Unexpected Reaction Pathways in the Reaction of Alkoxyalkynylchromium(0) Carbenes with Aromatic Dinucleophiles**

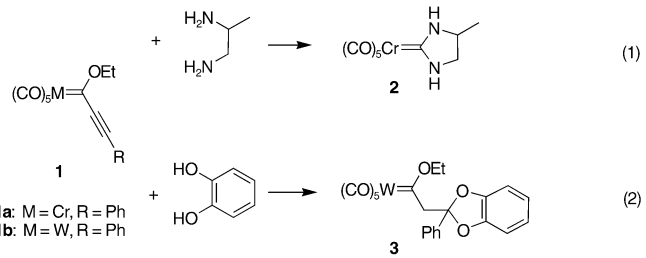
Miguel A. Sierra,* María J. Mancheño, Juan C. del Amo, Israel Fernández, and Mar Gómez-Gallego[a]

Abstract: Thermal- or SiO_2-induced reactions of the Michael adducts of 1,2-aromatic dinucleophiles and alkynylchromium(0) carbene complexes, compounds **7**–**10**, form different products in good yields depending on the nature of the aromatic dinucleophile used. Thus, 1,2-diaminobenzene derivatives **7** and **8** rearrange to pentacarbonylchromium(0) isocyanide complexes **11**, **12**, **14**, and **15** in a process that occurs through bicyclic intermediates **24**. Adducts **9** derived from *o*-aminophenol give 2,3-dihydro-1,5-benzoxazepine derivatives **17** by intramolecular 1,2-addition, followed by protonation at the chromium center and reductive elimination. In contrast, base-promoted addition of the phenolic hydroxy group in compound **9a** affords 3-ethoxy-5-phenyl-5,6-dihydro-2*H*-1,6-benzoxazocin-2-one (**18**), together with the expected adduct **17a**. Compound **18** is formed by a nucleophilic addition to a CO ligand in a preformed carbene complex. This is a new example of the rare attack of a nucleophile on a CO ligand in a Fischer carbene complex. Adducts **10** form seven-membered-ring carbene complexes **19** and **20** by intramolecular aminolysis. In contrast, reaction of alkynyl carbene complexes with 1,8-diaminonaphthalene under very mild conditions leads to 2-substituted perimidines **33** together with the corresponding ethoxymethylmetal carbene complex **32** through an unprecedented fragmentation process in a formal retro-Aumann reaction.

Keywords: addition reactions · carbene complexes · dinucleophiles · isocyanide complexes · perimidines · rearrangements

Introduction

Many reactions of α,β-unsaturated Group 6 Fischer carbene complexes and nucleophiles are analogous to those experienced by organic esters and amides.[2] However, in many cases, the presence of the metal fragment resulted in the formation of more sophisticated products than those expected from the standard 1,4- or 1,2-addition of the nucleophile.[3] The chemistry developed therefrom has resulted in an impressive array of synthetically useful processes.[4] Recently, we and others have demonstrated that the metal fragment of α,β-unsaturated chromium(0) carbene complexes also participates in the addition reactions of simple nucleophiles.[5] Simple amines may also produce other processes than the expected Michael additions in their reactions with α,β-unsaturated Group 6 (Fischer) carbenes. For example, Ricart recently reported the formation of cyclic diaminocarbene **2** in low yields by the reaction of complex **1a** and 1,2-diaminopropane (Reaction (1) of Scheme 1).[6] Additionally, the reaction of catechol with tungsten complex **1b** formed the bicyclic ketal **3** in a process claimed to be a double 1,4-addition process (Reaction (2) of Scheme 1).[7]



Scheme 1.

In spite of the number of reactions reported for α,β-unsaturated Fischer carbene complexes,[8] reactions in which a fragmentation of the carbon skeleton is involved are rare. At the beginning of this work, only one example of this kind of process had been described.[9a] Thus, Dötz and co-workers reported the spontaneous retro-Fischer fragmentation of complex **4** to form enyne **5** (Scheme 2). While this work was

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[**] A communication on part of this work has been published see ref. [1].

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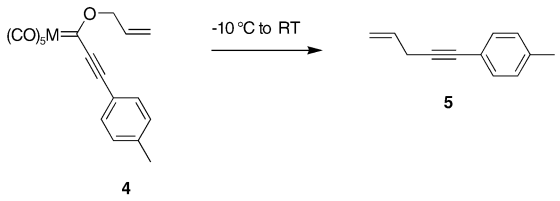
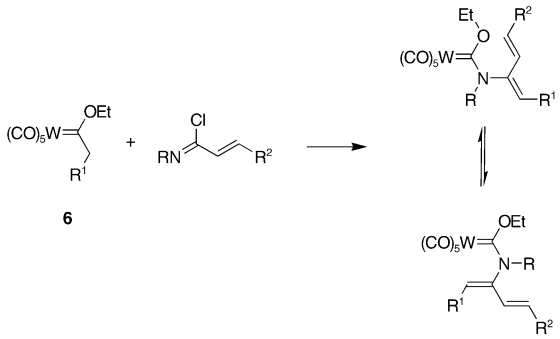


Scheme 2.

in progress, Aumann and co-workers described one more example of this type of fragmentation in the reaction of tungsten complexes **6** with 2-chloro-1,4-azadiene (Scheme 3).[9b]



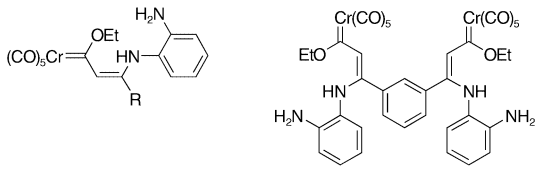
Scheme 3.

Abstract in Spanish: *Las reacciones, inducidas térmicamente o por tratamiento con SiO_2, de los aductos de tipo Michael derivados de la adición de 1,2-dinucleófilos aromáticos a alquinilcromo carbenos dan lugar a distintos productos con buenos rendimientos en función de la naturaleza del dinucleófilo aromático empleado. Así, los derivados de 1,2-diaminobenceno, **7** y **8**, sufren un reordenamiento del esqueleto para formar los complejos de isonitrilo coordinados a cromo **11**, **12**, **14** y **15** en un proceso que ocurre a través de los intermedios bicíclicos **24**. Los aductos **9** provenientes de o-aminofenol forman los derivados 2,3-dihidro-1,5-benzoxacepina **17** mediante adición 1,2-intramolecular, seguida de protonación en el centro metálico y eliminación reductora. En cambio, la adición promovida por base del grupo fenólico en el compuesto **9a** proporciona 3-etoxi-5-fenil-5,6-dihidro-2H-1,6-benzoxazocin-2-ona, **18**, junto con el aducto esperado **17a**. El compuesto **18** se forma mediante adición nucleófila a un ligando CO en un complejo carbénico preformado. Este proceso constituye un nuevo ejemplo de la poco estudiada reactividad derivada del ataque de un nucleófilo a un ligando CO en un complejo de Fischer. Por otro lado, los aductos **10** forman los complejos cíclicos de siete eslabones **17** y **20** mediante aminolisis intramolecular. Esto contrasta con la reactividad de los complejos alquinilcarbenoides **1** con 1,8-diaminonaftaleno que conducen en condiciones de reacción muy suaves a las perimidinas 2-sustituidas **33** junto con el correspondiente etoximetilmetalcarbeno **34**, a través de un proceso de fragmentación sin precedentes que puede considerarse como una reacción de tipo "retro-Aumann".*

These precedents make it probable that even the well-known addition of amines and phenols to α,β-unsaturated chromium(0) carbenes may, under some conditions, occur with the participation of the metal center to afford products other than the Michael or 1,2-adducts.[10] In our ongoing project directed towards the synthesis of polymetallic structures,[11] as well as in the development of methods for the addition of radicals to α,β-unsaturated complexes,[12] we obtained some anomalous results for the addition of aromatic 1,2-dinucleophiles to alkynylchromium(0) carbene complexes. Different addition processes were observed as a function of the dinucleophile employed and led to 2,3-dihydro-1,5-benzoxazepine derivatives, unprecedented rearrangement of alkoxychromium(0) carbene complexes to pentacarbonylisocyanide chromium complexes, as well as novel fragmentation processes. Reported herein is a detailed account of these processes.

Results and Discussion

The substrates used in our study (complexes **7**–**10**) were prepared by 1,4-addition of 1,2-diaminobenzene (compounds **7** and **8**), *o*-aminophenol (compounds **9** and **10c**), catechol (compound **10a**), and *o*-aminothiophenol (compound **10b**) to the corresponding alkynylchromium(0) carbene complexes, following the standard reported method.[6, 13]



7a R = Ph
7b R = Fc
7c R = *n*Pr

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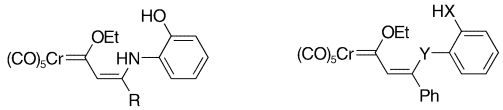
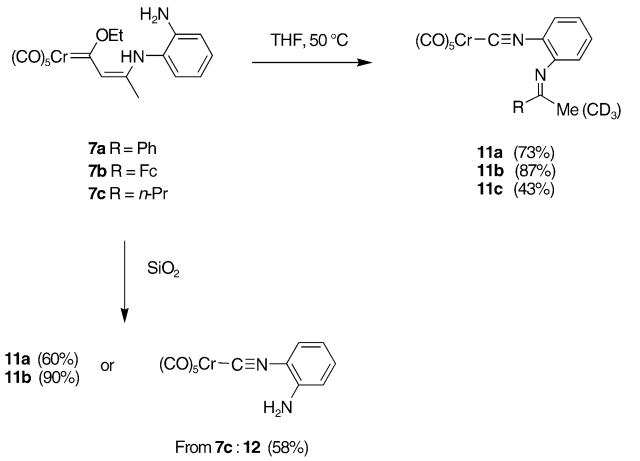


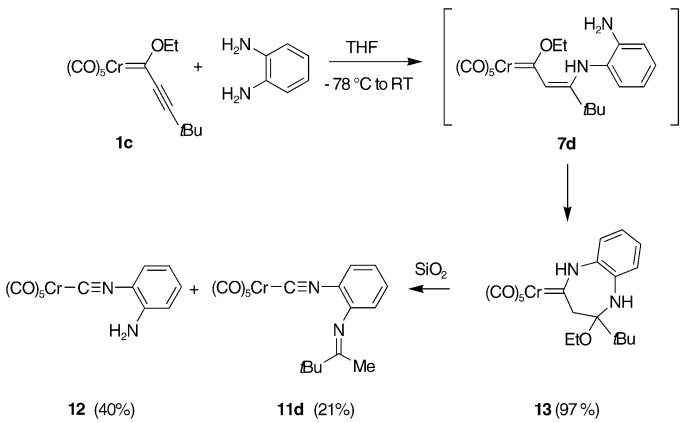
9a R = Ph
9b R = Fc

10a X = Y = O
10b X = NH, Y = S
10c X = NH, Y = O

Complexes **7a**–**c**, which contain a 1,2-diaminobenzene moiety, smoothly react to give new chromium complexes on gentle heating in THF (Scheme 4). These new products lack the carbene ligand and their outstanding NMR characteristics were the presence of a signal attributable to a methyl group ($\delta = 1.76-2.27$ and $16.1-20.4$ ppm for ^{1}H and ^{13}C NMR, respectively), as well as a signal assignable to a quaternary carbon between $\delta = 214.2-214.5$ ppm in their ^{13}C NMR spectra. Additionally, when complex **7b** was heated in THF containing CD_3OD, the signal attributable to the CH_3 group disappeared, indicating the complete incorporation of deuterium in this group. A single monocrystal of the product derived from complex **7b** was analyzed by X-ray diffraction.[1] The structure of isocyanide complex **11b** was thus established for this compound (Scheme 4), and hence for compounds **11a**



Scheme 4.

