the cascade triggered by a [4 + 2] cycloaddition with cyclopentadiene provided silylketene **13**. On the other hand, reaction with Danishefsky's diene gave the benzo[*a*]carbazole

Scheme 6. Cascade Reactions of Indole-Based Fischer Carbene Complex 11



14, which is derived from the addition of a second molecule of diene to the silylketene.

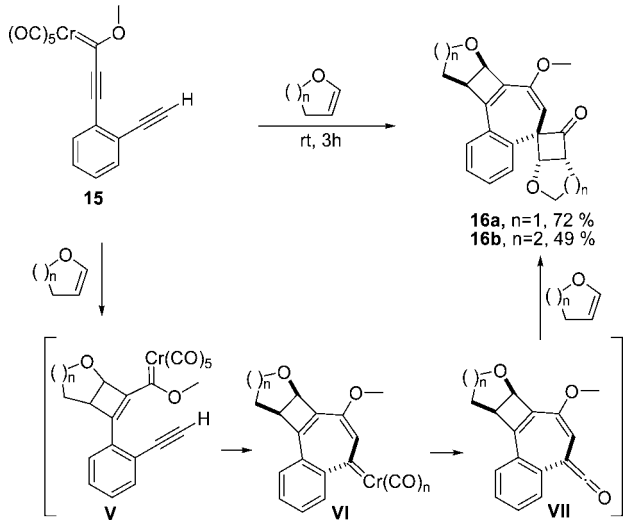
These results show that the cascade benzannulation process involving an intramolecular exo alkyne insertion is a very general process, which can be triggered by [2 + 2], [3 + 2], and [4 + 2] cycloadditions and can involve five- and six-membered-ring aromatic systems.

Finally, the sequential process was also examined employing carbene complex **15**, which features a terminal C−H bond. When the reaction was started by the [2 + 2] cycloaddition with 2,3-dihydrofuran, the polycycle **16a** was obtained as a single diastereoisomer after stirring at room temperature for 3 h (Scheme 7). In this case it was not necessary to increase the temperature to promote the evolution of the [2 + 2] adduct. The structure of **16a** was unambiguously established by X-ray diffraction.[17] A similar product, **16b**, although in slightly lower yield, was obtained from 3,4-dihydro-2*H*-pyran. The main feature of this new reaction is the formation of a seven-

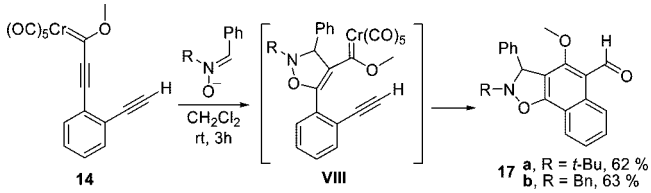
(16) CCDC-680526 contains the supplementary crystallographic data for compound **12**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre viawww.ccdc.cam.ac.uk/data_request/cif.

(17) CCDC-680527 contains the supplementary crystallographic data for compound **16a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre viawww.ccdc.cam.ac.uk/data_request/cif.

Scheme 7. Unexpected Formation of Benzo[7]annulenes 16 from Fischer Carbene Complex 15



Scheme 8. Formation of Naphthoisooxazoles 17 from Fischer Carbene Complex 14



membered ring, which must occur through a mechanistic pathway different from that of the preceding reactions. Moreover, as in the reactions with the phenyl-substituted terminal alkyne **1**, two molecules of enol ether and a CO ligand are incorporated. The second enol ether subunit must come from a [2 + 2] cycloaddition from a ketene. Thus, we might consider again the presence of the ketene **VII**, which could be derived from the CO insertion of Fischer carbene complex **VI**. The divergent behavior of carbene **V**, which undergoes an endo cyclization into a seven-membered ring instead of alkyne insertion to give a six-membered ring, can be rationalized by considering the different steric requirements of the terminal alkyne in comparison with the substituted alkynes, which determines the reactivity of the triple bond. A more detailed computational-based mechanistic rationale is provided below.

However, this anomalous behavior of carbene complex **15** turned out to be a rare exception. When the process was started by the [3 + 2] cycloaddition with the nitrone, naphthoisoxazole carboxaldehydes **17** were obtained in good yield (Scheme 8). Thus, the behavior of the intermediate carbene **VIII** is identical with that of **III**, that features a phenyl-substituted triple bond. It seems that, in order to evolve to the formation of the seven-membered ring, a very precise combination of low steric requirements and geometric arrangement (which is only met in the four-membered ring) is required.

Mechanistic Considerations. To gain a better understanding of the mechanisms of these transformations, we performed some computational DFT calculations.[18,19] The quantum mechanics computations were carried out by employing starting models **A1** and **B1**, which feature the geometric constraints of the four-membered ring and the correct substitution on the triple bond (Figure 1).

The reaction pathway found for system **A** (R = TMS) is in agreement with the mechanistic proposal postulated in Scheme

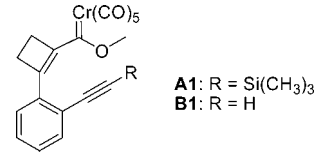


Figure 1. Model systems for DFT calculations.

