Group 6 Pyrrolocarbene Complexes as Alkoxycarbene Complex Analogs

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Chromium, molybdenum, and tungsten carbene complexes having the pyrrole group as the heteroatom-containing substituent were synthesized and characterized. Their thermal and photochemical reactivity more nearly resembled that of alkoxycarbene complexes than that of aminocarbene complexes. Thus, they cyclopropanated electron deficient olefins, produced hydroquinones rather than indenes in the Dötz annulation process, and underwent photochemical 2 + 2 cycloaddition with alkenes to produce cyclobutanones and with imines to produce β-lactams. With cyclohexadiene and cycloheptadiene, an unusual 4 + 2 cycloaddition of the diene across the ketene carbonyl group was observed. The pyrrole group was oxidatively cleaved to the corresponding formamide, the hydrolysis of which gave the free NH_2 group, making the pyrrole group functionally equivalent to the amino group.

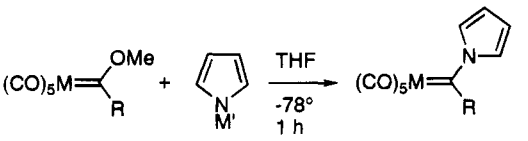
Introduction

Group 6 alkoxycarbene complexes have recently found extensive use in organic synthesis,[1] both in their thermal reactions with alkenes to form cyclopropanes[2] and with alkynes to form quinone derivatives (Dötz benzannulation reaction)[3] and in their photochemical reactions to produce ketene-derived products, such as β-lactams,[4] cyclobutanones,[5] amino acids and peptides,[6] allenes,[7] and, with dienyl carbene complexes, benzannulation products.[8] Chromium aminocarbene complexes differ substantially from alkoxycarbene complexes in their reactivity.[9] They tend to undergo C–H insertion into alkenes, rather than to cyclopropanate them;[2b] they undergo benzannulation with alkynes to give indenes, rather than quinones;[10] and they fail to undergo photochemical 2 + 2 cycloaddition to alkenes to produce cyclobutanones.[5] This difference in reactivity can be somewhat mitigated by placing electron-withdrawing groups (e.g., aryl[11] or acyl[12] groups), on the nitrogen, reducing the electron-donating ability of the amino groups, although no systematic study of this phenomenon has been reported.

Pyrrole is a nitrogen heterocycle that has roughly the pK_a of methanol (≈17),[13] and can be converted to the NH_2 group after oxidative cleavage,[14] making this heterocycle functionally equivalent to the amino group.[15] Since the basicity of the heteroatom in chromium carbene complexes affects both the stability and the mode of reactivity, it seemed possible that chromium pyrrolocarbene complexes might have the reactivity profile of alkoxycarbene complexes, but would introduce an amino functionality in their reaction products. Experiments addressing these questions are described below.

Results and Discussion

The requisite pyrrolocarbene complexes **2a–d** were synthesized from the corresponding alkoxycarbene complexes **1a–d** by exchange with the lithium or potassium salt of pyrrole (eq 1). The resulting pyrrolocarbene



(Eq. 1)

M' = Li, K

M = Cr, R = Ph **1a**	**2a** 88%
M = Mo, R = Ph **1b**	**2b** 78%
M = W, R = Ph **1c**	**2c** 89%
M = W, R = Me **1d**	**2d** 39%

complexes **2a–d** were stable solids which could be stored in the freezer and handled without decomposition. The phenyl carbene complexes **2a–c** were obtained from the lithium salt of pyrrole in good yields.

[⊗] Abstract published in *Advance ACS Abstracts,* April 15, 1995.

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(2) For a review see: Reissig, H. U. Organometallics in Organic Synthesis; Werner, H., Erker, G., Eds.; Springer-Verlag: Berlin, 1989, Vol. 2, p 311. (b) Weinand, A.; Reissig, H. U. *Organometallics* **1990**, *9*, 3133 and references therein.

(3) Wulff, W. D.; Bax, B. M.; Brandvold, T. A.; Chan, K. S.; Gilbert, A. M.; Hsung, R. P. *Organometallics* **1994**, *13*, 102 and references therein.

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(13) Yagil, G. *Tetrahedron* **1967**, *23*, 2855.

(14) Kashima, C.; Maruyama, T.; Fujioka, Y.; Harada, K. *J. Chem. Soc., Perkin Trans. 1* **1989**, 1041.

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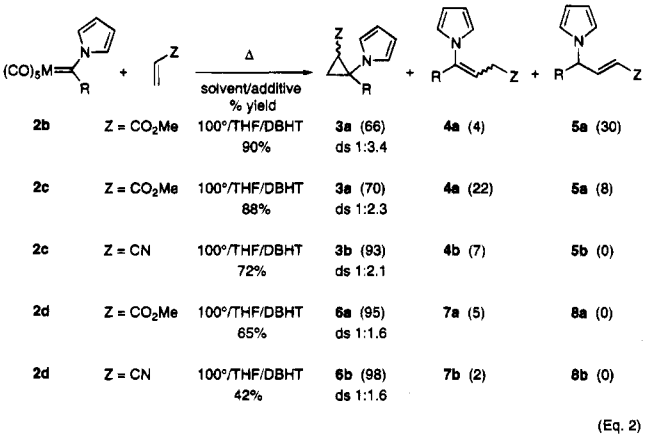
The tungsten methoxymethyl carbene complex **1d** was inert to pyrrol-1-yl lithium, and the corresponding pyrrolocarbene complex **2d** was formed from pyrrol-1-yl potassium, although in lower yield. The corresponding methyl chromium carbene complex could not be prepared.

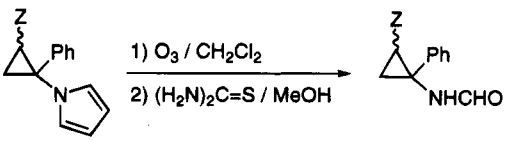
The ^{13}C chemical shift of the carbene carbon is characteristic for Group 6 carbene complexes, with these signals for alkoxycarbene complexes appearing in the 330–360 ppm region, while those for aminocarbene complexes are seen substantially upfield, in the 250–290 ppm region.[16] Pyrrolocarbene chromium complex **2a** had this signal at δ 320 (vs δ 352 for the corresponding methoxycarbene and δ 275 for the dimethylaminocarbene complex).[16] Pyrrolocarbene tungsten complex **2c** similarly had the ^{13}C-signal for the carbene carbon intermediate (δ 291) between the corresponding (methoxy)(phenyl)carbene complex,[17] (δ 322.0), and the (dibenzylamino)(phenyl)carbene complex (δ 262.1),[18] while the signal for the carbene carbon of the molybdenum complex **2c** appeared at δ 309.4 vs δ 349.9 for the (benzyloxy)(methyl)carbene complex[18] and δ 275.0 for the (methylamino)(phenyl)carbene complex.[12b]