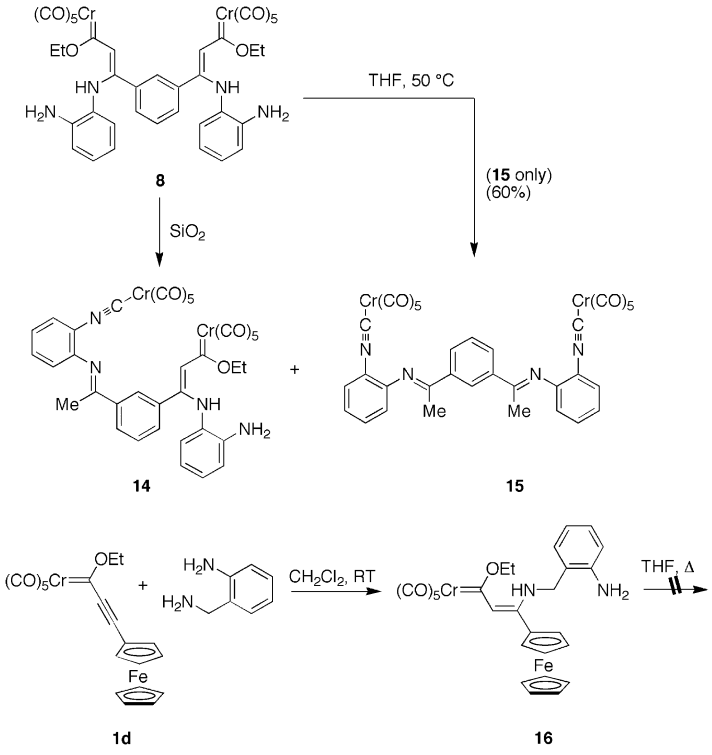


Scheme 5.

and **11c** obtained from complexes **7a** and **7c**, respectively.[14] The rearrangement alkoxychromium(0) carbene → pentacarbonylchromium(0) isocyanide also occurred in the presence of silica gel, and compounds **11** could be obtained from compounds **7** either by column chromatography or by stirring a solution of complexes **7** in THF in the presence of SiO_2. Under these conditions compound **7c** produced complex **12** as a result of the hydrolysis of the imine group of the initially formed isocyanide complex **11c**. This is an expected result because aliphatic imines are considerably more prone to hydrolysis than aromatic imines.

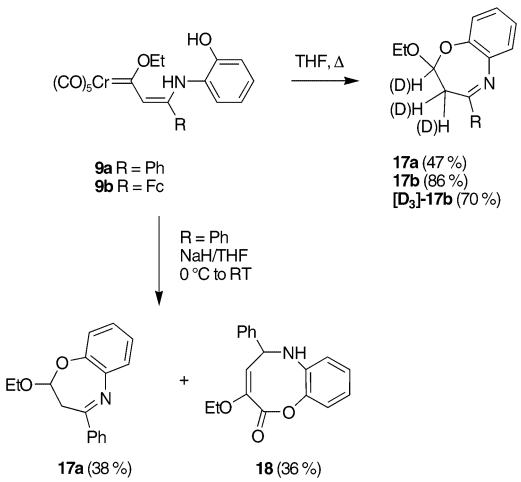
A different reaction outcome was obtained when complex **1c** was reacted with 1,2-diaminobenzene in THF from $-78\,^{\circ}C$ to room temperature. Under these conditions, instead of the expected isocyanide complex **11d** or its hydrolysis product **12**, a new chromium complex was obtained. As representative features, this compound retained the $[(CO)_5Cr]$ moiety ($\delta =$ 223.0 ppm (CO_{trans}) and ($\delta = 217.4$ ppm (CO_{cis})), a carbene carbon ($\delta = 285.1$ ppm), and two diastereotopic methylene groups, one of which corresponded to the OCH_2 group ($\delta =$ 3.45 and 3.30 ppm). Additionally, the carbene signal at $\delta =$ 285.1 ppm clearly correlated with the signals corresponding to the additional CH_2 group $\delta = 4.21$ and 2.52 ppm) in an HMBC experiment. These and the additional data collected (see the Experimental Section) allowed us to assign structure **13** to this compound. Furthermore, while complex **13** remained unchanged after prolonged heating in THF, it rapidly gave a mixture of the isocyanide complexes **11d** and **12** upon silica-gel chromatography. Therefore, we can conclude that complex **13** is a product derived from the quenching of an intermediate in the rearrangement of the nonisolated primary addition product, **7d**, to the isocyanide complex **11d** (Scheme 5).

A double carbene → isocyanide rearrangement can also be performed in one step with the bisadduct **8**. Treatment of compound **8** with SiO_2 resulted in a mixture of complex **14**, that contained one rearranged carbene moiety and an unaltered metal carbene fragment, together with the doubly rearranged complex **15**, and unreacted starting material. The doubly rearranged product **15** was isolated in an acceptable yield of 60% by heating complex **8** in THF. Thus, two simultaneous rearrangements can be effected in a single operation (Scheme 6). The 1,2-disposition of the diamino groups is essential for the reaction to take place. Because adduct **16**, derived from the addition of the more basic aliphatic amino group of *o*-aminobenzylamine to complex **1d**, remained unaltered under the usual reaction conditions and only decomposed after prolonged heating. This behavior differs dramatically compared to that experienced by adducts **7** derived from 1,2-diaminobenzene (Scheme 6).



Scheme 6.

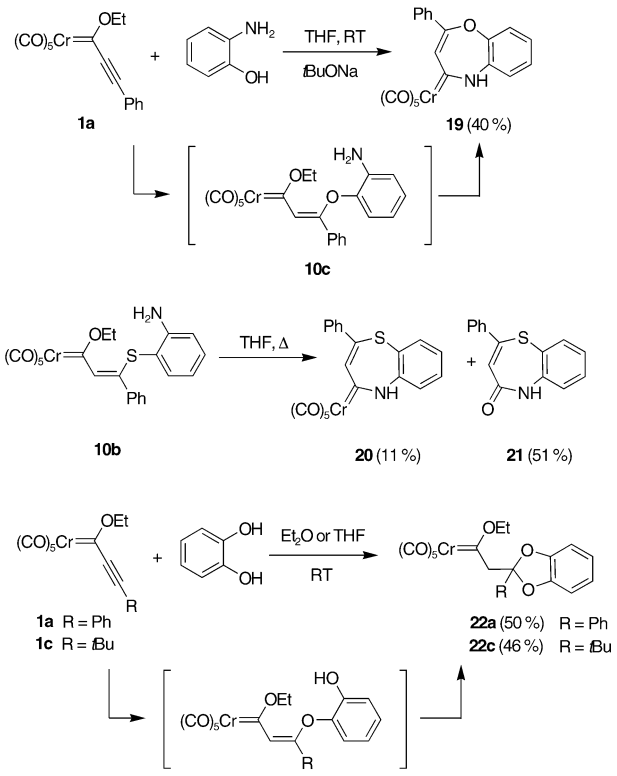
Complexes **9** derived from *o*-aminophenol were studied next. These compounds were stable on silica gel but also reacted to give a new class of compounds upon heating in THF. These new products did not retain the metallic moiety and their spectroscopic data were fully compatible with the 2,3-dihydro-1,5-benzoxazepine structure **17** (Scheme 7). In addition, the trideuterated compound [D_3]-**17b** was obtained when complex **9b** was heated in THF containing CD_3OD. In



Scheme 7.

an attempt to induce the cyclization at a low temperature by increasing the nucleophilicity of the phenol group, adduct **9a** was treated with NaH/THF at 0 °C. Upon warming to room temperature, a mixture of 2,3-dihydro-1,5-benzoxazepine (**17a**) and a new compound **18** were obtained in 38% and 36% yields, respectively. This new compound incorporated one additional carbon in its structure which suggested the incorporation of one CO ligand. Based on extensive 1D and 2D NMR studies and analytical data, the structure of 3-ethoxy-5-phenyl-5,6-dihydro-2*H*-1,6-benzoxazocin-2-one (**18**) was assigned to this compound (Scheme 7).

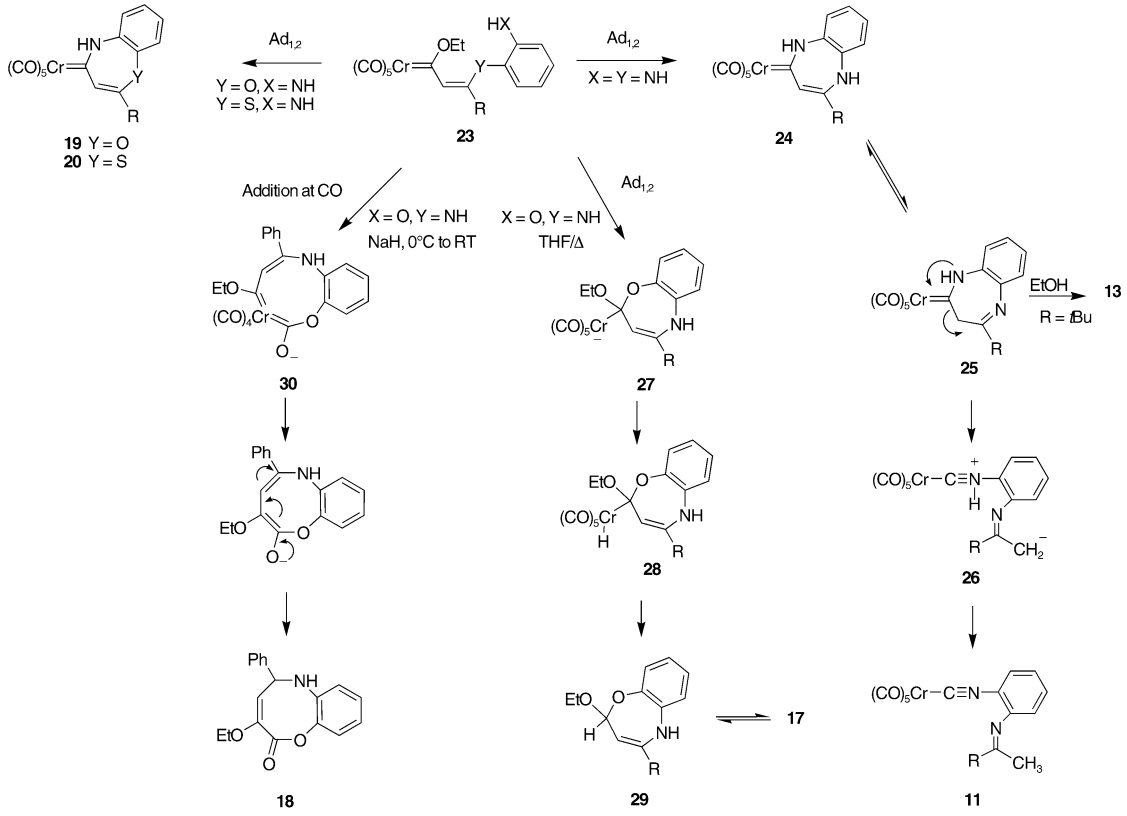
To reverse the regiochemistry of the addition of *o*-aminophenol to the carbene triple bond, the phenol group was deprotonated with *t*BuONa and the resulting phenolate reacted with chromium complex **1a**. Under these conditions, 1,4-addition takes place and the cyclic complex **19** arising from the intramolecular aminolysis was obtained. No 1,4-adduct **10c** was observed. The trend observed in the addition of the phenoxide anion derived from *o*-aminophenol was maintained for adduct **10b** derived from *o*-aminothiophenol and complex **1a**. In this case, carbene complex **20** together with its oxidation product **21** were obtained in 11% and 51% yields, respectively, by heating compound **10b** in THF. Finally, 1,2-dihydroxybenzene reacted with complexes **1a** and **1c** to form the bicyclic dioxolane complexes **22**. These results are analogous to those reported for the tungsten derivative **1b** (R = Ph) (Scheme 8).[7]



Scheme 8.