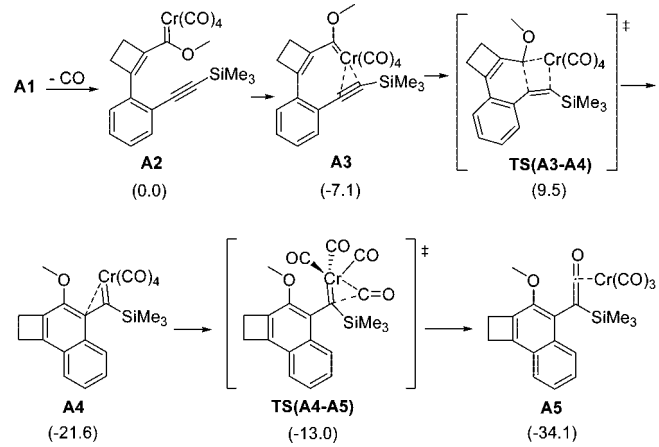


Figure 2. Reaction pathway calculated for model **A**. Relative ΔG values (kcal mol^{-1}) including solvation energy at the B3LYP/LANL2DZ+6-311++G**//B3LYP/LANL2DZ+6-31G* level are indicated in parentheses.

1 (Figure 2). Thus, the initial steps must be the dissociation of a CO ligand to give the coordinatively unsaturated tetracarbonylchromium carbene complex **A2**, followed by complexation with the triple bond to give complex **A3**. Then, complex **A3** undergoes an intramolecular alkyne insertion to form carbene complex **A4** through the transition state **TS(A3-A4)**, which features a metallacyclobutene structure and resembles the transition state of Ru-catalyzed enyne metathesis reactions.[20] An activation free energy of 16.4 kcal mol^{-1} was obtained for this step, which is the rate-limiting step in this reaction pathway. Then **A4** undergoes CO insertion to give the $Cr(CO)_3$-complexed silylketene **A5**. The overall reaction is highly exergonic (ΔG = −34.1 kcal mol^{-1}).

The formation of the seven-membered ring, however, proceeds through a completely different mechanism. We found that the intramolecular attack of the triple bond at the highly electrophilic carbenic carbon of the pentacarbonyl Fischer carbene complex is a process that is energetically very accessible when R = H (ΔG_{act} = 17 kcal mol^{-1}), and therefore, it will occur in preference to the CO dissociation required for the

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(19) Geometry optimizations were carried out employing the LANL2DZ ECP for Cr and the 6-31G* basis set for the rest of the atoms. Single-point energy calculations at the stationary points were carried out by employing the 6-311++G** basis set for H, C, O, and Si and again the LANL2DZ basis set for Cr. Solvation free energy was calculated by employing the SRCF PCM model. See the Supporting Information for further details.

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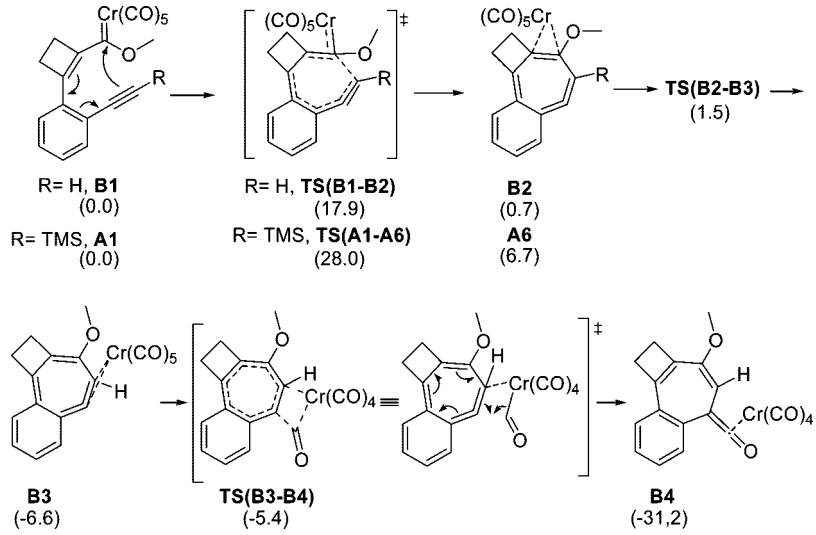

Figure 3. Reaction pathway calculated for model **B**. Relative ΔG values (kcal mol^{-1}) including solvation energy at the B3LYP/LANL2DZ+6-311++G**//B3LYP/LANL2DZ+6-31G* level are indicated in parentheses.

formation of the six-membered ring.[21] Nucleophilic attack gives the strained cumulene **B2**. Then, after a 1,2-Cr migration, to give complex **B3**, a CO transposition leads to ketene **B4**. Both transformations feature very low activation barriers. Clearly, the driving force for the evolution from **B2** to ketene **B4** is the recovery of the aromaticity of the six-membered ring and the release of the strain of the two consecutive double bonds in the seven-membered ring. The overall process is again highly exergonic (Figure 3).

The differential reactivity between the TMS -substituted system **A** and the terminal alkyne **B** relies on the relative activation free energies of the CO dissociation and the intramolecular nucleophilic attack of the triple bond at the carbenic carbon, which determines the formation of the naphthalene or the benzo[7]annulene, respectively. For system **A** the nucleophilic attack of the triple bond at the chromium pentacarbonyl carbenic carbon features a very high activation free energy, 28 kcal mol^{-1}, as a result of the steric hindrance between the $Cr(CO)_5$ moiety and the bulky substituent at the triple bond, and is a very endergonic process. Therefore, CO dissociation is the preferred pathway.[22] In contrast, in the terminal system **B**, the lack of a substituent in the triple bond allows intramolecular attack, which has a lower free energy barrier of 17 kcal mol^{-1}, and therefore this reaction occurs in preference to CO dissociation.