The reactivity of these complexes was next addressed, starting with the thermal cyclopropanations of electron deficient alkenes (eq 2). In contrast to carbene complexes of saturated amines, which are far less reactive in the cyclopropanation process than are alkoxycarbene complexes and result in only formal C–H insertion products such as **4**, **7**, **5**, and **8**,[2b] the pyrrolocarbene complexes **2a–d** underwent reaction with electron deficient alkenes to give cyclopropanes (as a *cis/trans* mixture) as the major products, accompanied by varying amounts of C–H insertion products. The reaction of the carbene chromium complex **2a** with methyl acrylate in cyclohexane at reflux gave cyclopropane **3a** and olefin **4a** in a 36:64 ratio. The presence of DMAP inverted this ratio, and **3a** was obtained as the major product (61:39), although the reaction was not efficient (~25% yield), and pure products were not obtained. Molybdenum and tungsten carbene complexes were more efficient than the chromium complex, with tungsten strongly favoring cyclopropanation over insertion. THF was the better solvent for cyclopropanation selectivity, compared to cyclohexane or acetonitrile, which favored the insertion reaction. (A free-radical scavenger, DBHT, was added to suppress polymerization of the olefin substrates.) The pyrrole group was readily converted to the formamide group by ozonolysis (eq 3).[14] Further hydrolysis to the free amino group resulted in cleavage of the cyclopropane ring, a common occurrence with 2-aminocyclopropane carboxylic acids.[19]



2b	Z = CO_2Me	100°/THF/DBHT 90%	**3a** (66) ds 1:3.4	**4a** (4)	**5a** (30)
2c	Z = CO_2Me	100°/THF/DBHT 88%	**3a** (70) ds 1:2.3	**4a** (22)	**5a** (8)
2c	Z = CN	100°/THF/DBHT 72%	**3b** (93) ds 1:2.1	**4b** (7)	**5b** (0)
2d	Z = CO_2Me	100°/THF/DBHT 65%	**6a** (95) ds 1:1.6	**7a** (5)	**8a** (0)
2d	Z = CN	100°/THF/DBHT 42%	**6b** (98) ds 1:1.6	**7b** (2)	**8b** (0)

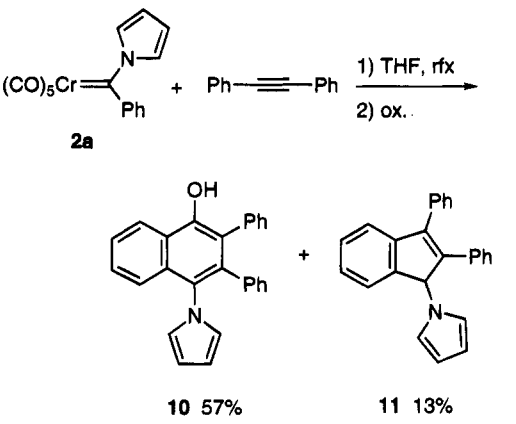
(Eq. 2)



(Eq. 3)

Z = CO_2Me **3a** **9a** 73%
Z = CN **3b** **9b** 71%

Chromium pyrrolocarbene complex **2a** was subjected to Dötz benzannulation conditions with diphenyl acetylene, resulting in the production of a crude product consisting of a 2.5/1 mixture of CO-insertion product **10** and indene **11**, in moderate yield (eq 4). Aminonaphthol **10** was rather unstable and underwent air oxidation to produce 3,4-diphenylnaphthoquinone. Because of this and because of the low selectivity of this process, benzannulation reactions with pyrrolocarbene complexes **2** were not further pursued.



2a

10 57% **11** 13%

(Eq. 4)

Although alkylaminocarbene chromium complexes failed to react with alkenes under photochemical conditions, the less electron rich arylaminocarbene complexes did react to form cyclobutanones, albeit in modest yield.[11] Similarly, chromium carbene complex **2a** underwent photochemical cycloaddition to a number of alkenes to give cyclobutanones in modest yield, and as only one diastereoisomer (eqs 5–10). The reactions were quite slow, requiring 40–60 h to go to completion. The stereoselectivity (both large groups *syn*) was typical of ketene olefin cycloadditions.[20] With ethyl vinyl ether, metathesis was a competitive reaction, and when the reaction was performed at room temperature, olefin was the major product (57% yield vs 6% of cyclobutanone).

(16) It has been noted that there is no *direct* correlation between electron density at the carbene carbon and its ^{13}C chemical shift value. See: Hafner, A.; Hegedus, L. S.; deWeck, G.; Hawkins, B.; Dötz, K. H. *J. Am. Chem. Soc.* **1988**, *110*, 8413.

(17) $(CO)_5W{=}C(OMe)(Ph)$ δ (ppm) ($CDCl_3$, 300 MHz): 322.0 (W=C), 203.4 (*cis* CO), 197.1 (*trans* CO), 155.1 (ipso), 131.7, 128.0, 126.2 (Ph), 70.0 (OMe).

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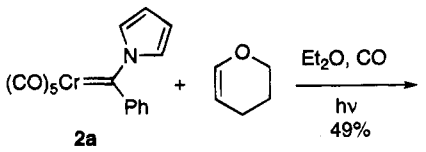
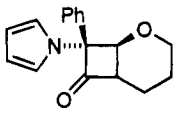
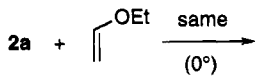
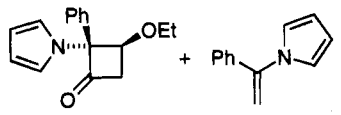


2a

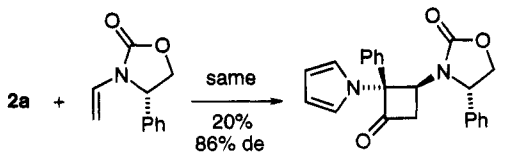


12a (Eq. 5)

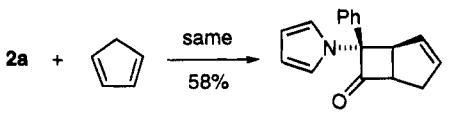




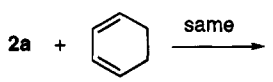
12b 35% **12b'** 17% (Eq. 6)

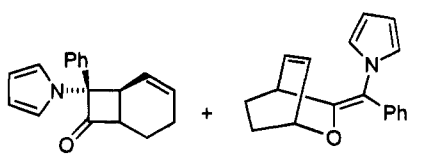


12c (Eq. 7)

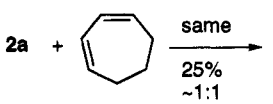


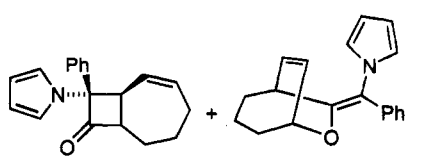
12d (Eq. 8)





12e 24% **12e'** 18% (Eq. 9)

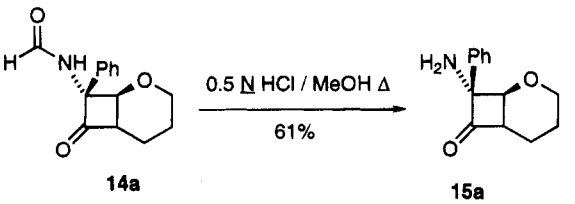




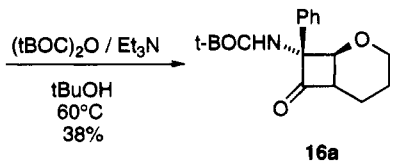
12f **12f'** (Eq. 10)

This metathesis reaction was suppressed by carrying out photolysis at 0 °C. Remarkably, with cyclohexadiene (eq 9) and cycloheptadiene (eq 10), a second cycloaddition product corresponding to 4 + 2 cycloaddition of the diene across the ketene carbonyl group was observed. The reaction was also diastereoselective in the formation of the 4 + 2 adducts, which were obtained as single diastereoisomers. The disposition of the groups in compound **12e'** was determined by X-ray crystallography. Although precedented,[21] this mode of reactivity is rare.