The nature of the reaction products, in the processes discussed above, depends on the additional nucleophile group once an amino group has been added to the triple bond, and on the structure of the 1,2-adducts formed by evolution of the intermediates **23**. Thus, the results obtained may be rationalized through two divergent reaction pathways (Scheme 9). Compounds **7** and **8** would form intermediates **24** by intramolecular 1,2-addition and afford **26** through breakage of the bond α to chromium center in their imine tautomers **25**. Finally, protonation of enolate **26** would give compounds **11**. Support for this proposal can be found in the isolation of hemiaminal complex **13**, which should be formed by EtOH addition to intermediate **25** (R = *t*Bu) and which produces isonitrile complexes **11d** and **12** by acid hydrolysis. Compounds **9** also form the corresponding 1,2-adducts **27**. In these cases, the electron-donor ability of the heteroatom (O) joined to the carbene is less than that observed for a nitrogen derivative and α-bond breakage does not occur. Thus, the intermediates **27** primarily formed by intramolecular 1,2-addition are protonated at the metal center followed by reductive elimination in **28** to yield benzoxazepines **17** after imine–enamine tautomerism of **29**. In these cases, the incorporation of the label occurs at the former carbene carbon and at the methylene group. No label incorporation was observed when compound **17b** (R = Fc) was heated in the presence of CD_3OD. Therefore, the deuterium should be incorporated in the enamine **29** to imine **17** tautomerism, which explains the appearance of two additional labels in compound [D_3]-**17b**. In contrast, compound **18** is formed through the competitive addition of *o*-aminophenolate to one CO ligand to form intermediate **30** that gives the isolated compound **18** by reductive elimination. This is one of the rare examples of nucleophilic attack on a CO ligand in a preformed Group 6 metal carbene complex.[15] Finally, the reaction of deprotonated *o*-aminophenol leads to the initial conjugated addition of phenolate, followed by base-catalyzed 1,2-addition of the amino group and ethoxide elimination to form the cyclic carbene complexes **19**. However, reaction of *o*-aminothiophenol with carbene complex **1a** allows the isolation of adduct **10b** that gives carbene complex **20** (11%) and its oxidation product **21** (51%) on refluxing in THF.

From the above results it is clear that if the 1,2-addition process can be inhibited, maybe, new processes could be discovered. Therefore, the *peri*-interaction present in 1,8-diaminonaphtalene **31** should inhibit the 1,2-addition. Reaction of carbene complexes **1** with **31** in CH_2Cl_2 at room

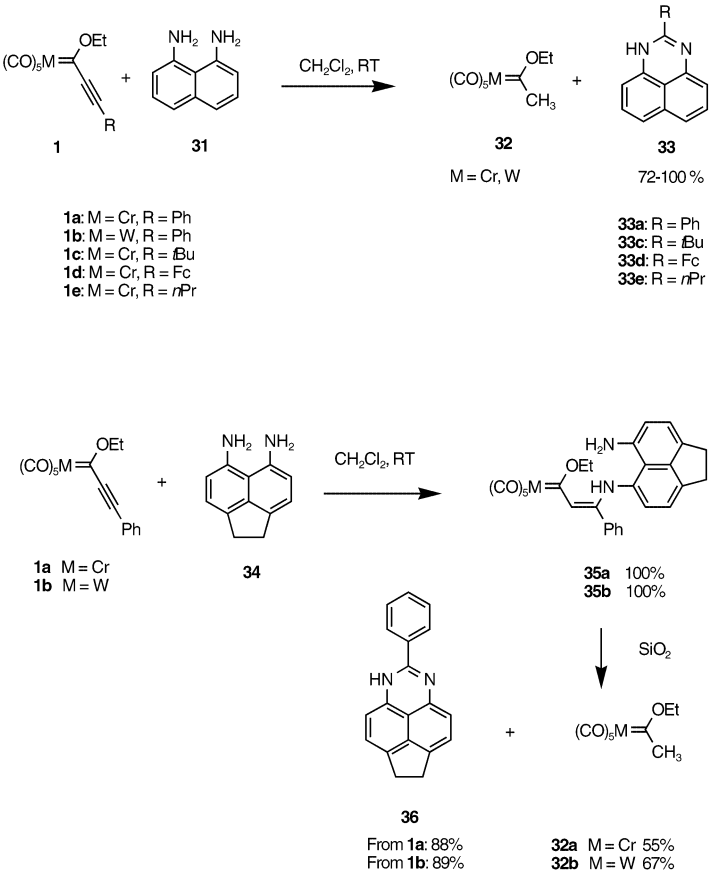


Scheme 9.

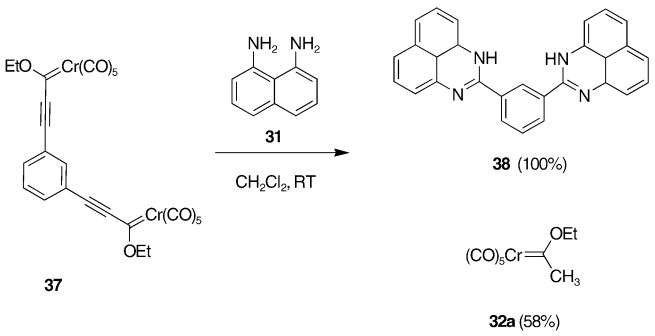
temperature produced a new complex identified as pentacarbonyl[(ethoxy)methylcarbene]metal(0) **32**, together with a new nonmetallic compound (Scheme 10). The spectroscopic and analytical data for this compound were consistent with the perimidine structure **33**. The reaction is independent of the nature of the substituent attached to the triple bond. Thus, aryl, ferrocenyl, and alkyl substituents produce the heterocyclic compounds **33** in excellent yields. The reaction is general for cyclic systems having diamino groups in a relative *peri*-position, as proved by the reaction of carbene complexes **1a** and **1b** with 5,6-diaminoacenaphthene **34**[16] that forms compounds **35**. These products can be converted into the heterocyclic compound **36** in 88% and 89% yields, respectively, together with the corresponding metal–carbene complex **32** (55% and 67% yield) by silica-gel treatment (Scheme 10).

More sophisticated structures can be obtained by this procedure in a single step. A double rearrangement was performed on biscarbene complex **37** with 1,8-diaminonaphthalene **31** (1:2 stoichiometric ratio) to give quantitative yields of compound **38**, which contains two 1,3-diazaphenalenyl moieties. The metallic fragment was recovered again as complex **32a** (Scheme 11).

To establish the mechanism of this novel rearrangement, the reaction of complex **1a** (M = Cr, R = Ph) and diamine **31** was carried out in CD_3OD. The deuterated perimidine [D_1]-**33** (R = Ph) was obtained together with the monodeuterated carbene complex [D_1]-**32a**. This result suggests the participation of a chromium carbene enolate as an intermediate in the



Scheme 10.

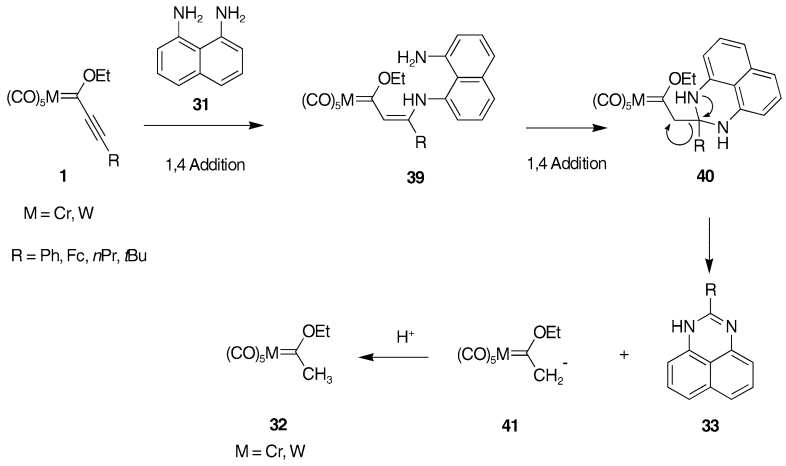


Scheme 11.

formation of complex **32a**. Deuterium could be incorporated by deuteration of this enolate to yield the labeled compound [D_1]-**32a**. The isolation of compounds **35** in the reaction implies that the observed rearrangement is initiated by the Michael addition of diamine **31** to the alkynyl carbene complex to form the intermediate complex **39**. This intermediate should afford complex **40** by conjugated addition. Intermediate **40** should have a strong *peri*-interaction released by cleavage to form perimidine **33** together with enolate **41**, that protonates to yield chromium carbene complex **32**. This transformation, which leads to the ethoxymethyl carbene complex by the cleavage of the α-carbon bond of the carbene, might be considered to be an unprecedented "retro-Aumann reaction" (Scheme 12).[17]

Conclusion

The thermal- or SiO_2-induced reactions of the Michael adducts of 1,2-aromatic dinucleophiles and alkynylchromium(0)carbene complexes form different products in excellent yields, depending on the nature of the dinucleophile. Thus, 1,2-diaminobenzene derivatives **7** and **8** rearranged to pentacarbonylchromium(0) isocyanide complexes **11** and **15**, respectively, through bicyclic intermediates **25**. The evidence for intermediates **25** was obtained by the isolation of compound **13** in the reaction of complex **1c** and 1,2-diaminobenzene. *o*-Aminophenol-derived adducts give 2,3-dihydro-1,5-benzoxazepine derivatives **17** by intramolecular 1,2-addition, followed by protonation at the chromium center and reductive elimination. When the intramolecular addition was promoted by base-deprotonation of the phenol, 3-ethoxy-5-phenyl-5,6-dihydro-2*H*-1,6-benzoxazocin-2-one (**18**) was isolated together with the expected adduct **17a**. Finally, adducts **10b** and **10c** form seven-membered-ring carbene complexes **20** and **19** by intramolecular aminolysis. In contrast, the use of 1,8-diaminonaphthalene promotes a new reaction pathway through a fragmentation process that might be considered to be an unprecedented "retro-Aumann" reaction. This novel cleavage allows the synthesis of perimidines in good yields under mild reaction conditions.[18]



Scheme 12.