Conclusion

In summary, we have reported novel cascade processes of dialkynyl Fischer carbene complexes triggered by [2 + 2], [3 + 2], and [4 + 2] cycloaddition reactions that give rise to highly complex and functionalized polycyclic compounds in a predictable manner. The outcome of the reactions depends on the substitution of the appended triple bond. Reactions of carbenes featuring a substituted triple bond give rise to substituted naphthalene derivatives in a cascade process which includes an intramolecular exo insertion of the triple bond.

In particular, the use of TMS -substituted alkynes results in a very convenient alternative, which allows in most of the examples the isolation of silylketenes, avoiding the subsequent evolution of these highly reactive species. On the other hand, a different behavior was observed with terminal triple bonds when the reactions were initiated by a [2 + 2] cycloaddition. Mechanistic rationales for the different observations have been provided with the aid of DFT computations.

The results presented herein show once again the potency of Fischer carbene complexes in the design of cascades of reactions that produce highly complex molecules from readily available starting materials.

Experimental Section

General Considerations. All reactions were carried out under an argon atmosphere. THF was distilled over benzophenone/sodium under a nitrogen atmosphere. CH_2Cl_2 was distilled over CaH_2 under a nitrogen atmosphere. Column chromatography was carried out on silica gel 60 (230−400 mesh). All other reagents were of the best commercial grade available. ^{1}H NMR spectra were recorded on a Bruker DPX-300 (75 MHz), Bruker NAV-300 (75 MHz), Bruker AMX-400 (100 MHz), or Bruker NAV-400 spectrometer (100 MHz). Chemical shifts are reported in ppm from tetramethylsilane with the residual solvent resonance as the internal standard ($CHCl_3$: δ 7.26). Data are reported as follows: chemical shift, multiplicity (s, singlet; d, doublet; dd, double doublet; td, triplet of doublets; t, triplet; q, quartet; br, broad; m, multiplet), coupling constants (J in Hz), integration, and assignment. ^{13}C NMR spectra were recorded on a Bruker AV-300, Bruker DPX-300 (75 MHz), Bruker NAV-300 (75 MHz), Bruker AMX-400 (100 MHz), or Bruker NAV-400 spectrometer (100 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$: δ 76.95). Carbon multiplicities were assigned by DEPT techniques. Two-dimensional NMR experiments (COSY, HMQC, HMBC, and NOESY) were recorded on a Bruker AMX-400 (100 MHz) or Bruker NAV-400 spectrometer (100 MHz). Electron impact (EI)

(21) The seven-membered ring could also be formed by an endo insertion of the triple bond in the chromium tetracarbonyl complex. This route was also studied, and the transition state for the endo insertion turned out to be 6.5 kcal mol^{-1} to higher energy than the transition state of the exo insertion (gas-phase Gibbs free energy with the smaller basis set combination). Therefore, this route was discarded.

(22) We obtained a value of 24.5 kcal mol^{-1} for the bond dissociation potential energy for the CO ligand in both models **A** and **B** at the B3LYP/LANL2DZ+6-311++G**//B3LYP/LANL2DZ+6-31G* level. Although the determination of the activation free energy of the CO dissociation in solution is not straightforward, due to the overestimation of the entropic contributions in ligand dissociation reactions, we can assume that the value of the activation free energy will be below 24.5 kcal mol^{-1}. Therefore, for system **A** the reaction pathway initiated by the CO dissociation will be favoured. See (a) Sumimoto, M.; Iwane, N.; Takahama, T.; Sakaki, *J. Am. Chem. Soc.* **2004**, *126*, 10457–10471, See the Supporting Information for further details.

high-resolution mass spectrometry was carried out on a Finnigan-Mat 95 spectrometer.

General Procedure for the Preparation of Alkynyl Fischer Carbene Complexes 1, 6, 11, and 14. Carbene complexes **1**, **6**, **11**, and **15** were prepared from hexacarbonylchromium and the corresponding terminal acetylenes following a variation of the original method described by Fischer.[23]

To a suspension of hexacarbonylchromium (10 mmol) and the corresponding alkyne (11 mmol) in THF (60 mL) cooled at −78 °C was added BuLi (1.6 M in hexanes, 11 mmol) dropwise. The mixture was slowly warmed to room temperature over 12 h. Then it wass cooled to −15 °C and methyl trifluoromethanesulfonate (20 mmol) was added in one portion. The resulting solution was stirred at room temperature for 10 min, and then it was quenched with a saturated aqueous solution of $NaHCO_3$ (20 mL). The organic layer was extracted with diethyl ether (3 × 15 mL) and dried with Na_2SO_4. The crude product was purified by column chromatography using hexane (or a mixture of hexane and ethyl acetate (15:1) for carbene complex **11**) as eluent. The resulting complex was recrystallized in hexanes at −20 °C.