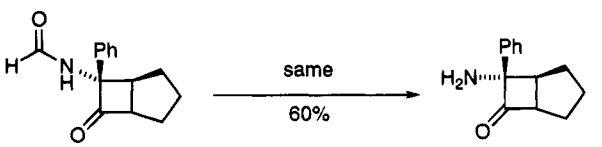
The pyrrole group in **12a** was converted to the formamide **14a** in excellent yield (88%) by ozonolysis. The same process with **12d** resulted in ozonolysis of the alkene. Reduction of the double bond followed by ozonolysis gave the saturated bicyclic cyclobutanone **14d** with a pendant formamide group in good (72%) yield. The formamido group was hydrolyzed under acidic conditions to give the corresponding α-aminocyclobutanones **15a** and **15d** in ~60% yield. These products were converted to their *t*-BOC derivatives **16a** and **16d** (eqs 11 and 12).



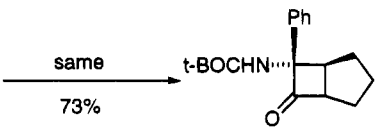
14a **15a**



16a (Eq. 11)



14d **15d**

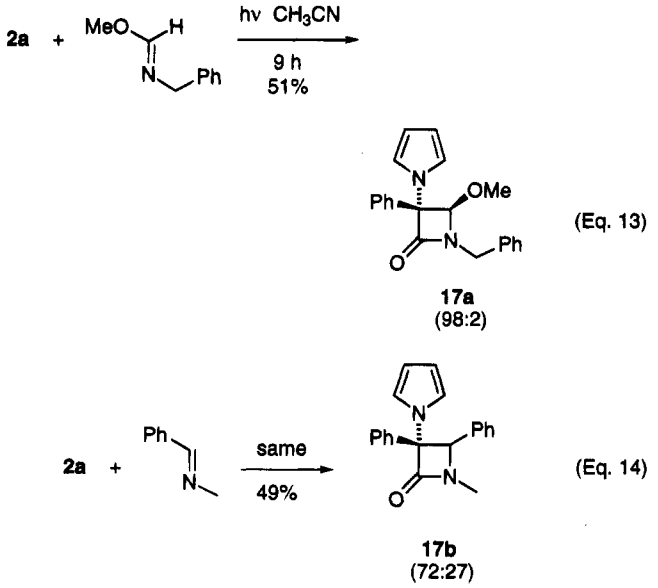


16d (Eq. 12)

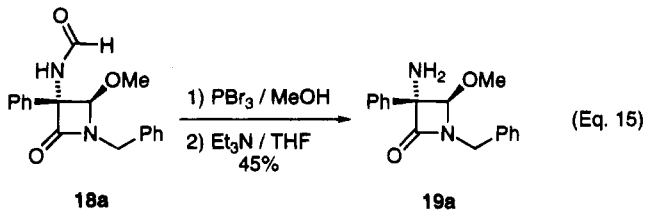
Both chromium (aryl)(alkoxy)carbene complexes and (hydrido)(amino)carbene complexes undergo facile photocycloadditions to imines to produce β-lactams,[4] but (aryl)(amino)carbene complexes undergo this reaction little if at all.[16] Chromium pyrrolocarbene complex **2a** underwent photocycloaddition to imines to give β-lactams in modest yields (eqs 13 and 14). The stereoselectivity observed was similar to that observed with other classes of carbene complexes.[22] The pyrrole group in compounds **17a** and **17b** was converted to the formamido group in 86% and 63% yield, respectively, by ozonolysis. Deprotection of the 3-amino group in β-lactam **18a** was accomplished by hydrolysis of the forma-

(21) (a) Pittol, C. A.; Roberts, S. M.; Sutton, P. W.; Williams, J. O. *J. Chem. Soc., Chem. Commun.* **1994**, 803. (b) Mayr, H.; Heigl, U. W. *J. Chem. Soc., Chem. Commun.* **1987**, 1804 and references therein. (c) For a review on ketene cycloadditions see: Hyatt, J.; Raynolds, R. W. *Org. React.* **1994**, *45*, 159.

(22) For an extensive compilation see: Dumas, S.; Hegedus, L. S. *J. Org. Chem.* **1994**, *59*, 4967.



mido group with PBr_3 in MeOH,[23] followed by treatment with Et_3N (eq 15).



In summary, group 6 pyrrolocarbene complexes resemble alkoxycarbene complexes more than aminocarbene complexes in their reactivity pattern, but generate amino substituted products.

Experimental Section

General Methods. Melting points were taken on a Mel-Temp apparatus and are uncorrected. ^{1}H-NMR (300 MHz) and ^{13}C-NMR (75 MHz) spectra were obtained on Bruker ACE-300, Bruker ACP-300, or Bruker AM-500 MHz spectrometers. NMR were recorded in $CDCl_3$, and chemical shifts are given in ppm relative to tetramethylsilane (0 ppm, ^{1}H) and $CDCl_3$ (76.95 ppm, ^{13}C). Infrared spectra were recorded on a Perkin-Elmer 1600 Series FTIR. Mass spectra were obtained on a VG Quattro-SQ or VG Autospec (Fisons Instruments). Optical rotations were recorded on a Rudolph Research automatic polarimeter Autopol III. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

Flash chromatography was performed on Merck silica gel (230–400 mesh). Radial chromatography was performed on a Chromatotron Model 7924, and the plates were prepared with silica gel 60 PF_{254} (EM Science). THF (Mallinckrodt) and Et_2O (Mallinckrodt) were distilled from sodium/benzophenone under a nitrogen atmosphere. MeOH (Mallinckrodt) and CH_2Cl_2 (technical grade) were distilled from CaH_2 and stored over 4 Å molecular sieves. Acetonitrile was distilled from P_2O_5 and stored under argon. Hexane (technical grade) was distilled at atmospheric pressure. Photoreactions were performed with dry degassed solvents (freeze–thaw method).