Experimental Section

General procedures: ^{1}H NMR and ^{13}C NMR spectra were recorded at 25 °C as specified on a Varian XL-300S (300.1 and 75.4 MHz), Bruker Avance 300 (300.1 and 75.4 MHz) and Bruker 200-AC (200.1 and 50 MHz) spectrometers. Chemical shifts are given relative to TMS ($\delta(^1H) = 0.0$ ppm) or $CDCl_3$ ($\delta(^{13}C) = 77.0$ ppm). IR spectra were taken on a Perkin–Elmer 781 spectrometer. Mass spectra were carried out on a GC-MS HP-5989 (60 eV) mass spectrometer with methanol as the solvent. Melting points were determined on a Gallenkamp apparatus and are uncorrected. All solvents used in this work were purified by distillation and were freshly distilled immediately before use. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium benzophenone, CH_2Cl_2 and Et_3N from CaH_2. Flame-dried glassware and standard Schlenk techniques were used for moisture-sensitive reactions. Merck silica gel (230–400 mesh) was used as the stationary phase for the purification of crude reaction mixtures by flash column chromatography. Products were identified by TLC (kiesegel 60F-254), UV light ($\lambda = 254$ nm); 5% phosphomolybdic acid solution in 95% EtOH was used to develop the plates. All commercially available compounds were used without further purification. The following products were prepared according to literature methods:

Ethynylferrocene,[19] pentacarbonyl[(ethoxy)(2-phenylethynyl)carbene]-chromium(0),[20] decacarbonyl-[μ-1,3-phenylenediethynyl)bis(ethoxycarbene)]dichromium(0),[11a] pentacarbonyl[(ethoxy)(2-propyl-ethynyl)carbene]chromium(0),[21] pentacarbonyl[(ethoxy)(2-*tert*-butylethynyl)carbene]-chromium(0).[21]

Pentacarbonyl[(ethoxy)(2-ferrocenylethynyl)carbene]chromium(0) (1d): To a solution of ethynylferrocene (1.6 g, 7.62 mmol) in dry Et_2O (30 mL) at −78 °C was added dropwise *n*-butyllithium (5.3 mL, 8.38 mmol, 1.6 M in hexanes). The mixture was stirred at −78 °C for 45 min and then the solution was transferred via cannula at 0 °C to a suspension of chromium hexacarbonyl (1.75 g, 7.62 mmol) in dry Et_2O (40 mL) at 0 °C. The mixture was allowed to reach room temperature and was stirred for 15 min. Anhydrous THF (40 mL) was added and the mixture was stirred at room temperature overnight. Et_3OBF_4 (2.89 g, 15.24 mmol) was added in one portion at −78 °C. The solution was stirred at this temperature for 15 min and then allowed to reach room temperature for an additional hour. Solvents were removed under reduced pressure and the residue was dissolved in Et_2O and filtered on silica gel. The solvent was evaporated and the residue was subjected to flash column chromatography under argon pressure (SiO_2, hexanes) to give complex **1d** (2.29 g, 66%) as a deep purple solid. ^{1}H NMR (200 MHz, $CDCl_3$):

$\delta = 4.58$ (q, $J = 7.1$ Hz, 2H; OCH_2), 4.55 (m, 4H; CH), 4.22 (s, 5H; Cp), 1.48 ppm (t, $J = 7.1$ Hz, 3H; CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 309.0$ (Cr=C), 225.6 (CO_{trans}), 216.7 (CO_{cis}), 145.4 (Cq), 92.6 (Cq), 75.4 (OCH_2), 73.4 (CH), 72.7 (CH), 71.0 (Cp), 60.4 (Cq), 14.9 ppm (CH_3); IR (CCl_4): $\tilde{\nu} =$ 2131, 2056, 1988, 1952, 1292, 1198 cm^{-1}; elemental analysis calcd (%) for $C_{20}H_{14}CrFeO_6$: C 52.43, H 3.08; found: C 52.71, H 3.33.

Synthesis of α,β-unsaturated alkoxychromium(0) carbenes 7, 8, 16, 9, 10, 35, and 13: These compounds were synthesized following the method described by Ricart et al.[6]

Pentacarbonyl[(ethoxy)(2-phenyl-2-(*o*-phenylenediamine)ethenyl)carbene]chromium(0) (7a): To a solution of pentacarbonyl[(ethoxy)(2-phenylethynyl)carbene]chromium(0) (**1a**, 350 mg, 1 mmol) in anhydrous THF (50 mL) at $-78\,^{\circ}C$ was added *o*-phenylenediamine (108 mg, 1 mmol). The mixture was allowed to reach room temperature and was then stirred until the starting material had disappeared (2 h, checked by TLC). The solvent was removed in vacuo, and the residue was subjected to flash column chromatography under argon pressure (SiO_2, hexanes) to give carbene complex **7a** (388 mg, 85%) as a red solid. ^1H NMR (300 MHz, $CDCl_3$): $\delta =$ 10.02 (brs, 1H; NH), 7.24 (m, 5H; ArH), 6.86 (t, ^1J (H, H) = 6.7 Hz, 1H; ArH), 6.66 (d, $J = 8.0$ Hz, 1H; ArH), 6.59 (s, 1H; CH), 6.44–6.30 (m, 2H; ArH), 4.88 (q, $J = 7.0$ Hz, 2H; OCH_2), 3.76 (brs, 2H; NH_2), 1.57 ppm (t, $J =$ 7.0 Hz, 3H; CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 300.5$ (Cr=C), 224.0 (CO_{trans}), 218.3 (CO_{cis}), 149.3, 140.2, 134.8, 130.2, 128.6, 128.5, 127.1, 126.3, 125.3, 121.7, 118.9, 116.3 (aromatic C and CH), 74.7 (OCH_2), 15.8 ppm (CH_3); IR (CCl_4): $\tilde{\nu} = 2050$, 1921, 1539, 1188 cm^{-1}; elemental analysis calcd (%) for $C_{22}H_{18}CrN_2O_6$: C 57.64, H 3.96, N 6.11; found: C 57.79, H 4.23, N 6.27.

Pentacarbonyl[(ethoxy)(2-ferrocenyl-2-(*o*-phenylenediamine)ethenyl)carbene]chromium(0) (7b): To a solution of pentacarbonyl[(ethoxy)(2-ferrocenylethynyl) carbene]chromium(0) (**1d**, 458 mg, 1 mmol) in anhydrous THF (50 mL) at $-30\,^{\circ}C$ was added *o*-phenylenediamine (108 mg, 1 mmol). The mixture was allowed to reach room temperature and was then stirred until the starting material had disappeared (5 h, checked by TLC). The solvent was removed in vacuo, and the crude residue was crystallized at low temperature in pentane/Et_2O (1:1) to afford carbene complex **7b** (419 mg, 74%) as a dark red solid. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 10.22$ (brs, 1H; NH), 6.98 (m, 1H; ArH), 6.96 (s, 1H; CH), 6.68 (d, $^1J = 7.8$ Hz, 1H; ArH), 6.61–6.52 (m, 2H; ArH), 4.75 (q, $J = 6.9$ Hz, 2H; OCH_2), 4.28 (d, $J =$ 2.1 Hz, 2H; CH), 4.26 (d, $J = 2.1$ Hz, 2H; CH), 4.16 (s, 5H; Cp), 3.71(brs, 2H; NH_2), 1.48 ppm (t, $J = 6.9$ Hz, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 286.1$ (Cr=C), 224.1 (CO_{trans}), 219.0 (CO_{cis}), 153.7, 140.9, 128.0, 126.7, 124.9, 121.2, 118.7, 116.3 (aromatic C and CH), 81.3 (Cq), 76.8 (OCH_2), 73.7 (CH), 71.2 (CH), 70.8 (Cp), 15.8 ppm (CH_3); IR (CCl_4): $\tilde{\nu} = 2046$, 1925, 1545, 1508, 1194 cm^{-1}; elemental analysis calcd (%) for $C_{26}H_{22}CrFeN_2O_6$: C 55.14, H 3.92, N 4.95; found: C 55.29, H 4.18, N 5.13.

Pentacarbonyl[(2-propyl-2-(*o*-phenylenediamine)ethenyl)carbene](ethoxy)chromium(0) (7c): To a solution of pentacarbonyl[(ethoxy)(2-propylethynyl)carbene]chromium(0) (**1e**, 150 mg, 0.47 mmol) in anhydrous THF (25 mL) at $-78\,^{\circ}C$ was added *o*-phenylenediamine (51 mg, 0.47 mmol). The mixture was allowed to reach room temperature and was then stirred until the starting material had disappeared (45 min, checked by TLC). The solvent was removed in vacuo to give carbene complex **7c** (200 mg, 99%) as a dark yellow oil. No further purification was required. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 9.95$ (brs, 1H; NH), 7.10 (t, $J = 7.5$ Hz, 1H; ArH), 6.92 (d, $J = 7.5$ Hz, 1H; ArH), 6.74–6.69 (m, 2H; ArH), 6.35 (s, 1H; CH), 4.79 (q, $J = 6.9$ Hz, 2H; OCH_2), 3.73 (brs, 2H; NH_2), 2.08 (t, $J = 7.5$ Hz, 2H; CH_2), 1.47 (t, $J = 6.9$ Hz, 3H; CH_3), 1.45 (m, 2H; CH_2), 0.81 ppm (t, $J =$ 7.2 Hz, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 293.2$ (Cr=C), 223.9 (CO_{trans}), 218.6 (CO_{cis}), 157.1, 142.2, 129.3, 127.5, 122.3, 119.0, 118.6, 116.2 (aromatic C and CH), 74.0 (OCH_2), 34.2 (CH_2), 21.8 (CH_2), 15.8 (CH_3), 13.8 ppm (CH_3); IR (CCl_4): $\tilde{\nu} = 2050$, 1927, 1547, 1190 cm^{-1}; elemental analysis calcd (%) for $C_{19}H_{20}CrN_2O_6$: C 53.77, H 4.75, N 6.60; found: C 53.94, H 4.89, N 6.77.

Synthesis of *bis*-carbene complex (8): To a solution of decacarbonyl[(μ-1,3-phenylenediethynyl)bis(ethoxycarbene)]dichromium(0)[11a] (**37**, 200 mg, 0.32 mmol) in anhydrous THF (15 mL) at $-78\,^{\circ}C$ was added *o*-phenylenediamine (70 mg, 0.64 mmol). The mixture was allowed to reach room temperature and was then stirred until the starting material had disappeared (30 min, checked by TLC). The solvent was removed in vacuo to yield biscarbene complex **8** (270 mg, 100%) as a deep red solid. No further purification was required. ^1H NMR (200 MHz, $CDCl_3$): $\delta = 9.84$ (brs, 2H; NH), 7.27–7.07 (m, 4H; ArH), 6.83 (t, $J = 7.4$ Hz, 2H; ArH), 6.67 (d, $J =$ 7.6 Hz, 2H; ArH), 6.43 (s, 2H; CH), 6.40 (d, $J = 7.3$ Hz, 2H; ArH), 6.08 (m, 2H; ArH), 4.90 (q, $J = 7.0$ Hz, 4H; OCH_2), 3.77 (brs, 4H; NH_2), 1.57 ppm (t, $J = 7.0$ Hz, 6H; CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 302.9$ (Cr=C), 224.0 (CO_{trans}), 218.1 (CO_{cis}), 147.5, 140.6, 135.6, 130.3, 128.7, 128.4, 127.3, 126.3, 124.9, 121.5, 118.6, 116.5 (aromatic C and CH), 74.9 (OCH_2), 15.7 ppm (CH_3); IR (CCl_4): $\tilde{\nu} = 2050$, 1931, 1541, 1184 cm^{-1}; elemental analysis calcd (%) for $C_{38}H_{30}Cr_2N_4O_{12}$: C 54.42, H 3.61, N 6.68; found: C 54.70, H 3.85, N 6.83.