Pentacarbonyl[3-(2-(phenylethynylphenyl)-1-methoxypropynylidene]chromium(0) (1). Dark red solid (3.00 g; 69%). R_f 0.44 (HxH). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.85−7.41 (m, 4H), 4.38 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 314.2 (Cr═C), 225.7 (CO), 216.2 (4 × CO), 135.2 (CH), 132.5 (CH), 131.4 (2 × CH), 131.3 (CH), 128.9 (CH), 128.6 (CH), 128.5 (2 × CH), 125.4 (C), 123.3(C), 122.5 (C), 95.3 (C), 94.6 (C), 87.4 (C), 81.1 (C), 66.3 (OCH_3).

Pentacarbonyl[3-(2-trimethylsilylethynylphenyl)-1-methoxypropynylidene]chromium(0) (6). Dark red solid (3.41 g; 79%). R_f 0.46 (HxH:AcOEt 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (dd, J = 7.2, 2.9 Hz, 1H), 7.58 (dd, J = 7.6, 2.9 Hz, 1H), 7.45−7.42 (m, 2H), 4.49 (s, 3H), 0.25 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 314.2 (Cr═C), 225.8 (CO), 216.2 (4 × CO), 135.2 (CH), 133.4 (CH), 131.2 (CH), 128.8 (CH), 125.0 (C), 123.2 (C), 102.8 (C), 101.0 (C), 98.2 (C), 94.5 (C), 66.4 (OCH_3), −0.1 (3 × CH_3).

Pentacarbonyl[3-(1-methyl-3-trimethylsilylethynyl-1*H*-indol-2-yl)-1-methoxypropynylidene]chromium(0) (11). Violet solid (3.64 g; 72%). R_f 0.39 (HxH:AcOEt 5:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.64 (d, J = 7.4 Hz, 1H), 7.34−7.11 (m, 3H), 4.41 (s, 3H), 3.84 (s, 3H), 0.17 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 307.0 (Cr═C), 225.4 (CO), 216.3 (4 × CO), 139.4 (C), 128.3 (C), 126.6 (CH), 124.0 (C), 123.1 (C), 121.8 (CH), 121.6 (CH), 110.1 (CH), 107.8 (C), 103.2 (C), 102.3 (C), 96.9 (C), 66.0 (OCH_3), 31.2 (NCH_3), 0.0 (3 × CH_3).

Pentacarbonyl[3-(2-ethynylphenyl)-1-methoxypropynylidene]chromium(0) (15). Violet solid (1.87 g; 52%). R_f 0.41 (HxH). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.74−7.41 (m, 4H), 4.49 (s, 3H), 3.42 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 314.4 (Cr═C), 225.7 (CO), 216.1 (4 × CO), 134.6 (CH), 133.0 (CH), 131.2 (CH), 129.1 (CH), 124.3 (2 × C), 94.3 (CH), 83.1 (CH and C), 81.5 (C), 66.4 (OCH_3).

General Procedure for the Preparation of Polycycles 3, 5, 7−10, and 12−14. To a solution of alkynyl Fischer carbene complex **1**, **6**, or **11** (0.5 mmol) in THF (10 mL) was added 2,3-dihydrofuran (2 mmol), and the mixture was stirred at room temperature under an argon atmosphere until the TLC analysis showed the disappearance of the alkynyl carbene complex. Then the tube was sealed and the solution was heated to 80 °C over 2−4 h. The mixture was diluted with hexane (30 mL) and was exposed to air and sunlight in order to oxidize the metallic species to the corresponding organic compounds. Finally, the mixture was filtered through a pad of Celite, solvents were removed under reduced pressure, and the crude product was purified by column chromatography using a mixture of hexane and ethyl acetate as eluent to afford **3**, **7**, or **12**.

5, **8**, **9**, **10**, **13**, and **14** were prepared by following the same procedure using *N*-benzylidene-*N*-*tert*-butylamine oxide (1.5 mmol) for **5** and **8** (a 4:1 mixture of THF and CH_2Cl_2 (10 mL) was used in these cases), 1-methoxy-3-trimethylsilyloxy-1,3-butadiene (1.5 mmol) for **10** and **14**, or freshly distilled cyclopentadiene (10 mmol) for **9** and **13**, instead of 2,3-dihydrofuran.

(6b*R,9a*R**)-5-(2,3,3a,4,5,5a-Hexahydro-5-phenyl-4-oxocyclobuta[*b*]furan-5-yl)-6b,8,9,9a-tetrahydro-6-methoxynaphtho[1′,2′:3,4]cyclobuta[*b*]furan (3).** Yellow oil (85 mg; 41%). R_f 0.32 (HxH:AcOEt 3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.28 (m, 1H), 7.75 (m, 2H), 7.69 (m, 1H), 7.51−7.23 (m, 5H), 5.70 (d, J = 3.2 Hz, 1H), 5.08 (d, J = 3.4 Hz, 1H), 4.35 (m, 1H), 4.22−4.00 (m, 4H), 3.67 (m, 4H), 2.07 (m, 2H), 1.90 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 211.3 (C), 153.7 (C), 142.0 (CH), 139.3 (C), 134.3 (C), 129.3 (C), 129.1 (CH), 128.3 (2 × CH), 127.3 (CH), 126.0 (2 × CH), 125.2 (CH), 124.9 (CH), 123.1 (CH), 119.2 (CH), 111.2 (C), 79.9 (CH), 77.2 (CH), 68.9 (CH_2), 65.3 (CH_2), 59.4 (C) 55.1 (CH_3), 46.3 (CH), 44.7 (CH), 28.7 (CH_2), 26.1 (CH_2). HRMS (EI): m/z calcd for $C_{27}H_{24}O_4$ 412.1675 [M^+], found 412.1679.