The following chemicals were prepared according to literature procedures: pentacarbonyl[(methoxy)(phenyl)carbene]-chromium(0),[24] pentacarbonyl[(methoxy)(phenyl)carbene]-molybdenum(0),[24] pentacarbonyl[(methoxy)(phenyl)carbene]-tungsten(0),[24] 3-vinyl-(*S*)-4-phenyl-2-oxazolidinone,[25] cyclopentadiene,[26] methyl *N*-benzylformimidate,[27] and *N*-methylbenzilidineimine.[28] Palladium on carbon was purchased from Lancaster, and the rest of the chemicals from Aldrich and were used as received.

General Procedure for the Synthesis of (Phenyl)(pyrrol-1-yl)carbene Complexes 2. All of the operations were carried out under an argon atmosphere. Pyrrol-1-yl lithium was prepared by adding *n*-BuLi (2 equiv) to a solution of pyrrole (2 equiv) in THF at 0 °C. The resulting faint yellow solution was stirred for 10 min at 0 °C and for 30 min at room temperature. The lithium reagent was added via canula to an Airless flask containing a solution of the corresponding (methoxy)(phenyl)carbene complex **1** (1 equiv) in THF at −78 °C. The initial red solution turned to yellow after the addition was concluded. The reaction mixture was stirred at −78 °C for 1 h and then quenched with water. After warming to room temperature, THF was evaporated under reduced pressure and the residue was extracted with hexane (**2a**) or ether (**2b,c**) several times until the aqueous phase no longer remained brown in color. The resulting dark brown organic layer was dried ($MgSO_4$), filtered through Celite, and concentrated under reduced pressure to afford the crude carbenes **2a–c** as brown-black solids. Purification via flash chromatography on silica using a 9/1 mixture of hexane/CH_2Cl_2 as eluent gave the pure carbenes **2a–c**.

Pentacarbonyl[(phenyl)(pyrrol-1-yl)carbene]chromium(0) (2a). Pentacarbonyl[(methoxy)(phenyl)carbene]-chromium(0) (**1a**) (2.714 g, 8.70 mmol) in THF (45 mL) was treated with pyrrol-1-yl lithium, prepared from pyrrole (1.21 mL, 17.40 mmol) and *n*-BuLi (8.50 mL, 17.40 mmol) in THF (10 mL), according to the general procedure. Purification of the crude reaction product afforded 2.680 g (7.72 mmol, 88% yield) of carbene **2a** as bright black needles: mp 80–82 °C; ^{1}H-NMR δ 7.39 (m, 3H), 7.24 (m, 3H), 6.86 (m, 2H), 6.56 (bs, 2H); ^{13}C-NMR δ 320.8 (Cr=C), 225.7 (*trans* CO), 215.9 (*cis* CO), 154.8 (ipso), 127.5, 127.2, 120.3 (Ph), ≈120 (b, pyrrole ring); IR (film) ν 2063, 1991, 1966, 1936, 1911 cm^{-1}; MS (EI) *m/z* 155 ($M^+ - (CO)_5Cr$, 41%), 105 (100%), 77 (Ph, 75%), 67 (pyrrole, 55%). Anal. Calcd for $C_{16}H_9CrNO_5$: C, 55.34; H, 2.61; N, 4.03. Found: C, 55.20; H, 2.84; N, 3.83.

Pentacarbonyl[(phenyl)(pyrrol-1-yl)carbene]molybdenum(0) (2b). Pentacarbonyl[(methoxy)(phenyl)carbene]-molybdenum(0) (**1b**) (0.579 g, 1.63 mmol) in THF (12 mL) was treated with pyrrol-1-yl lithium, prepared from pyrrole (0.23 mL, 3.26 mmol) and *n*-BuLi (2.05 mL, 3.26 mmol) in THF (4 mL), according to the general procedure. Purification of the crude reaction product afforded 0.497 g (1.27 mmol, 78% yield) of carbene **2b** as a brown solid: mp 180–181 °C; ^{1}H-NMR δ 7.37 (m, 3H), 7.23 (m, 2H), 6.90 (m, 2H), 6.6 (b, 2H); ^{13}C-NMR δ 309.4 (Mo=C), 215.3 (*trans* CO), 205.3 (*cis* CO), 154.6 (ipso), 127.5, 127.3, 120.7 (Ph), ≈120 (b); IR (film) ν 2068 (*trans* CO), 1944 (*cis* CO) cm^{-1}. Anal. Calcd for $C_{16}H_9MoNO_5$: C, 49.12; H, 2.31; N, 3.58. Found: C, 48.86; H, 2.13; N, 3.48.

Pentacarbonyl[(phenyl)(pyrrol-1-yl)carbene]tungsten(0) (2c). Pentacarbonyl[(methoxy)(phenyl)carbene]tungsten-(0) (**1c**) (0.888 g, 2.00 mmol) in THF (8 mL) was treated with pyrrol-1-yl lithium, prepared from pyrrole (0.28 mL, 4.00

(23) Cowley, B. R.; Humber, D. C.; Laundon, B.; Long, A. G.; Lynd, A. L. *Tetrahedron* **1983**, *39*, 461.

(24) Fischer, E. O.; Aumann, R. *Chem. Ber.* **1968**, *101*, 963. The method for the preparation of pentacarbonyl[(methoxy)(methyl)carbene]-chromium(0) was used for the phenyl-substituted chromium, molybdenum, and tungsten complexes. PhLi was prepared *in situ* from ^{n}BuLi and bromobenzene in Et_2O at −20 °C (1 h).

(25) Miller, M.; Hegedus, L. S. *J. Org. Chem.* **1993**, *58*, 6779.

(26) *Organic Synthesis*; Wiley: New York, 1963; Collect. Vol. 4, p 242.

(27) Guzman, A.; Muchowski, J. M.; Naal, N. T. *J. Org. Chem.* **1981**, *46*, 1224. The method for the preparation of methyl *N*-(2-phenylethyl)-formimidate was used for this benzyl derivative: bp 45–50 °C (0.4 mmHg).

(28) Hegedus, L. S.; McGuire, M. A.; Schultze, L. M.; Yijun, C.; Anderson, O. P. *J. Am. Chem. Soc.* **1984**, *106*, 2680.

mmol) and *n*-BuLi (1.95 mL, 4.00 mmol) in THF (4 mL), according to the general procedure. Purification of the crude reaction product afforded 0.857 g (1.79 mmol, 89% yield) of carbene **2c** as a crystalline black solid: mp 98–99 °C (d); ^{1}H-NMR δ 7.40 (m, 3H), 7.27 (m, 2H), 6.96 (m, 2H), 6.62 (bs, 2H); ^{13}C–NMR δ 291.7 (W=C), 205.9 (*trans* C=O), 197.1 (*cis* C=O), 155.7 (ipso), 127.6, 127.4, 120.7 (Ph), ≈120 (b, pyrrole); IR (film) ν 2068, 1987, 1947 cm^{-1}. Anal. Calcd for $C_{16}H_9NO_5W$: C, 40.11; H, 1.89; N, 2.92. Found: C, 39.93; H, 2.01; N, 2.86.