Pentacarbonyl[(ethoxy)(2-ferrocenyl-2-(*o*-aminobenzylamino)ethenyl)carbene]chromium(0) (16): To a solution of pentacarbonyl[(ethoxy)(2-ferrocenylethynyl)carbene]chromium(0) (**1d**, 100 mg, 0.22 mmol) in anhydrous CH_2Cl_2 (5 mL) at room temperature was added *o*-aminobenzylamine (27 mg, 0.22 mmol). The mixture was stirred until the starting material had disappeared (3 h, checked by TLC). The solvent was removed in vacuo to afford carbene complex **16** (120 mg, 95%) as a dark orange solid. No further purification was required. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 9.29$ (brs, 1H; NH), 7.11 (t, $J = 7.2$ Hz, 1H; ArH), 7.05 (d, $J = 7.5$ Hz, 1H; ArH), 6.76 (s, 1H; CH), 6.73 (t, $J = 7.5$ Hz, 1H; ArH), 6.66 (d, $J = 7.8$ Hz, 1H; ArH), 4.60 (s, 2H; CH), 4.50 (q, $J = 7.2$ Hz, 2H; OCH_2), 4.45 (s, 2H; CH), 4.34 (d, $J = 5.1$ Hz, 2H; CH_2), 4.25 (s, 5H; Cp), 3.51 (s, 2H; NH_2), 0.98 ppm (t, $J = 7.2$ Hz, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 280.2$ (Cr=C), 224.2 (CO_{trans}), 219.3 (CO_{cis}), 156.4, 144.3, 129.8, 129.5, 120.6, 119.6, 119.1, 116.4 (aromatic C and CH), 81.3 (Cq), 73.2 (CH), 71.4 (CH), 71.1 (OCH_2), 70.8 (Cp), 47.2 (CH_2), 14.7 ppm (CH_3); IR (CCl_4): $\tilde{\nu} = 2046$, 1923, 1545 cm^{-1}; elemental analysis calcd (%) for $C_{27}H_{24}CrFeN_2O_6$: C 55.88, H 4.17, N 4.83; found: C 55.61, H 4.03, N 5.01.

Pentacarbonyl[(ethoxy)(2-phenyl-2-(*o*-hydroxyphenylamino)ethenyl)carbene]chromium(0) (9a): To a solution of pentacarbonyl[(ethoxy)(2-phenylethynyl)carbene]chromium(0) (**1a**, 700 mg, 2 mmol) in anhydrous THF (80 mL) at $-78\,^{\circ}C$ was added *o*-aminophenol (218 mg, 2 mmol). The mixture was allowed to reach room temperature and was then stirred until the starting material had disappeared (2 h, checked by TLC). The solvent was removed in vacuo to afford carbene complex **9a** (900 mg, 98%) as a red solid. No further purification was required. ^1H NMR (200 MHz, $CDCl_3$): $\delta = 10.38$ (brs, 1H; NH), 7.29 (m, 5H; ArH), 6.81 (brs, 2H; ArH), 6.54 (s, 1H; CH), 6.46 (t, $J = 7.5$ Hz, 1H; ArH), 6.19 (d, $J = 7.8$ Hz, 1H; ArH), 4.91 (q, $J = 7.0$ Hz, 2H; OCH_2), 1.60 ppm (t, $J = 7.0$ Hz, 3H; CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 300.7$ (Cr=C), 224.2 (CO_{trans}), 218.3 (CO_{cis}), 147.4, 146.7, 135.2, 130.2, 128.7, 126.4, 125.7, 123.9, 122.5, 120.4, 115.7 (aromatic C and CH), 74.9 (OCH_2), 15.7 ppm (CH_3); IR (CCl_4): $\tilde{\nu} = 2048$, 1969, 1929, 1547, 1221, 1197 cm^{-1}; elemental analysis calcd (%) for $C_{22}H_{17}CrNO_7$: C 57.52, H 3.73, N 3.05; found: C 57.74, H 3.91, N 2.92.

Pentacarbonyl[(ethoxy)(2-ferrocenyl-2-(*o*-hydroxyphenylamino)ethenyl)carbene]chromium(0) (9b): To a solution of pentacarbonyl[(ethoxy)(2-ferrocenylethynyl)carbene]chromium(0) (**1d**, 150 mg, 0.33 mmol) in anhydrous THF (15 mL) at $-78\,^{\circ}C$ was added *o*-aminophenol (36 mg, 0.33 mmol). The mixture was allowed to reach room temperature and was then stirred until the starting material had disappeared (4 h, checked by TLC). The solvent was removed in vacuo to afford carbene complex **9b** (185 mg, 100%) as a dark red solid. No further purification was required. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 10.32$ (brs, 1H; NH), 7.04 (s, 1H; CH), 6.95 (brs, 1H; ArH), 6.80 (brs, 1H; ArH), 6.64 (t, $J = 7.5$ Hz, 1H; ArH), 6.55 (d, $J = 7.5$ Hz, 1H; ArH), 5.34 (brs, 1H; OH), 4.76 (q, $J = 7.0$ Hz, 2H; OCH_2), 4.29 (m, 4H; CH), 4.18 (s, 5H; Cp), 1.49 ppm (t, $J = 7.0$ Hz, 3H; CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 288.6$ (Cr=C), 224.2 (CO_{trans}), 219.0 (CO_{cis}), 151.0, 148.2, 126.9, 126.2, 125.3, 122.4, 120.6, 116.0 (aromatic C and CH), 77.9 (Cq), 74.0 (OCH_2), 71.2 (CH), 71.0 (Cp), 70.5 (CH), 15.7 ppm (CH_3); IR (CCl_4): $\tilde{\nu}$ 2046, 1985, 1919, 1549, 1439 cm^{-1}; elemental analysis calcd (%) for $C_{26}H_{21}CrFeNO_7$: C 55.05, H 3.73, N 2.47; found: C 55.19, H 3.96, N 2.62.

Pentacarbonyl[(ethoxy)(2-phenyl-2-(*o*-aminobenzenethiol)ethenyl)carbene]chromium(0) (10b): To a solution of pentacarbonyl[(ethoxy)(2-phenylethynyl)carbene]chromium(0) (**1a**, 350 mg, 1 mmol) in anhydrous THF (50 mL) at $-78\,^{\circ}C$ was added *o*-aminobenzenethiol (125 mg, 1 mmol). The mixture was allowed to reach room temperature and was then stirred until the starting material had disappeared (1.5 h, checked by TLC). The solvent was removed in vacuo and the crude reaction was submitted to flash column chromatography to yield carbene complex **10b** (226 mg, 48%) as a dark red solid. ^1H NMR (200 MHz, $CDCl_3$): $\delta = 7.38–7.19$ (m, 7H; ArH),

6.82 – 6.73 (m, 3H; ArH and CH), 4.47 (q, $J = 7.0$ Hz, 2H; OCH_2), 4.33 (br s, 2H; NH_2), 0.75 ppm (t, $J = 7.0$ Hz, 3H; CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 326.0$ (Cr=C), 224.0 (CO_{trans}), 216.5 (CO_{cis}), 149.0, 144.5, 138.2, 137.1, 135.1, 132.6, 128.6, 128.2, 119.3, 115.9, 111.6 (aromatic C and CH), 75.8 (OCH_2), 13.8 ppm (CH_3); IR (CCl_4): $\tilde{\nu} = 2054$, 1979, 1940, 1610, 1541, 1230 cm^{-1}; elemental analysis calcd (%) for $C_{22}H_{17}CrNO_6S$: C 55.58, H 3.60, N 2.95, S 6.74; found: C 55.79, H 3.83, N 2.82, S 6.58.

[(2*Z*)(3-(6-aminoacenaphthen-5-ylamino)-3-phenyl-2-propenyliden]pentacarbonylchromium(0) (35a): Complex **1a** (150 mg, 0.43 mmol) and 5,6-diaminoacenaphthene (**34**, 79 mg, 0.43 mmol) in CH_2Cl_2 (15 mL) were stirred for 6.5 h at room temperature to give complex **35a** (229 mg, 100%) as a dark red solid. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 10.96$ (br s, 1H; NH), 7.31 – 7.15 (m, 5H; ArH), 7.04 (d, $J = 7.4$ Hz, 1H; ArH), 6.74 – 6.70 (m, 2H; ArH), 6.65 (s, 1H; CH), 6.35 (d, $J = 7.4$ Hz, 1H; ArH), 4.91 (q, $J = 7.0$ Hz, 2H; OCH_2), 4.30 (s, 2H; NH_2), 3.18 (m, 4H; $2CH_2$), 1.57 ppm (t, $J = 7.0$ Hz, 3H; CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 300.7$ (Cr=C), 224.1 (CO_{trans}), 218.3 (CO_{cis}), 147.9, 144.8, 141.5, 139.2, 137.0, 135.3, 131.2, 129.8, 129.3, 128.7, 128.5, 126.0, 125.5, 122.6, 118.7, 114.4 (aromatic C and CH), 75.0 (OCH_2), 30.3 (CH_2), 29.7 (CH_2), 15.7 ppm (CH_3); IR (CCl_4): $\tilde{\nu} = 2050$, 1983, 1927, 1535, 1219 cm^{-1}; elemental analysis calcd (%) for $C_{28}H_{22}CrN_2O_6$: C 62.92, H 4.15, N 5.24; found: C 63.15, H 4.32, N 5.41.

[(2*Z*)(3-(6-aminoacenaphthen-5-ylamino)-3-phenyl-2-propenyliden]pentacarbonyltungsten(0) (35b): Analogously to complex **35a**, complex **1b** (150 mg, 0.31 mmol) and 5,6-diaminoacenaphthene (**34**, 57 mg, 0.31 mmol) in CH_2Cl_2 (15 mL) were stirred at room temperature for 6 h to give complex **35b** (206 mg, 100%) as a dark red solid. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 11.10$ (br s, 1H; NH), 7.31 – 7.17 (m, 5H; ArH), 7.04 (d, $J = 7.4$ Hz, 1H; ArH), 6.74 – 6.70 (m, 3H; ArH and CH), 6.37 (d, $J = 7.4$ Hz, 1H; ArH), 4.76 (q, $J = 7.1$ Hz, 2H; OCH_2), 4.29 (br s, 2H; NH_2), 3.18 (m, 4H; $2CH_2$), 1.54 ppm (t, $J = 7.1$ Hz, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 277.3$ (W=C), 203.8 (CO_{trans}), 199.0 (CO_{cis}), 151.5, 144.9, 141.5, 139.1, 137.1, 135.2, 131.1, 130.0, 129.1, 128.6, 125.5, 125.4, 120.4, 118.8, 117.6, 114.5 (aromatic C and CH), 77.6 (OCH_2) , 30.3 (CH_2), 29.7 (CH_2), 15.5 ppm (CH_3); IR (CCl_4): $\tilde{\nu} = 2058$, 1969, 1929, 1537, 1219 cm^{-1}; elemental analysis calcd (%) for $C_{28}H_{22}N_2O_6W$: C 50.47; H 3.33; N 4.20; found, C 50.70, H 3.21, N 4.36.