5-Benzoyl-2-*tert*-butyl-2,3-dihydro-4-methoxy-3-phenylnaphtho[2,1-*d*]isoxazole (5). Orange solid (109 mg; 50%). Mp: 221−223 °C. R_f 0.27 (HxH:AcOEt 3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.85 (d, J = 7.0 Hz, 1H), 7.62 (d, J = 7.0 Hz, 1H), 7.70−7.40 (m, 12H), 5.78 (s, 1H), 3,67 (s, 3H), 1.23 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.3 (C), 163.6 (C), 160.2 (C), 142.3 (C), 139.7 (C), 133.7 (C), 132.5 (CH), 130.3 (2 × CH), 130.4 (C), 128.5 (2 × CH), 128.7 (2 × CH), 128.0 (CH), 127.7 (2 × CH), 125.9 (CH), 125.7 (CH), 125.5 (CH), 122.1 (CH), 116.1 (C), 116.0 (C), 66.4 (CH), 63.5 (CH_3), 62.0 (C), 25.2 (3 × CH_3). HRMS (EI): m/z calcd for $C_{29}H_{27}NO_3$ 437.1991 [M^+], found 437.1990.

(6b*R,9a*R**)-2-(6b,8,9,9a-Tetrahydro-6-methoxynaphtho[1′,2′:3,4]cyclobuta[1,2-*b*]furan-5-yl)-2-trimethylsilyl-1-ethenone (7).** Yellow oil (88 mg; 52%). R_f 0.42 (HxH:AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, J = 8.6 Hz, 1H), 7.74 (d, J = 8.1 Hz, 1H), 7.51 (t, J = 8.2 Hz, 1H), 7.38 (t, J = 7.3 Hz, 1H), 5.81 (d, J = 3.0 Hz, 1H), 4.36 (dd, J = 8.0, 3.0 Hz, 1H), 4.17 (t, J = 8.5 Hz, 1H), 4.15 (s, 3H), 3.66 (ddd, J = 11.4, 9.5, 5.0 Hz, 1H), 2.11 (dd, J = 12.5, 4.9 Hz, 1H), 2.00−1.90 (m, 1H), 0.21 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.5 (C), 151.3 (C), 142.3 (C), 136.5 (C), 128.0 (C), 126.8 (CH), 126.5 (CH), 124.6 (C), 123.7 (CH), 122.9 (CH), 110.3 (C), 81.5 (OCH), 67.0 (OCH_2), 57.8 (OCH_3), 47.7 (CH), 28.2 (CH_2), 13.5 (C), −0.2 (3 × CH_3). HRMS (EI): m/z calcd for $C_{20}H_{22}O_3Si$ 338.1333 [M^+], found 338.1332.

2-(2-*tert*-Butyl-2,3-dihydro-4-methoxy-3-phenylnaphtho[2,1-*d*]isoxazol-5-yl)-2-(trimethylsilyl)ethenone (8). Yellow oil (102 mg; 46%). R_f 0.37 (HxH:AcOEt 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, J = 8.5 Hz, 1H), 7.99 (d, J = 8.1 Hz, 1H), 7.53 (t, J = 7.1 Hz, 1H), 7.44 (t, J = 7.2 Hz, 1H), 7.37−7.25 (m, 5H), 5.87 (s, 1H), 3.37 (s, 3H), 1.26 (s, 9H), 0.15 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.5 (C), 153.2 (C), 152.8 (C), 143.4 (C), 135.5 (C), 128.6 (2 × CH), 127.9 (2 × CH), 127.6 (CH), 126.8 (CH), 125.8 (CH), 124.3 (CH), 122.3 (CH), 117.4 (C), 116.2 (C), 109.7 (C), 66.9 (CH), 61.7 (C), 60.3 (OCH_3), 25.3 (3 × CH_3), 12.7 (C), −0.3 (3 × CH_3). HRMS (EI): m/z calcd for $C_{27}H_{31}NO_3Si$ 445.2068 [M^+], found 445.2066.

2-(1,4-Dihydro-1,4-methano-10-methoxyphenanthren-9-yl)-2-(trimethylsilyl)ethenone (9). Yellow oil (92 mg; 55%). R_f 0.50 (HxH:AcOEt 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, J = 9.4 Hz, 1H), 7.94 (d, J = 9.4 Hz, 1H), 7.45−7.42 (m, 2H), 7.08−7.00 (m, 2H), 4.56 (bs, 1H), 4.44 (bs, 1H), 3.96 (s, 3H), 2.51 (d, J = 6.7 Hz, 1H), 2.44 (d, J = 6.7 Hz, 1H), 0.28 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.9 (C), 152.7 (C), 150.9 (C), 143.8 (CH), 143.7 (CH), 143.1 (C), 132.9 (C), 126.9 (C), 126.6 (CH), 125.0 (CH), 124.3 (CH), 123.4 (CH), 114.0 (C), 71.9 (CH_2), 61.4

(23) Fischer, E. O.; Kreissl, F. R. *J. Organomet. Chem.* **1972**, *35*, C47–C51.