Synthesis of Pentacarbonyl[(methyl)(pyrrol-1-yl)carbene]tungsten(0) (2d). Airless flasks (50 and 200 mL) were flame dried and filled with argon. A 35% oil dispersion of KH (1.146 g) was placed into the 50 mL flask, and the oil was removed by washing with freshly distilled hexane (3 × 10 mL) and removing via syringe. After drying the clean KH under vacuum to produce 0.402 g (10.00 mmol), 22 mL of dry THF was introduced into the flask, which was cooled to 0 °C. Pyrrole (0.69 mL, 10.00 mmol) was added to the suspension, and the reaction mixture was stirred for 10 min at 0 °C and for 2 h at room temperature, until evolution of H_2 stopped. The resulting suspension of pyrrol-1-yl potassium was transferred via cannula into an addition funnel attached to the 200 mL Airless flask, which contained a solution of pentacarbonyl-[(methoxy)(methyl)carbene]tungsten(0) **1d** (3.51 g, 9.19 mmol) in 80 mL of THF, and then the suspension was added dropwise at −78 °C. The reaction mixture was stirred for 3 h and quenched with water. After warming to room temperature, THF was removed under reduced pressure and the brown residue was extracted with ether several times, until the aqueous layer lost its red color. The resulting dark red organic layer was dried ($MgSO_4$), filtered through Celite, and evaporated to give a garnet solid. Purification of this crude material was performed by chromatography on silica (hexane/CH_2Cl_2, 95/5). Contamination of $W(CO)_6$ that could not be removed in the column was eliminated by precipitation in MeOH, giving 1.400 g (3.36 mmol, 39% yield) of pure carbene **2d** as a garnet solid: mp 90–91 °C; ^{1}H-NMR δ 7.69 (bs, 1H), 7.18 (bs, 1H), 6.61 (bs, 2H), 3.22 (s, 3H, CH_3); ^{13}C-NMR δ 295.2 (W=C), 205.0 (*trans* CO), 197.5 (*cis* C=O), 134.3, 119.8, 118.8, 116.4, 46.8; IR (film) ν 2067, 1938 cm^{-1}. Anal. Calcd for $C_{11}H_7NO_5W$: C, 31.68; H, 1.69; N, 3.35. Found: C, 31.75; H, 1.46; N, 3.28.

General Procedure for the Synthesis of Cyclopropanes 3 from Pentacarbonyl[(phenyl)(pyrrol-1-yl)carbene]molybdenum(0) (2b) and Pentacarbonyl[(phenyl)-(pyrrol-1-yl)carbene]tungsten(0) (2c). A pressure tube was sealed with a rubber septum, flame dried, evacuated, and filled with Ar. The carbene complex was added in one portion followed by THF to produce a 0.02–0.03 M solution. To this solution were added 0.2 equiv of 2,6-di-*tert*-butyl-4-methylphenol (DBHT) and 1.1 equiv of the corresponding olefin. The tube was sealed with a pressure cap and heated at 100 °C behind a blast shield for 3–5 h. At this point, the initial brown (carbenes **2b** and **2c**) or red (carbene **2d**) transparent solution turned into a dark brown suspension, and the carbene complex was completely consumed as evidenced by TLC analysis. After cooling to room temperature, the reaction mixture was transferred to a round-bottomed flask and THF was removed by rotary evaporation. The residue was taken up in EtOAc, air was bubbled into the suspension for a few minutes, and then the suspension was filtered through Celite. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by flash chromatography on silica to separate molybdenum or tungsten hexacarbonyl and DBHT from the reaction products. These organic reaction products were further purified as described in each synthesis.

Synthesis of Cyclopropane 3a from Pentacarbonyl-[(phenyl)(pyrrol-1-yl)carbene]molybdenum(0) (2b). Carbene complex **2b** (0.156 g, 0.40 mmol), methyl acrylate (36 μL, 0.40 mmol), and DBHT (18 mg, 0.08 mmol) in THF (15 mL) were allowed to react according to the general procedure for 3 h. Flash chromatography (hexane/AcOEt, 9/1) of the crude reaction mixture separated $Mo(CO)_6$ and DBHT and gave 88.3 mg (0.36 mmol, 90% crude yield) of an oil containing a mixture of cyclopropane **3a** and olefins **4a** and **5a** in a ratio of 66:4:30. Purification of this mixture by radial-layer chromatography (hexane/AcOEt, 70/1, 40/1, and 95/5) separated **4a** and gave 72.8 mg of an oil formed by **3a** and **5a** in a ratio of 74:26, indicating a 56% yield in cyclopropane. Separation of this mixture could not be accomplished quantitatively.[29] Compound **3a** was obtained as a 1/3.4 mixture of diastereoisomers.

Synthesis of Cyclopropane 3a from Pentacarbonyl-[(phenyl)(pyrrol-1-yl)carbene]tungsten(0) (2c). Carbene complex **2c** (0.144 g, 0.30 mmol), methyl acrylate (27 μL, 0.30 mmol), and DBHT (13.2 mg, 0.06 mmol) in THF (12 mL) were allowed to react according to the general procedure for 5 h. Flash chromatography (hexane/AcOEt, 9/1) of the crude reaction mixture separated $W(CO)_6$ and DBHT and gave 63.6 mg (0.26 mmol, 88% crude yield) of an oil containing a mixture of cyclopropane **3a** and olefins **4a** and **5a** in a ratio of 70:22:8. Purification of this mixture by radial chromatography (2 mm plate; hexane/AcOEt, 70/5, 40/5, and 95/5) separated **4a** and gave 45.70 mg of an oil formed by **3a** and **5a** in a ratio of 90:10, indicating a 57% yield in cyclopropane. Separation of this mixture could not be accomplished quantitatively,[29] but a sample of **3a** could be obtained for complete characterization of the product. Compound **3a** was produced as a 2.3/1 mixture of diastereoisomers: R_f = 0.25 (hexane/EtOAc, 4/1); ^{1}H-NMR (2 diastereoisomers, a/b = 2.3/1) δ 7.32–7.20 (m, 4H, Ph), 6.81 (m, 1H, Ph), 6.88 (b), 6.73 (a) (t, 2H, J = 2.2 Hz), 6.16 (a), 6.09 (b) (t, 2H, J = 2.2 Hz), 3.58 (a), 3.50 (b) (s, 3H, OMe), 2.76 (b), 2.65 (a) (dd, 1H, J = 9.2, 6.6 Hz), 2.47 (a), 2.21 (b) (dd, 1H, J = 6.8, 5.7 Hz), 1.86 (b), 1.74 (a) (dd, 1H, J = 9.2, 5.7 Hz); ^{13}C-NMR δ 169.4 (C=O, b), 168.7 (C=O, a), 141.9 (ipso, a), 137.0 (ipso, b), 128.5, 128.3, 128.0, 127.8, 127.2, 124.4 (Ph), 121.5, (pyrrole, a), 120.3 (pyrrole, b), 108.8 (pyrrole, b), 108.7 (pyrrole, a), 52.2 (OMe, a), 51.9 (OMe, b), 50.1 (Ph*C*N, b), 48.5 (Ph*C*N, a), 30.8 (CH, a), 29.1 (CH, b), 22.6 (CH_2, a), 18.8 (CH_2, b); IR (film) ν 1739 (CO_2Me) cm^{-1}. Anal. Calcd for $C_{15}H_{15}NO_2$: C, 74.67; H, 6.26; N, 5.80. Found: C, 74.80; H, 6.33; N, 5.78.