Complex 13: To a solution of pentacarbonyl[(ethoxy)(2-*tert*-butylethynyl)-carbene]chromium(0) (**1c**, 225 mg, 0.68 mmol) in anhydrous THF (22 mL) at $-78\,^\circ C$ was added *o*-phenylenediamine (74 mg, 0.68 mmol). The mixture was allowed to reach room temperature and was then stirred until the starting material had disappeared (1.5 h, checked by TLC). The solvent was removed in vacuo to give complex **13** (290 mg, 97%) as a dark yellow solid. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 10.32$ (br s, 1H; NH), 7.11 – 7.00 (m, 2H; ArH), 6.80 (t, $J = 7.5$ Hz, 1H; ArH), 6.72 (d, $J = 8.1$ Hz, 1H; ArH), 4.63 (s, 1H; NH), 4.21 (d, $J = 12.9$ Hz, 1H; CH_2), 3.45 (m, 1H; OCH_2), 3.30 (m, 1H; OCH_2), 2.52 (d, $J = 12.9$ Hz, 1H; CH_2), 1.05 (t, $J = 7.0$ Hz, 3H; CH_3), 1.03 ppm (s, 9H; CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 285.1$ (Cr=C), 223.0 (CO_{trans}), 217.4 (CO_{cis}), 139.0, 128.6, 126.8, 123.6, 119.5, 119.2 (aromatic C and CH), 99.0 (Cq), 60.2 (OCH_2), 53.4 (CH_2), 42.9 (Cq), 25.4 (CH_3), 15.3 ppm (CH_3); IR (CCl_4): $\tilde{\nu} = 2056$, 1944, 1913, 1473 cm^{-1}.

Synthesis of isocyanidechromium(0) complexes:

Isocyanide complex 11a

Method A: SiO_2 (500 mg) was added to a solution of carbene complex **7a** (50 mg, 0.11 mmol) in hexanes/AcOEt 10:1 at room temperature. The heterogeneous mixture was stirred under argon pressure until the starting material disappeared (48 h, checked by TLC). The crude reaction mixture was dissolved in AcOEt and filtered through a short pad of Celite. Flash column chromatography yielded compound **11a** (27 mg, 60%) as a pale yellow solid.

Method B: A solution of complex **7a** (100 mg, 0.22 mmol) in anhydrous THF (5 mL) was heated at $50\,^\circ C$ under an argon atmosphere until the starting material had disappeared (8 h, checked by TLC). The crude reaction mixture was dissolved into a mixture of hexanes/Et_2O (2:1) and filtered through a double pad of Celite and SiO_2 to yield, after removing the solvent, compound **11a** (66 mg, 73%). M.p. 94 – 96 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.97$ (d, $J = 7.5$, 2H; ArH), 7.44 – 7.32 (m, 3H; ArH), 7.29 (t, $J = 7.2$ Hz, 2H; ArH), 7.03 (t, $J = 7.2$ Hz, 1H; ArH), 6.82 (d, $J = 7.8$ Hz, 1H; ArH), 2.23 ppm (s, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 216.6$ (CO_{trans}), 214.5 (Cr-CN), 214.3 (CO_{cis}), 168.6 (C=N), 148.5, 137.9, 131.4, 129.7, 128.4, 128.4, 127.5, 126.2, 123.7, 120.5 (aromatic C and CH), 18.0 ppm (CH_3); IR (CCl_4): $\tilde{\nu} = 2137$ (CN), 2054, 1998, 1958, 1639 cm^{-1}; elemental analysis calcd (%) for $C_{20}H_{12}CrN_2O_5$: C 58.26, H 2.93, N 6.79; found: C 58.51, H 3.17, N 6.65.

Isocyanide complex 11b: Complex **7b** (1.13 g, 2 mmol) was subjected to flash column chromatography on silica gel under argon pressure to yield complex **11b** (935 mg, 90%) as an orange solid. M.p. 135 °C (decomp); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.32 – 7.24$ (m, 2H; ArH), 7.01 (t, $J = 7.3$ Hz, 1H; ArH), 6.79 (d, $J = 7.8$ Hz, 1H; ArH), 4.77 (s, 2H; CH), 4.40 (s, 2H; CH), 4.16 (s, 5H; Cp), 2.08 ppm (s, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 216.7$ (CO_{trans}), 214.5 (Cr-CN), 214.3 (CO_{cis}), 171.2 (C=N), 148.8, 129.5, 126.2, 123.4, 120.7 (aromatic C and CH), 82.0 (Cq), 71.2 (CH), 69.5 (Cp), 68.8 (CH), 18.6 ppm (CH_3); IR (CCl_4): $\tilde{\nu} = 2141$ (CN), 2056, 1998, 1954, 1626, 1464, 1215 cm^{-1}; MS (ESI): 521.1 $[M+H]^+$; elemental analysis calcd (%) for $C_{24}H_{16}CrFeN_2O_5$: C 55.41, H 3.10, N 5.38; found: C 55.64, H 3.27, N 5.55.

Deuteration experiments: A solution of carbene **7b** (100 mg, 0.18 mmol) in anhydrous THF (2.5 mL) and CD_3OD (0.5 mL) was heated at $50\,^\circ C$ under an argon atmosphere until the starting material had disappeared (10 h, checked by TLC). The solvent was removed under reduced pressure and the crude reaction mixture was dissolved in hexanes/Et_2O (2:1) and filtered through a double pad of Celite and SiO_2 to yield, after removing the solvent, compound **[D_3]-11b** (80 mg, 87%).

Isocyanide complex 11c: A solution of complex **7c** (100 mg, 0.24 mmol) in anhydrous THF was heated at $50\,^\circ C$ under an argon atmosphere until the starting material had disappeared (29 h, checked by TLC). The solvent was removed under reduced pressure and the crude reaction mixture was dissolved in hexanes/Et_2O (1:1) and filtered through a short pad of Celite. The solvent was evaporated to yield (37 mg, 43%) complex **11c** as a yellow oil. No further purification was required. ^1H NMR (200 MHz, $CDCl_3$): $\delta = 7.28 – 7.19$ (m, 2H; ArH), 6.99 (m, 1H; ArH), 6.71 (d, $J = 7.7$ Hz, 1H; ArH), 2.43 (t, $J = 7.3$ Hz, 2H; CH_2), 1.77 (s, 3H; CH_3), 1.68 (m, 2H; CH_2), 0.97 ppm (t, $J = 7.3$ Hz, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 216.7$ (CO_{trans}), 214.5 (CO_{cis}), 175.7 (C=N), 148.3, 129.7, 126.5, 123.5, 120.7 (aromatic C and CH), 42.9 (CH_2), 20.4 (CH_3), 19.3 (CH_2), 13.7 ppm (CH_3). The signal attributable to the isonitrile group could not be detected; IR (CCl_4): $\tilde{\nu} = 2139$ (CN), 2056, 1996, 1956, 1664, 1477, 1446, 1257 cm^{-1}.

Isocyanide complex 12: To a solution of complex **7c** (100 mg, 0.24 mmol) in hexanes/AcOEt 10:1 at room temperature was added SiO_2 (1.0 g). The mixture was stirred under an argon atmosphere until the starting material had disappeared (46 h, checked by TLC). The solvent was removed under reduced pressure and the crude reaction mixture was dissolved in AcOEt and filtered through a short pad of Celite. Flash column chromatography yielded compound **12** (43 mg, 58%) as a white solid. M.p. 195 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.15 – 7.08$ (m, 2H; ArH), 6.75 – 6.65 (m, 2H; ArH), 3.99 ppm (br s, 2H; NH_2); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 216.6$ (CO_{trans}), 214.5 (CO_{cis}), 142.8, 130.1, 126.4, 118.5, 115.8 ppm (aromatic C and CH). The signal attributable to the isonitrile group could not be detected; IR (CCl_4): $\tilde{\nu} = 2143$ (CN), 2058, 1940, 1495 cm^{-1}; elemental analysis calcd (%) for $C_{12}H_6CrN_2O_5$: C 46.47, H 1.95, N 9.03; found: C 46.72, H 2.17, N 9.18.

Isocyanide complexes 11d and 12: To a solution of complex **1c** (102 mg, 0.76 mmol) in 25 mL of anhydrous THF at $-78\,^\circ C$ was added 1,2-diaminobenzene (82 mg, 0.76 mmol). The mixture was allowed to reach room temperature and stirred under an argon atmosphere until the starting material had disappeared (1 h, checked by TLC). The solvent was removed under reduced pressure and the crude reaction mixture was purified by flash column chromatography to yield compound **11d** (63 mg, 21%) as an oil and complex **12** (93 mg, 40%).

11d: ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.30 – 7.20$ (m, 2H; ArH), 6.98 (t, $J = 7.4$ Hz, 1H; ArH), 6.63 (d, $J = 7.9$ Hz, 1H; ArH), 1.76 (s, 3H; CH_3), 1.22 ppm (s, 9H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 216.7$ (CO_{trans}), 214.5 (CO_{cis}), 181.8 (C=N), 148.0, 129.7, 127.4, 123.4, 120.4 (aromatic C and CH), 40.8 (Cq), 27.8 (CH_3), 16.1 ppm (CH_3). The signal corresponding to the isonitrile group could not be detected; IR (CCl_4): $\tilde{\nu} = 2139$ (CN), 2056, 1996, 1958, 1655, 1475 cm^{-1}; elemental analysis calcd (%) for $C_{18}H_{16}CrN_2O_5$: C 55.11, H 4.11, N 7.14; found: C 55.35, H 4.29, N 7.33.

Decacarbonyl[bisisocyanide]dichromium(0)] complex (15): A solution of complex **8** (100 mg, 0.12 mmol) in anhydrous THF (5 mL) was heated at $50\,^\circ C$ under an argon atmosphere until the starting material had disappeared (17 h, checked by TLC). The mixture was subjected to flash chromatography under argon pressure (SiO_2, hexanes) to yield complex **15**

(54 mg, 60%) as an oil. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.64$ (s, 1H; ArH), 8.13 (m, 2H; ArH), 7.32–7.25 (m, 5H; ArH), 7.05 (t, $J = 7.3$ Hz, 2H; ArH), 6.82 (d, $J = 7.5$ Hz, 2H; ArH), 2.27 ppm (s, 6H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 216.6$ (CO_{trans}), 214.3 (Cr-CN), 214.3 (CO_{cis}), 168.0 (C=N), 148.4, 138.0, 130.4 129.7, 128.6, 128.4, 126.2, 123.8, 120.5, 118.1 (aromatic C and CH), 18.0 ppm (CH_3); IR (CCl_4): $\tilde{\nu} = 2137$ (CN), 2054, 1998, 1959, 1637, 1223 cm^{-1}; elemental analysis calcd (%) for $C_{34}H_{18}Cr_2N_4O_{10}$: C 54.70, H 2.43, N 7.51; found: C 54.94, H 2.27, N 7.68.

Synthesis of decacarbonyl[isocyanide-carbene]dichromium(0) complex (14) and bisisocyanide complex (15): To a solution of decacarbonyl[(μ-1,3-phenylenediethynyl)bis(ethoxycarbene)]dichromium(0) (**37**, 250 mg, 0.4 mmol) in anhydrous THF (20 mL) at −78 °C was added *o*-phenylenediamine (86 mg, 0.8 mmol). The mixture was stirred until the starting material had disappeared (30 min, checked by TLC). The solvent was removed in vacuo, and the crude reaction mixture was submitted to flash column chromatography to yield the bisisocyanide complex **15** (86 mg, 29%), complex **14** (80 mg, 25%), as a deep red solid, and the starting biscarbene complex (40 mg, 12%).