(OCH_3), 49.1 (CH), 48.5 (CH), 13.6 (C), 0.0 (3 × CH_3). HRMS (EI): *m/z* calcd for $C_{21}H_{22}O_2Si$ 334.1384 [M^+], found 334.1382.

(1*E*,5*E*)-5-Hydroxy-1-methoxy-6-(10-methoxy-3-trimethylsilyloxyphenanthren-9-yl)-6-trimethylsilylhexa-1,5-dien-3-one (10). Brown solid (119 mg; 47%). Mp: 151−155 °C. R_f 0.18 (HxH:AcOEt 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 (d, *J* = 8.0 Hz, 1H), 8.05 (d, *J* = 8.8 Hz, 1H), 8.01 (s, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.50−7.42 (m, 2H), 7.33 (d, *J* = 12.5 Hz, 1H), 7.19 (d, *J* = 8.7 Hz, 1H), 6.77 (bs, 1H), 5.48 (d, *J* = 12.5 Hz, 1H), 3.88 (s, 3H), 3.47 (s, 3H), 3.29 (d, *J* = 17.1 Hz, 1H), 3.13 (d, *J* = 17.1 Hz, 1H), 0.36 (s, 9H), 0.13 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.8 (CO), 162.9 (CH), 154.9 (C), 154.0 (C), 150.1 (C), 133.4 (C), 132.6 (C), 127.6 (C), 126.7 (CH), 126.6 (CH), 125.1 (C), 124.9 (CH), 124.7 (CH), 122.7 (CH), 122.3 (C), 116.9 (CH), 116.7 (C), 107.2 (CH), 104.4 (CH), 60.7 (OCH_3), 57.3 (OCH_3), 47.2 (CH_2), 1.4 (3 × CH_3), −0.2 (3 × CH_3). HRMS (EI): *m/z* calcd for $C_{28}H_{36}O_5Si_2$ 508.2096 [M^+], found 508.2088.

(3a*R,10c*R**)-2-{1,2,3a,10c-Tetrahydro-10-methyl-4-methoxy-10*H*-furo[3′,2′:3,4]cyclobuta[*i*]carbazol-5-yl}-2-trimethylsilyl-1-ethenone (12).** Yellow solid (133 mg; 68%). Mp: 167−171 °C. R_f 0.37 (HxH:AcOEt 3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.37 (d, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 8.2 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.20 (t, *J* = 8.1 Hz, 1H), 5.85 (d, *J* = 3.3 Hz, 1H), 4.39 (dd, *J* = 7.7, 3.3 Hz, 1H), 4.14 (dd, *J* = 9.2, 6.5 Hz, 1H), 4.05 (s, 3H), 3.86 (s, 3H), 3.60 (ddd, *J* = 11.0, 9.2, 5.4 Hz, 1H), 2.08−1.92 (m, 2H), 0.19 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 176.9 (C), 146.8 (C), 141.5 (C), 130.8 (C), 125.7 (C), 125.5 (CH), 125.3 (C), 123.7 (C), 122.9 (C), 122.6 (CH), 118.5 (CH), 110.2 (CH), 108.1 (CH), 82.5 (OCH), 66.6 (OCH_2), 57.7 (OCH_3), 47.1 (NCH_3), 30.5 (CH), 29.9 (CH_2), 15.1 (C), −0.2 (3 × CH_3). HRMS (EI): *m/z* calcd for $C_{23}H_{25}NO_3Si$ 391.1598 [M^+], found 391.1603.

2-(1,4-Dihydro-1,4-methano-5-methoxy-11-methyl-11*H*-benzo[*a*]carbazol-6-yl)-2-(trimethylsilyl)ethenone (13). Yellow oil (130 mg; 67%). R_f 0.44 (HxH:AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (d, *J* = 7.9 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.22 (t, *J* = 7.2 Hz, 1H), 6.98 (bs, 2H), 4.68 (bs, 1H), 4.37 (bs, 1H), 4.01 (s, 3H), 3.89 (s, 3H), 2.47 (d, *J* = 6.9 Hz, 1H), 2.43 (d, *J* = 6.9 Hz, 1H), 0.30 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.1 (C), 147.9 (C), 143.6 (CH), 143.4 (CH), 142.8 (C), 142.4 (C), 133.8 (C), 131.5 (C), 125.3 (CH), 123.7 (C), 123.6 (C), 122.2 (CH), 118.5 (CH), 112.4 (C), 107.8 (C), 70.5 (CH_2), 62.3 (OCH_3), 48.8 (CH), 47.7 (CH), 31.2 (NCH_3), 14.8 (C), 0.0 (3 × CH_3). HRMS (EI): *m/z* calcd for $C_{24}H_{25}NO_2Si$ 387.1649 [M^+], found 387.1643.