Synthesis of Cyclopropane 3b. Carbene **2c** (0.335 g, 0.70 mmol), acrylonitrile (46 μL, 0.70 mmol), and DBHT (46 mg, 0.21 mmol) in THF (22 mL) were allowed to react according to the general procedure for 4.5 h. Flash chromatography (hexane/AcOEt, 9/1) of the crude reaction mixture separated $W(CO)_6$ and DBHT and gave the products as a yellow oil due to complexation with chromium. This oil was taken up in hexane/AcOEt (4/1). Air was bubbled into the solution, and then the solution was air oxidized in sunlight and in a light box (6 × 20 Vitalite fluorescent bulbs). After 2–3 h, the resulting brown suspension was filtered through Celite and the filtrate was air oxidized again. These operations were successively repeated until a clear colorless solution was obtained (12–15 h).[30] Solvent removal on a rotary evaporator gave 105 mg (0.50 mmol, 72% crude yield) of an oil containing a mixture of cyclopropane **3b** and olefin **4b** in a ratio of 93:7. Cyclopropane **3b** was produced as a 1/2.1 mixture of diastereoisomers. Purification by radial layer chromatography (hexane/EtOAc, 70/1, 40/1, and 95/5) gave 88 mg (0.42 mmol, 61% yield) of cyclopropane **3b**. First diastereoisomer: R_f = 0.31 (hexane/EtOAc, 4/1); mp 86–7 °C; ^{1}H-NMR δ 7.38–7.31 (m, 3H, Ph), 7.18 (m, 2H, Ph), 6.83 (t, J = 2.2 Hz, 2H, pyrrole), 6.17 (t, J = 2.2 Hz, 2H, pyrrole), 2.51 (dd, J = 10.0, 6.8 Hz, 1H), 2.14 (dd, 1H, J = 6.8, 6.1 Hz), 2.11 (dd, 1H, J = 10.0, 6.1 Hz); ^{13}C-NMR δ 136.0 (ipso), 128.8, 128.7, 126.6 (Ph), 120.7 (pyrrole), 117.4 (CN), 109.6 (pyrrole), 48.3 (C(Ph)(N)), 21.2 (CH_2), 14.2 (CH); IR (film) ν 2243 (CN) cm^{-1}. Second diastereoisomer: R_f = 0.23 (hexane/EtOAc, 4/1); mp 90–91 °C;

(29) This was not an inconvenience for the next step, since ozonolysis could be performed with the contaminated cyclopropane. The α-formamidocyclopropanes were easily purified and isolated via chromatography.

(30) Air oxidation of the crude reaction mixture without separation of DBHT and $W(CO)_6$ resulted in decomposition of the products and lower yields.

^{1}H-NMR δ 7.32–7.25 (m, 3H, Ph), 6.89 (t, J = 2.1 Hz, 2H, pyrrole), 6.80 (m, 2H, Ph), 6.25 (t, J = 2.1 Hz, 2H, pyrrole), 2.34 (dd, J = 8.7, 6.5 Hz, 1H), 2.29 (dd, 1H, J = 6.5, 5.2 Hz), 1.95 (dd, 1H, J = 8.7, 5.2 Hz); ^{13}C-NMR δ 139.3 (ipso), 128.8, 128.1, 124.6 (Ph), 121.4 (pyrrole), 117.4 (CN), 109.8 (pyrrole), 47.4 (PhCN), 23.5 (CH_2), 14.5 (CH); IR (film) ν 2243 (CN) cm^{-1}. Anal. Calcd for $C_{14}H_{12}N_2$: C, 80.74; H, 5.80; N, 13.45. Found: C, 80.92; H, 5.71; N, 13.49.

Synthesis of Cyclopropane 6a. Carbene complex **2d** (0.333 g, 0.80 mmol), methyl acrylate (72 μL, 0.80 mmol), and DBHT (35.2 mg, 0.16 mmol) in THF (22 mL) were allowed to react according to the general procedure for 5 h. Flash chromatography of the crude reaction mixture (silica; hexane/EtOAc, 9/1) separated $W(CO)_6$ and DBHT and gave 94.0 mg (0.52 mmol, 65% crude yield) of an oil containing a mixture of cyclopropane **6a** and olefin **7a** in a ratio of 95:5. This mixture was purified by radial chromatography (2 mm plate; hexane/AcOEt, 40/1 and 95/5) to afford 42.5 and 27.1 mg of the two diasteromeric cyclopropanes: 69.6 mg, 0.39 mmol, 48% yield. Data for the major isomer: R_f = 0.34 (hex/EtOAc, 9/1); ^{1}H-NMR δ 6.76 (t, 2H, J = 2.1 Hz, pyrrole), 6.11 (t, 2H, J = 2.1 Hz, pyrrole), 3.76 (s, 3H, CO_2Me), 2.23 (dd, 1H, J = 9.5, 6.5 Hz), 1.65 (dd, 1H, J = 9.6, 5.5 Hz), 1.63 (s, 3H, CH_3), 1.50 (dd, 1H, J = 6.5, 5.5 Hz); ^{13}C-NMR δ 171.1 (C=O), 119.8 (pyrrole), 108.4 (pyrrole), 51.9 (OCH_3), 43.8 (MeCN), 27.5 ($CHCO_2Me$), 20.4 (CH_2), 20.2 (CH_3); IR (film) ν 1732 cm^{-1}. Anal. Calcd for $C_{10}H_{13}NO_2$: C, 67.01; H, 7.31; N, 7.81. Found: C, 66.97; H, 7.39; N, 7.69. Data for the minor isomer: R_f = 0.29 (hexane/EtOAc, 9/1); ^{1}H-NMR δ 6.68 (t 2H, J = 2.1 Hz, pyrrole), 6.09 (t, 2H, J = 2.1 Hz, pyrrole), 3.50 (s, 3H, CO_2Me), 2.09–1.99 (m, 2H), 1.63 (s, 3H, CH_3), 1.31 (dd, 1H, J = 7.6, 5.1 Hz); ^{13}C-NMR δ 169.5 (C=O), 120.2 (pyrrole), 108.2 (pyrrole), 51.9 (OCH_3), 43.5 (MeCN), 28.3 ($CHCO_2Me$), 26.7 (CH_3), 19.8 (CH_2); IR (film) ν 1732 cm^{-1}.