14: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 9.95$ (brs, 1H; NH), 8.10 (s, 1H; ArH), 7.97 (s, 1H; ArH), 7.28 (m, 4H; ArH), 7.05 (m, 1H; ArH), 6.89–6.78 (m, 2H; ArH), 6.68–6.64 (m, 2H; CH and ArH), 6.43–6.40 (m, 2H; ArH), 4.92 (q, $J = 6.9$ Hz, 2H; OCH_2), 3.79 (brs, 2H; NH_2), 2.14 (s, 3H; CH_3), 1.59 ppm (t, $J = 6.9$ Hz, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 301.8$ (Cr=C), 224.1 (CO_{trans}), 218.2 (CO_{cis}), 216.5 (CO_{trans}), 214.2 (CO_{cis}), 173.5, 167.3, 148.2, 140.4, 138.2, 135.1, 131.4, 129.7, 129.2, 128.6, 128.1, 127.4, 126.5, 126.1, 125.0, 123.9, 121.9, 120.3, 119.1, 118.0, 116.4 (aromatic C and CH), 74.8 (OCH_2), 17.6 (CH_3), 15.8 ppm (CH_3). The signal corresponding to the isonitrile group could not be detected.; IR (CCl_4): $\tilde{\nu} = 2137$ (CN), 2052, 1998, 1959, 1932, 1541, 1373, 1188 cm^{-1}; elemental analysis calcd (%) for $C_{36}H_{24}Cr_2N_4O_{11}$: C 54.55, H 3.05, N 7.07; found: C 54.74, H 3.21, N 7.26.

2-Ethoxy-4-phenyl-2,3-dihydro-1,5-benzoxazepine (17a): A solution of complex **9a** (100 mg, 0.22 mmol) in anhydrous THF (5 mL) was refluxed under argon atmosphere until the starting material had disappeared (5 h, checked by TLC). The solvent was removed in vacuo, the crude reaction mixture was dissolved in hexanes/Et_2O (2:1) and filtered through a double pad of SiO_2 and Celite. The solvent was removed under reduced pressure to give compound **17a** (27 mg, 47%) as a brown solid. M.p. 64–66 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.95$–7.92 (m, 2H; ArH), 7.42–7.40 (m, 3H; ArH), 7.26–7.23 (m, 1H; ArH), 7.15 (m, 1H; ArH), 7.08 (m, 1H; ArH), 7.02–7.00 (m, 1H; ArH), 5.54 (dd, $^1J = 9.7$ Hz, $^2J = 3.8$ Hz, 1H; CH), 4.01 (m, 1H; OCH_2), 3.64 (m, 1H; OCH_2), 3.26 (dd, $^1J = 13.8$ Hz, $^2J = 3.8$ Hz, 1H; CH_2), 2.70 (dd, $^1J = 13.8$ Hz, $^2J = 9.7$ Hz, 1H; CH_2), 1.60 ppm (t, $J = 7.1$ Hz, 3H; CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 165.5$ (C=N), 145.0 (Cq), 142.4 (Cq), 138.6 (Cq), 130.7, 128.6, 127.3, 126.7, 126.2, 124.7 and 123.4, (aromatic CH), 109.3 (CH), 64.1 (OCH_2), 35.8 (CH_2), 15.1 ppm (CH_3); IR (CCl_4): $\tilde{\nu} = 1608$, 1572, 1477, 1221, 1097 cm^{-1}; MS (ESI): 268.3 $[M+H]^+$.

2-Ethoxy-4-ferrocenyl-2,3-dihydro-1,5-benzoxazepine (17b): A solution of complex **9b** (96 mg, 0.17 mmol) in anhydrous THF (5 mL) was refluxed under argon atmosphere until the starting material had disappeared (5 h, checked by TLC). The solvent was removed in vacuo, the crude reaction mixture was dissolved in hexanes/Et_2O (2:1) and filtered through a double pad of SiO_2 and Celite. The solvent was removed under reduced pressure to give compound **17b** (54 mg, 86%) as an orange solid. M.p. 89–91 °C; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.16$–6.95 (m, 4H; ArH), 5.54 (dd, $^1J = 9.6$ Hz, $^2J = 4.1$ Hz, 1H; CH), 4.86 (brs, 1H; CH), 4.76 (brs, 1H; CH), 4.44 (brs, 2H; CH), 4.16 (s, 5H; Cp), 4.09 (m, 1H; OCH_2), 3.66 (m, 1H; OCH_2), 2.88 (dd, $^1J = 13.7$ Hz, $^2J = 4.1$ Hz, 1H; CH_2), 2.61 (dd, $^1J = 13.7$ Hz, $^2J = 9.6$ Hz, 1H; CH_2), 1.26 ppm (t, $J = 7.1$ Hz, 3H; CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 167.9$ (C=N), 144.9 (Cq), 142.8 (Cq), 126.3, 125.4, 124.8, 123.4 (aromatic CH), 109.3 (CH), 82.6 (Cq), 71.6 (CH), 71.1 (CH), 69.7 (Cp), 68.3 (CH), 68.2 (CH), 63.9 (OCH_2), 36.9 (CH_2), 15.1 ppm (CH_3); IR (CCl_4): $\tilde{\nu} =$ 1605, 1585, 1472, 1097 cm^{-1}; elemental analysis calcd (%) for $C_{21}H_{21}FeNO_2$: C 67.22, H 5.64, N 3.73; found: C 67.05, H 5.81, N 3.89.

Deuteration experiment: A solution of complex **9b** (100 mg, 0.18 mmol) in anhydrous THF (5 mL) and CD_3OD (0.5 mL) was heated at 50 °C under an argon atmosphere until the starting material had disappeared (24 h, checked by TLC). The solvent was removed under reduced pressure and the crude reaction mixture was dissolved in hexanes/Et_2O (1:1) and filtered through a double pad of Celite and SiO_2 to give, after removing the solvent, compound **[D_3]-17b** (46 mg, 70%) with 33% of deuteration grade in the CH group, and 58% and 72% of deuteration grade in the methylene group.

3-Ethoxy-5-phenyl-5,6-dihydro-2*H*-1,6-benzoxazocin-2-one (18): To a solution of complex **9a** (100 mg, 0.22 mmol) in anhydrous THF (2 mL) at 0 °C was added 10.5 mg of NaH (0.26 mmol, 60% in mineral oil). The reaction was stirred at 0 °C during 1 h, left to reach room temperature, then stirred until the starting material had disappeared (4 h, checked by TLC). The mixture was quenched with H_2O, dried over $MgSO_4$, and filtered through a short pad of Celite. Flash column chromatography on silica gel yielded compound **17a** (23 mg, 39%), and compound **18** (23 mg, 36%) as a pale yellow solid.

18: M.p. 165–167 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.09$ (s, 1H; NH), 7.20–7.13 (m, 3H; ArH), 7.07–6.91 (m, 5H; ArH), 6.73 (t, $J = 8.0$ Hz, 1H; ArH), 5.88 (d, $J = 2.3$ Hz, 1H; CH), 5.68 (d, $J = 2.3$ Hz, 1H; CH), 3.94 (q, $J = 7.0$ Hz, 2H; OCH_2), 1.39 ppm (t, $J = 7.0$ Hz, 3H; CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 166.4$ (Cq), 150.9 (Cq), 148.2 (Cq), 135.2 (Cq), 129.1, 128.5, 128.0, 126.5, 125.6 (Cq), 123.0, 121.0, 120.9 (aromatic CH), 113.2 (CH), 66.3 (OCH_2), 63.1 (CH), 14.2 ppm (CH_3); IR (CCl_4): $\tilde{\nu} = 1684$, 1647, 1497, 1321, 1138 cm^{-1}; MS (EI), *m*/*z* (%): 295 (100) $[M]^+$, 266 (44), 238 (38), 220 (36), 196 (48), 131 (70), 103 (96), 77 (66); elemental analysis calcd (%) for $C_{18}H_{17}NO_3$: C 73.20, H 5.80, N 4.74; found: C 73.42, H 5.99, N 4.58.

Pentacarbonylchromium(0) carbene complex (19): To a solution of 2-aminophenol (55 mg, 0.5 mmol) in anhydrous THF (2 mL) at room temperature was added *t*BuONa (49 mg, 0.5 mmol) in one portion. The mixture was stirred for 30 min and then a solution of complex **1a** (175 mg, 0.5 mmol) in anhydrous THF (4 mL) was added. The starting material had disappeared after 15 min. The solvent was removed under reduced pressure, and the crude reaction mixture was subjected to flash chromatography under argon pressure on silica gel (hexanes) to give carbene complex **19** (80 mg, 40%) as a dark red solid. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 10.00$ (brs, 1H; NH), 7.81–7.77 (m, 2H; ArH), 7.42–7.40 (m, 3H; ArH), 7.23 (s, 1H; CH), 7.18 (m, 2H; ArH), 7.09 ppm (t, $J = 7.8$ Hz, 2H; ArH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 274.7$ (Cr=C), 223.1 (CO_{trans}), 217.3 (CO_{cis}), 153.7, 150.4, 132.9, 132.8, 131.2, 129.1, 129.0, 127.5, 127.5, 126.1, 121.8, 119.0 ppm (aromatic C and CH); IR (CCl_4): $\tilde{\nu} = 2052$, 1938, 1560 cm^{-1}; elemental analysis calcd (%) for $C_{22}H_{11}CrNO_6$: C 58.12, H 2.68, N 3.39; found: C 58.38, H 2.89, N 3.21.

Pentacarbonylchromium(0) carbene complex (20) and 2-phenyl-1,5-benzothiazepin-4(5*H*)-one (21): A solution of complex **10b** (100 mg, 0.21 mmol) in anhydrous THF (5 mL) was heated at 50 °C under argon atmosphere until the starting material had disappeared (29 h, checked by TLC). The solvent was removed in vacuo, the crude reaction was subjected to flash column chromatography to give compound **21** (27 mg, 51%) as a white solid and carbene complex **20** (10 mg, 11%) as a dark red oil.

21: M.p. 106–108 °C; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 8.06$–8.00 (m, 3H; ArH), 7.84 (d, $J = 8.0$ Hz, 1H; ArH), 7.47–7.40 (m, 5H; ArH), 7.32 ppm (t, $J = 7.5$ Hz, 1H; ArH); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 168.0$, 154.1, 135.0. 133.6, 130.9, 129.0, 127.5, 126.3, 125.2, 123.2, 121.6 ppm (aromatic C and CH); IR (CCl_4): $\tilde{\nu} = 1635$, 1578, 1554, 1514, 1481, 1435, 1225 cm^{-1}; MS (70 eV): *m*/*z* (%): 253 (6) $[M]^+$, 236 (16), 212 (10), 211 (100), 108 (21), 82 (14), 69 (33); elemental analysis calcd (%) for $C_{15}H_{12}NOS$: C 71.12, H 4.38, N 5.53, S 12.66; found: C 71.37, H 4.54, N 5.72, S 12.83.

20: ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 10.63$ (brs, 1H; NH), 7.75 (m, 2H; ArH), 7.49 (m, 2H; ArH), 7.34 ppm (m, 6H; ArH and CH); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 280.6$ (Cr=C), 227.9 (CO_{trans}), 217.16 (CO_{cis}), 161.8, 141.4, 138.2, 136.7, 136.2, 134.1, 133.4, 129.9, 128.7, 128.6, 128.1, 123.0 ppm (aromatic C and CH); IR (CCl_4): $\tilde{\nu} = 2054$, 1940, 1551, 1472, 1254 cm^{-1}.