(1*E*,5*E*)-5-Hydroxy-1-methoxy-6-(5-methoxy-11-methyl-2-trimethylsiloxy-11*H*-benzo[*a*]carbazol-6-yl)-6-trimethylsilyl-hexa-1,5-dien-3-one (14). Brown solid (182 mg; 65%). Mp: 148−153 °C. R_f 0.31 (HxH:AcOEt 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (d, *J* = 8.0 Hz, 1H), 8.12 (d, *J* = 8.8 Hz, 1H), 7.93 (s, 1H), 7.47−7.41 (m, 2H), 7.23−7.19 (m, 1H), 7.22 (d, *J* = 12.5 Hz, 1H), 7.09 (d, *J* = 7.7 Hz, 1H), 6.30 (bs, 1H), 5.36 (d, *J* = 12.5 Hz, 1H), 4.14 (bs, 3H), 3.91 (s, 3H), 3.38 (s, 3H), 3.37 (d, *J* = 17.0 Hz, 1H), 3.21 (d, *J* = 17.0 Hz, 1H), 0.40 (s, 9H), 0.17 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.4 (CO), 162.7 (CH), 153.2 (C), 153.1 (C), 146.4 (C), 141.0 (C), 131.9 (C), 125.3 (CH), 124.2 (CH), 123.8 (C), 123.7 (C), 122.9 (C), 122.7 (C), 122.4 (CH), 118.7 (CH), 118.1 (C), 117.4 (C), 115.8 (CH), 108.6 (CH), 105.7 (CH), 104.5 (CH), 61.5 (OCH_3), 57.2 (OCH_3), 47.0 (CH_2), 33.7 (NCH_3), 1.6 (3 × CH_3), 0.0 (3 × CH_3). HRMS (EI): *m/z* calcd for $C_{31}H_{39}NO_5Si_2$ 561.2361 [M^+], found 561.2364.

General Procedure for the Preparation of Polycycles 16. Alkynyl carbene complex **15** (0.1 mmol) was dissolved in the corresponding enol ether (0.5 mL). The mixture was stirred at room temperature until TLC analysis showed the disappearance of the starting alkynyl carbene complex. Then the excess enol ether was removed under reduced pressure and a 9:1 mixture of hexane and AcOEt was added (20 mL). The resulting suspension was exposed to air and sunlight. Finally, the mixture was filtered through a pad of Celite, solvents were removed under reduced pressure, and the crude product was purified by column chromatography using a 3:1 mixture of hexane and ethyl acetate as eluent.

(3′a*R,5*S**,5′a*S**,7b*R**,10a*R**)-2′,3′,3′a,6′a,7b,9,10,10a-Octahydro-7-methoxy-4′-oxospiro{benzo[6′,7′]cyclohepta[3,4]cyclobuta[*b*]furan-5,5′-4′H-cyclobuta[*b*]furan} (16a).** Orange solid (25 mg; 72%). Mp: 200 °C dec. R_f 0.21 (HxH:AcOEt 3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51−7.26 (m, 4H), 5.32 (d, *J* = 3.0 Hz, 1H), 4.58 (s, 1H), 4.49 (d, *J* = 4.1 Hz, 1H), 4.29−3.88 (m, 4H), 3.66 (m, 1H), 3.58 (s, 3H), 3.09−2.96 (m, 1H), 2.22−1.72 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 213.7 (C), 154.2 (C), 149.0 (C), 135.2 (C), 132.6 (C), 131.0 (C), 130.4 (CH), 126.8 (CH), 125.0 (CH), 124.7 (2 × CH), 95.8 (CH), 81.0 (C), 77.2 (CH), 68.8 (CH_2), 67.7 (CH_2), 61.0 (CH_3), 55.2 (CH), 45.4 (CH), 29.1 (CH_2), 26.6 (CH_2). HRMS (EI): *m/z* calcd for $C_{21}H_{20}O_4$ 336.3811 [M^+], found 336.3816. Anal. Calcd for $C_{21}H_{20}O_4$: C, 74.98; H, 5.99. Found: C, 75.10; H, 6.11.

(4′a*R,5*S**,6′a*S**,7b*R**,11a*R**)-2′3′,4′,4′a,5′,6′a,9,10,11,11a-Decahydro-7-methoxy-5′-oxospiro{7bH-benzo[6′,7′]cyclohepta[3,4]-cyclobuta[*b*]pyran-5,6′-cyclobuta[*b*]pyran} (16b).** Yellow solid (18 mg; 49%). Mp: 200 °C dec. R_f 0.22 (HxH:AcOEt 3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48−7.27 (m, 4H), 5.10 (d, *J* = 3.1 Hz, 1H), 4.44 (s, 1H), 4.32 (d, *J* = 4.3 Hz, 1H), 4.31−3.89 (m, 4H), 3.67 (m, 1H), 3.44 (s, 3H), 3.00 (m, 1H), 2.24−1.99 (m, 7H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 214.0 (C), 155.2 (C), 150.1 (C), 135.4 (C), 132.1 (C), 131.7 (C), 130.0 (CH), 126.0 (CH), 125.7 (C), 125.2 (CH), 124.1 (CH), 96.2 (CH), 81.3 (C), 77.4 (CH), 68.8 (CH_2), 67.2 (CH_2), 59.9 (CH_3), 55.0 (CH), 45.3 (CH), 29.5 (CH_2), 26.0 (CH_2), 24.3 (CH_2), 22.5 (CH_2). HRMS (EI): *m/z* calcd for $C_{23}H_{24}O_4$ 364.1675 [M^+], found 364.1679.

General Procedure for the Preparation of Polycycles 17. Alkynyl carbene complex **15** (0.5 mmol) and the corresponding nitrone (1.5 mmol) were dissolved in CH_2Cl_2 (5 mL). The mixture was stirred at room temperature until the TLC analysis showed the disappearance of **15**. Hexane was added (20 mL), and the resulting suspension was exposed to air and sunlight. Finally, the mixture was filtered through a pad of Celite, solvents were removed under reduced pressure, and the crude product was purified by column chromatography using a 3:1 mixture of hexane and ethyl acetate as eluent.