Synthesis of Cyclopropane 6b. Carbene **2d** (0.372 g, 0.89 mmol), acrylonitrile (58 μL, 0.80 mmol), and DBHT (49 mg, 0.22 mmol) in THF (22 mL) were allowed to react according to the general procedure for 5 h. Flash chromatography (hexane/AcOEt, 9/1) of the crude reaction mixture separated $W(CO)_6$ and DBHT and gave the products as a yellow oil due to complexation with chromium. This oil was taken up in hexane/AcOEt (4/1) and air oxidized as described above. Solvent removal of the colorless resulting solution gave a crude product formed by cyclopropane **6b** and olefin **7b** in 98:2 ratio. Purification of this material by flash chromatography afforded 14.2 and 34.5 mg of the two diastereomeric cyclopropanes: 48.8 mg, 0.33 mmol, 42% yield. Data for the first diastereoisomer: R_f = 0.45 (hexane/EtOAc, 4/1); ^{1}H-NMR δ 6.72 (t, 2H, pyrrole), 6.13 (t, 2H, pyrrole), 1.98 (dd, 1H, J = 10.0, 6.1 Hz), 1.83 (dd, 1H, J = 10.0, 5.7 Hz), 1.78 (s, 3H, CH_3), 1.44 (t, 1H, J = 5.9 Hz); ^{13}C-NMR δ 119.7 (pyrrole), 118.4 (CN), 109.3 (pyrrole), 41.8 (MeCN), 22.8 (CH_3), 21.0 (CH_2), 11.8 (CH); IR (film) ν 2241 (CN) cm^{-1}. Anal. Calcd for $C_9H_{10}N_2$: C, 73.94; H, 6.89; N, 19.16. Found: C, 73.81; H, 7.04; N, 19.02. Data for the second diastereoisomer: R_f = 0.13 (hexane/EtOAc, 4/1); ^{1}H-NMR δ 6.80 (t, 2H, J = 2.1 Hz, pyrrole), 6.20 (t, 2H, J = 2.1 Hz, pyrrole), 1.92 (t, 1H, J = 5.9 Hz), 1.74 (dd, 1H, J = 9.2, 5.9 Hz), 1.61 (s, 3H, CH_3), 1.50 (dd, 1H, J = 9.2, 5.9 Hz); ^{13}C-NMR δ 120.0 (pyrrole), 117.9 (CN), 109.5 (pyrrole), 42.2 (MeCN), 25.3 (CH_3), 21.0 (CH_2), 12.1 (CH); IR (film) ν 2244 (CN) cm^{-1}.

General Procedure for the Formamidocyclopropane Derivatives 9. The cyclopropanes **3** were placed in a round-bottomed flask equipped with a stir bar, followed by addition of CH_2Cl_2. The resulting colorless solution was ozonized at −78 °C (1 L per min) until the color of the solution turned blue (5–10 min). Then Ar was bubbled into the solution until the blue color disappeared (3–6 min), and a solution of thiourea (1 equiv) in MeOH was added. The reaction mixture was stirred at −78 °C for 15 min and at 0 °C for 1 h. Thiourea dioxide precipitated from the solution as a white solid, and the mixture was filtered through Celite. The filtrate was concentrated on a rotary evaporator, and the residue was taken up in CH_2Cl_2, washed with 1% $NaHCO_3$ aqueous solution (× 2), H_2O (× 1), and brine (× 2). The organic layer was dried ($MgSO_4$) and evaporated under reduced pressure to give a crude material whose ^{1}H-NMR and TLC showed that these compounds exist as a mixture of two rotamers about the formamide. Purification by column chromatography gave the pure compounds.

Synthesis of Formamidocyclopropane 9a. A 91 mg (0.38 mmol) amount of a mixture consisting of cyclopropane **3a** (2.5:1 diastereomeric ratio) and olefin **5a** in a 97:3 ratio, was ozonized in CH_2Cl_2 (7 mL) according to the general procedure. Addition of thiourea (30 mg, 0.39 mmol) in MeOH (3 mL) and workup of the reaction as described above gave 71 mg of the crude compound as a 98/2 mixture of two conformers. This material was purified by flash chromatography on silica (hexane/AcOEt, 1/1) to afford 58.2 mg (0.265 mmol, 73% yield) of cyclopropane **9a** (2.4:1 diastereomeric ratio) as the major conformer. Further separation (radial chromatography) of the two diastereoisomers furnished them as white solids. Data for the minor diastereoisomer: mp 69–70 °C; ^{1}H-NMR δ 8.84 (bs, 1H), 8.68 (bs, 1H), 7.50 (bs, 2H, Ph), 7.34–7.28 (m, 3H, Ph), 3.71 (s, 3H, CH_3), 2.60 (dd, 1H, J = 8.7, 7.3 Hz), 1.98 (t, 1H, J = 6.9 Hz), 1.92 (dd, 1H, J = 8.9, 6.4 Hz); ^{13}C-NMR δ 170.9 (CO_2Me), 163.8 (NHCHO), 138.1 (ipso), 128.6, 128.4 (Ph), 52.2 (CH_3), 41.9 (C(Ph)(N)), 26.5 (CH), 21.4 (CH_2); IR (film) ν 1728 (CO_2Me), 1681 (NHCHO) cm^{-1}. Data for the major diastereoisomer: mp 116–117 °C; ^{1}H-NMR δ 8.75 (bs, 2H, NHCHO), 7.53 (bs, 2H, Ph), 7.33–7.27 (m, 3H, Ph), 3.57 (s, 3H, OCH_3), 2.45 (dd, 1H, J = 9.2, 7.2 Hz), 2.23 (t, 1H, J = 6.9 Hz), 1.60 (dd, 1H, J = 9.2, 6.5 Hz); ^{13}C-NMR δ 169.5 (CO_2Me), 163.2 (NHCHO), 135.2 (ipso), 129.9, 128.8 (Ph), 52.1 (CH_3), 41.5 (PhCN), 27.6 (CH), 18.8 (CH_2); IR (film) ν 1731 (CO_2Me), 1681 (NHCHO) cm^{-1}. High-resolution exact mass spectrum (FAB) M + 1 calcd for $C_{12}H_{14}NO_3$: 220.0973. Found: 220.0972.

Synthesis of Formamidocyclopropane 9b. Cyclopropane **3b** (44 mg, 0.21 mmol, one diastereoisomer) was ozonized in CH_2Cl_2 according to the general procedure. Addition of thiourea (17 mg, 0.21 mmol) in MeOH (1.5 mL) and workup of the reaction as described above gave 35 mg of the crude product as a 98/2 mixture of two conformers. Flash chromatography of this material (hex/AcOEt, 1/1) gave a solid, which was washed with hexane to produce 28 mg (0.15 mmol, 71% yield) of pure cyclopropane **9b** as the major conformer: mp 138–139 °C; ^{1}H-NMR δ 8.88 (bs, 2H), 7.54–7.32 (m, 5H, Ph), 2.41 (t, 1H, J = 8.2 Hz), 1.99 (m, 2H); ^{13}C-NMR δ 163.1 (CO), 136.0 (ipso), 129.2, 128.8 (Ph), 118.1 (CN), 40.6 (PhCNHCHO), 21.4 (CH_2), 11.6 (CH); IR (film) ν 2246 (CN), 1685 (NHCHO) cm^{-1}. MS (EI) m/z 186 (M^+, 18%), 158 (M^+ − CO, 63%), 104 (PhCNH, 100%). High-resolution mass measurement (EI) calcd for $C_{11}H_{10}N_2O$: 186.0793. Found: 186.0785±0.000 18 (n = 4).