Complex 22a: To a solution of pentacarbonyl[(ethoxy)(2-phenylethynyl)-carbene]chromium(0) (**1a**, 175 mg, 0.5 mmol) and catechol (55 mg, 0.5 mmol) in anhydrous Et_2O (5 mL) at room temperature was added Et_3N (101 mg, 1 mmol). The mixture was stirred until the starting material had disappeared (48 h, checked by TLC). The solvent was removed in vacuo, and the reaction mixture was subjected to flash column chromatography under argon pressure (SiO_2, hexanes) to give carbene complex **22a** (115 mg, 50%) as an orange solid. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.50$–7.47 (m, 2H; ArH), 7.35–7.26 (m, 3H; ArH), 6.72 (s, 4H; ArH), 4.80 (q, $J = 7.1$ Hz, 2H; OCH_2), 4.22 (s, 2H; CH_2), 1.12 ppm (t, $J = 7.1$ Hz, 3H; CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 353.8$ (Cr=C), 223.4 (CO_{trans}), 215.9 (CO_{cis}), 146.8, 140.6, 129.0, 128.4, 124.9, 121.6, 115.2, 108.5 (aromatic C and CH), 78.5 (OCH_2), 69.3 (CH_2), 14.2 ppm (CH_3); IR (CCl_4): $\tilde{\nu} = 2064$, 1989,

1946, 1485, 1238 cm^{-1}; elemental analysis calcd (%) for $C_{22}H_{16}CrO_8$: C 57.40, H 3.50; found: C 57.67, H 3.71.

Complex 22c: To a solution of complex **1c** (165 mg, 0.5 mmol) in anhydrous THF (5 mL) was added a solution of catechol (55 mg, 0.5 mmol) and *t*BuONa (99 mg, 1 mmol) in THF (5 mL) at room temperature. The mixture was stirred for 24 h. The solvent was evaporated in vacuo and the reaction mixture was subjected to flash column chromatography under argon pressure (SiO_2, hexanes) to give carbene complex **22c** (102 mg, 46%) as an orange solid. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 6.68-6.59$ (m, 4H; ArH), 4.60 (q, $J = 7.1$ Hz, 2H; OCH_2), 3.89 (s, 2H; CH_2), 1.09 (t, $J = 7.1$ Hz, 3H; CH_3), 1.01 ppm (s, 9H; $3CH_3$); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 357.9$ (Cr=C), 223.5 (CO_{trans}), 215.9 (CO_{cis}), 148.5 (C_{ipso}), 121.7 (Cq), 120.9, 107.3 (CH aromatic), 78.7 (OCH_2), 63.4 (CH_2), 41.5 (Cq), 24.1 (CH_3), 14.2 ppm (CH_3); IR (CCl_4): $\tilde{\nu} = 2062$, 1985, 1946, 1489, 1238 cm^{-1}; elemental analysis calcd (%) for $C_{20}H_{20}CrO_8$: C 54.55, H 4.58. C 57.40; found: C 54.74, H 4.81.

Synthesis of 2-substituted perimidines. General procedure:

In a typical experiment, the carbene complex was dissolved in anhydrous CH_2Cl_2 and 1,8-diaminonaphtalene was added. The mixture reaction was stirred at room temperature under an argon atmosphere until the starting material had disappeared (checked by TLC). The solvent was removed in vacuo, and the crude reaction mixture was purified by flash column chromatography on silica gel under argon pressure.

2-Phenyl-1*H*-perimidine (33a)

Method A: Following the general procedure, a solution of carbene complex **1a** (150 mg, 0.43 mmol) and 1,8-diaminonaphtalene (68 mg 0.43 mmol) in CH_2Cl_2 (15 mL) gave, after 24 h, perimidine **33a** (84 mg, 80%) as an orange solid and carbene complex **32a** (90 mg , 80%).

Method B: A solution of carbene complex **1b** (150 mg, 0.31 mmol) and 1,8-diaminonaphtalene (49 mg, 0.31 mmol) in CH_2Cl_2 (15 mL) gave, after 7.5 h, perimidine **33a** (74 mg, 97%) and carbene complex **32b** (112 mg, 91%).

33a: M.p. 187–188 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.78$ (m, 2H; ArH), 7.44–7.37 (m, 3H; ArH), 7.14–7.04 (m, 4H; ArH), 6.53 ppm (br s, 2H; ArH); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 152.7$, 135.4, 134.0, 131.0, 128.9, 128.3, 126.2, 121.8, 119.8 ppm; IR (KBr): $\tilde{\nu} = 3051$, 1636, 1597, 1566, 1404, 1371 cm^{-1}; MS (70 eV): *m*/*z* (%): 245 (22) $[M+1]^+$, 244 (100) $[M]^+$, 166 (32), 122 (18); elemental analysis calcd (%) for $C_{17}H_{12}N_2$: C 83.58, H 4.95, N 11.47; found: C 83.71, H 4.86, N 11.35.

2-*tert*-Butyl-1*H*-perimidine (33c): Following the general procedure, a solution of carbene complex **1c** (160 mg, 0.48 mmol) and 1,8-diaminonaphtalene (76 mg, 0.48 mmol) in CH_2Cl_2 (16 mL) gave, after 24 h, perimidine **33c** as a yellow solid (83 mg, 77%) and carbene complex **32a** (79 mg, 62%).

33c: M.p. 162–163 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.19-6.98$ (m, 4H; ArH), 6.46 (br s, 2H; ArH), 1.27 ppm (s, 9H; CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 161.7$, 140.8, 135.2, 128.1, 121.4, 119.2, 108.2 (aromatic C and CH), 36.6 (Cq), 28.0 ppm (CH_3); IR (CCl_4): $\tilde{\nu} = 3452$, 2966, 1634, 1599, 1406, 1373 cm^{-1}; elemental analysis calcd (%) for $C_{15}H_{16}N_2$: C 80.32, H 7.19, N 12.49; found: C 80.15, H 7.25, N 12.63.

2-Ferrocenyl-1*H*-perimidine (33d): Following the general procedure, a solution of carbene complex **1d** (150 mg, 0.32 mmol) and 1,8-diaminonaphtalene (52 mg, 0.32 mmol) in CH_2Cl_2 (15 mL) gave, after 24 h, perimidine **33d** (113 mg, 100%) as an orange solid and carbene complex **32a** (72 mg, 83%).

33d: M.p. 253–255 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.14-7.04$ (m, 4H; ArH), 6.62 (d, $J = 6.2$ Hz, 2H; ArH), 4.87 (br s, 2H; CH), 4.31 (br s, 2H; CH), 4.19 ppm (s, 5H; Cp); ^{13}C NMR (125 MHz, $[D_6]$DMSO): $\delta = 155.1$ (C=N), 145.3, 138.4, 135.1, 128.9, 127.9, 121.2, 118.3, 117.2, 113.0, 102.0 (aromatic C and CH), 77.1 (Cq Fc), 70.2 (CH Fc), 69.5 (Cp), 67.6 ppm (CH Fc); IR (KBr): $\tilde{\nu} = 3422$, 1636, 1593, 1412, 1373 cm^{-1}; MS (EI): *m*/*z* (%): 352 (100) $[M]^+$, 286 (71), 176 (16), 56 (10); elemental analysis calcd (%) for $C_{21}H_{16}FeN_2$: C 71.61, H 4.58, N 7.95; found: C 71.78, H 4.44, N 8.03.

2-Propyl-1*H*-perimidine (33e): Following the general procedure, a solution of carbene complex **1e** (150 mg, 0.48 mmol) and 1,8-diaminonaphtalene (76 mg, 0.48 mmol) in CH_2Cl_2 (15 mL) gave, after 24 h, the perimidine **33e** (73 mg, 72%) as a yellow solid and carbene complex **32a** (84 mg, 66%).

33e: M.p. 157–159 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.09-7.00$ (m, 4H; ArH), 6.43 (d, $J = 6.8$ Hz, 2H; ArH), 4.62 (br s, 1H; NH), 2.26 (t, $J = 7.5$ Hz, 2H; CH_2), 1.70 (sextuplet, $J = 7.6$ Hz, 2H; CH_2), 0.97 ppm (t, $J = 7.3$ Hz, 3H; CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 156.9$ (C=N), 140.5, 135.3, 128.2, 121.7, 119.4, 107.8 (aromatic C and CH), 37.6 (CH_2), 20.7 (CH_2), 13.6 ppm (CH_3); IR (KBr): $\tilde{\nu} = 3393$, 2961, 1636, 1607, 1585, 1414, 1373 cm^{-1}; elemental analysis calcd (%) for $C_{14}H_{14}N_2$: C 79.97, H 6.71, N 13.32; found: C 80.06, H 6.62, N 13.25.

2-Phenyl-6,7-dihydro-1*H*-cyclopenta[*gh*]perimidine (36): Following the general procedure, from carbene complex **35a** (229 mg, 0.24 mmol) after flash column chromatography on silica gel were obtained perimidine **36** (102 mg, 88%) as a yellow solid, and carbene complex **32a** (62 mg, 55%). Analogously, from tungsten complex **1b** (206 mg, 0.31 mmol) were obtained perimidine **36** as an orange solid (75 mg, 89%) and carbene complex **32b** (83 mg, 67%).

36: M.p. 120–122 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.76-7.73$ (m, 2H; ArH), 7.40–7.38 (m, 3H; ArH), 6.82 (d, $J = 7.2$ Hz, 2H; ArH), 6.38 (br s, 2H; ArH), 3.16 ppm (s, 4H; $2CH_2$); ^{13}C NMR (50 MHz, $[D_6]$DMSO): $\delta = 153.5$ (C=N), 140.7, 135.7, 134.1, 130.7, 128.2, 126.6, 121.2, 119.4 (aromatic C and CH), 30.2 ppm ($2CH_2$); IR (KBr): $\tilde{\nu} = 3421$, 1635, 1593, 1560, 1550, 1458 cm^{-1}; elemental analysis calcd (%) for $C_{19}H_{14}N_2$: C 84.42, H 5.22, N 10.36; found: $C_{19}H_{14}N_2$ C 84.29, H 5.13, N 10.47.

2-[3-(1*H*-perimidin-2-yl)phenyl]-1*H*-perimidine (38): Following the general procedure, biscarbene complex **37** (160 mg, 0.24 mmol), 1,8-diaminonaphtalene (80 mg, 0.51 mmol), and CH_2Cl_2 (15 mL) gave, after 1.5 h, perimidine **38** (98 mg, 100%) as a dark yellow solid and carbene complex **32a** (73 mg, 58%).

38: M.p. 221 °C (decomp); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 10.84$ (s, 2H), 8.63 (s, 1H; ArH), 8.18 (d, $J = 6.6$ Hz, 2H; ArH), 7.72 (t, $J = 6.5$ Hz, 1H; ArH), 7.22–7.05 (m, 8H; ArH), 6.76 (d, $J = 6.2$ Hz, 2H; ArH), 6.60 ppm (d, $J = 4.6$ Hz, 2H; ArH); ^{13}C NMR (125 MHz, $[D_6]$DMSO): $\delta = 152.4$ (C=N), 144.8, 138.4, 135.1, 133.8, 129.2, 128.9, 128.6, 128.0, 125.4, 121.6, 119.4, 117.8, 114.0, 102.9 ppm (aromatic C and CH); IR (KBr): 3335, 3047, 1634, 1593, 1373 cm^{-1}; elemental analysis calcd (%) for $C_{18}H_{18}N_4$: C 81.93, H 4.42, N 13.65; found: C 82.10, H 4.45, N 13.86.

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