2-*tert*-Butyl-2,3-dihydro-4-methoxy-3-phenylnaphtho[2,1-*d*]isoxazole-5-carbaldehyde (17a). Orange oil (112 mg; 62%). R_f 0.23 (HxH:AcOEt 3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.51 (s, 1H), 9.39 (d, *J* = 7.3 Hz, 1H), 8.05 (d, *J* = 7.3 Hz, 1H), 7.70 (t, *J* = 6.9 Hz, 1H), 7.52 (t, *J* = 6.9 Hz, 1H), 7.40−7.21 (m, 5H), 5.90 (s, 1H), 3,56 (s, 3H), 1.23 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 189.5 (CH), 163.6 (C), 160.2 (C), 142.3 (C), 133.7 (C), 130.4 (C), 128.7 (2 × CH), 128.0 (CH), 127.7 (2 × CH), 125.9 (CH), 125.7 (CH), 125.5 (CH), 122.1 (CH), 116.1 (C), 116.0 (C), 66.4 (CH), 63.5 (CH_3), 62.0 (C), 25.2 (3 × CH_3). HRMS (EI): *m/z* calcd for $C_{23}H_{23}NO_3$ 361.1678 [M^+], found 361.1681. Anal. Calcd for $C_{23}H_{23}NO_3$: C, 76.43; H, 6.41. Found: C, 76.67; H, 6.76.

2-Benzyl-2,3-dihydro-4-methoxy-3-phenylnaphtho[2,1-*d*]isoxazole-5-carbaldehyde (17b). Orange oil (124 mg; 63%). R_f 0.26 (HxH:AcOEt 5:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.61 (s, 1H), 9.27 (d, *J* = 7.0 Hz, 1H), 8.00 (d, *J* = 7.3 Hz, 1H), 7.78 (t, *J* = 6.6 Hz, 1H), 7.52−7.18 (m, 11H), 5.95 (s, 1H), 3.59 (d, *J* = 11.2 Hz, 1H), 3,43 (s, 3H), 3.29 (d, *J* = 11.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 190.2 (CH), 163.9 (C), 160.9 (C), 145.3 (C), 134.6 (C), 130.0 (C), 129.4 (C), 128.1 (2 × CH), 127.6 (2 × CH), 127.5 (CH), 127.4 (2 × CH), 126.9 (2 × CH), 126.2 (CH), 125.3 (CH), 125.1 (CH), 125.0 (CH), 122.5 (CH), 116.3 (C), 116.0 (C), 68.9 (CH), 65.3 (CH_3), 51.6 (CH_2). HRMS (EI): *m/z* calcd for $C_{26}H_{21}NO_3$ 395.1521 [M^+], found 395.1516. Anal. Calcd for $C_{26}H_{21}NO_3$: C, 78.97; H, 5.35. Found: C, 79.13; H, 5.43.

Computational Details. All calculations were performed with the Gaussian03 package of programs.[24] Full geometry optimizations were carried out with the B3LYP density functional method.[25] This hybrid functional is generally considered as a reliable method for transition-metal-containing large molecules.[26] Geometry optimizations were performed employing the relativistic effective core potential LANL2DZ[27] for Cr and the standard 6-31G* basis set for H, C, O, and Si (basis set denoted as LANL2DZ+6-31G*). Single-point energy calculations on the optimized structures were calculated by employing the relativistic effective core potential LANL2DZ for Cr and the 6-311++G** basis set for C, H, O, and Si (basis set denoted as LANL2DZ+6-311++G**). Harmonic force constants were computed at the optimized geometries employing the smaller basis set to characterize the stationary points as minima or saddle points. Zero-point vibrational corrections were determined from the harmonic vibrational frequencies to convert the total energies E_e to ground-state energies E_0. Intrinsic reaction coordinate calculations were conducted to verify the connection between the transition states and the minimum employing the Gonzalez and Schlegel method[28] implemented in Gaussian 03.

ΔG_{gas} values were calculated within the ideal gas, rigid rotor, and harmonic oscillator approximations. A pressure of 1 atm and a temperature of 298.15 K were assumed in the calculations. To take into account condensed-phase effects, a self-consistent reaction field model (SCRF) was applied. To evaluate the solvation Gibbs energies, single-point energy calculations at the gas-phase structures were performed within the polarizable continuum model (PCM)[29] using the united atom Hartree−Fock (UAHF) parametrization.[30] ΔG_{soln} was obtained by addition of the solvation Gibbs energy to the ΔG_{gas} value. A relative permittivity of 7.58 was employed to simulate THF as the solvent used in the experimental work. Unless otherwise indicated, the relative energy values indicated along the discussion will refer to Gibbs energies including the solvation contribution. Computational data, three-dimensional models, and Cartesian coordinates for all the stationary points found are included in the Supporting Information.

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Supporting Information Available: CIF files giving crystallographic data for compounds **12** and **16a** and text, tables, and figures giving experimental details for the synthesis of the precursor terminal alkynes of the dialkynyl Fischer carbene complexes, computational details (energies, 3D models, and Cartesian coordinates for the stationary points found), and NMR spectra for the polycyclic compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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