Procedure for the Benzannulation Reaction. Synthesis of Aminonaphthol 10. A 25 mL Airless flask was flame dried, evacuated, and filled with Ar. Pentacarbonyl[(phenyl)(pyrrol-1-yl)carbene]chromium(0) (**2a**) (0.114 g, 0.33 mmol) was added into the flask, followed by the addition of THF (10 mL) and diphenylacetylene (53 mg, 0.30 mmol) to produce a dark brown solution that was heated at reflux temperature for 1 h and 40 min. The resulting clear red solution, which did not contain carbene (by TLC), was concentrated on a rotary evaporator, and the residue was taken up in hexane/AcOEt, 7/3, and filtered through Celite. Air was bubbled into the yellow filtrate for 30–40 min, and the resulting suspension was filtered through Celite. This operation was repeated two more times until the solution lost most of its yellow color.[31] Evaporation of the solvents under reduced pressure gave a crude product consisting in a 2.5/1 mixture of compounds **10**/**11**. This material was purified by flash chromatography on

(31) The use of light in the oxidation step led to oxidation of aminonaphthol **10** in 3,4-diphenylnaphthoquinone.

silica (hexane/AcOEt, 95/5) to afford 62 mg (0.17 mmol, 57% yield) of aminonaphthol **10** as a white solid. An analytical sample was recrystallized from hexane/CH_2Cl_2: mp 161–162 °C; ^{1}H-NMR δ 8.33 (dd, 1H, J = 9.0, 1.5 Hz), 7.55–7.44 (m, 2H), 7.36–7.14 (m, 6H), 6.97–6.87 (m, 5H), 6.63 (t, 2H, J = 2.1 Hz, pyrrole), 6.09 (t, 2H, J = 2.1 Hz, pyrrole), 5.67 (s, 1H, OH); ^{13}C-NMR δ 148.1 (C–OH), 137.6 (ipso), 137.1 (ipso), 134.6 (ipso), 131.8 (ipso), 131.0, 129.4, 129.0, 128.8 (ipso), 127.8, 127.0, 126.3, 125.9, 124.1 (pyrrole), 123.4, 123.3 (ipso), 122.3, 121.3 (ipso), 107.9 (pyrrole); IR (film) ν 3526 (OH) cm^{-1}. MS (EI) m/z 361 (M^+, 100%). High-resolution mass measurement calcd for $C_{26}H_{19}NO$: 361.1467. Found: 361.1465±0.0029 (n = 6).

General Procedure for the Synthesis of Cyclobutanones 12. An Ace pressure tube was sealed with a rubber septum, flame dried, evacuated, and filled with Ar twice. Pentacarbonyl[(phenyl)(pyrrol-1-yl)carbene]chromium(0) (**2a**) was added into the tube, followed by dry degassed ether (CH_2Cl_2 for **12c**) and an excess (5–7 equiv) of the corresponding olefin (for **12c** the carbene was used in excess) to produce a deep brown solution. Glass beads were added into the pressure tube to increase the light transmission of the reacting solution. The tube was equipped with a pressure head, and it was saturated with CO (3 cycles to 80 psi) and irradiated (450 W Conrad-Hanovia 7825 medium-pressure mercury lamp, Pyrex well) until the brown solution turned yellow (40–60 h) indicating complete consumption of the carbene. The solution was filtered through Celite and concentrated under reduced pressure to give a brown residue from which $Cr(CO)_6$ was recovered via sublimation (45 °C, 1 mmHg). The residue containing the crude cyclobutanone was purified by flash chromatography or by radial chromatography.

Synthesis of Cyclobutanone 12a. Pentacarbonyl[(phenyl)(pyrrol-1-yl)carbene]chromium(0) **2a** (0.590 g, 1.70 mmol) and dihydropyran (1.2 mL, 13 mmol) in ether (40 mL) were allowed to react according to the general procedure for 40 h. Flash chromatography of the crude reaction product (hexane/AcOEt, 9/1) yielded 222 mg (0.83 mmol, 49% yield) of cyclobutanone **12a** as a white solid: mp 90–92 °C; ^{1}H-NMR δ 7.29–7.16 (m, 5H, Ph), 6.83 (t, 2H, J = 2.2 Hz, pyrrole), 6.25 (t, 2H, J = 2.2 Hz, pyrrole), 4.91 (d, 1H, J = 5.9 Hz, C*H*–OCH_2), 3.88 (m, 1H), 3.65 (m, 1H, OC–C*H*–CH_2), 3.37 (m, 1H), 2.22 (m, 1H), 1.80–1.52 (m, 3H); ^{13}C-NMR δ 202.2 (CO), 134.8 (ipso), 128.1, 127.8, 127.5 (Ph), 119.0 (pyrrole), 109.7 (pyrrole), 85.3 (Ph*C*N), 70.8 (*C*H–OCH_2), 65.0 (CH–*O*CH_2), 55.1 (OC–*C*H–CH_2), 21.6 (CH_2), 18.5 (CH_2); IR (film) ν 1789 (CO) cm^{-1}; MS (EI) m/z 267 (M^+, 33%), 183 (M^+ – dihydropyran, 50%), 155 (PhCPyrrole, 100%). Anal. Calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.40; N, 5.24. Found: C, 76.34; H, 6.39; N, 5.25.

Synthesis of Cyclobutanone 12b. Pentacarbonyl[(phenyl)(pyrrol-1-yl)carbene]chromium(0) **2a** (0.213 g, 0.61 mmol) and ethyl vinyl ether (0.3 mL, 3.1 mmol) in ether (12 mL) at 0 °C were allowed to react according to the general procedure for 40 h to give a crude product consisting of a 2.1/1 mixture of cyclobutanone **12b** and the methathesis product **12b′**. This material was purified by filtration through a short column of silica (hexane/AcOEt, 7/3) followed by radial chromatography (2 mm plate; hex/AcOEt) to give 18 mg (0.11 mmol, 17% yield) of **12b′** followed by 55 mg (0.216 mmol, 35% yield) of cyclobutanone **12b** as a white solid. An analytical sample was recrystallized from hexane: mp 55–56 °C; ^{1}H-NMR δ 7.28 (m, 3H, Ph), 6.96 (m, 2H, Ph), 6.86 (t, 2H, J = 2.1 Hz, pyrrole), 6.25 (t, 2H, J = 2.1 Hz, pyrrole), 4.78 (dd, 1H, J = 8.4, 6.5 Hz, C*H*–OEt), 3.55 (dd, 1H, J = 18.7, 8.4 Hz, CH_2), 3.31 (dd, 1H, J = 18.7, 6.5 Hz, CH_2), 3.49, 3.28 (m, 2H, OCH_2), 1.00 (t, 3H, J = 7.0 Hz, CH_3); ^{13}C-NMR δ 201.6 (CO), 134.9 (ipso), 128.2, 128.1, 126.9 (Ph), 119.6 (pyrrole), 109.2 (pyrrole), 86.0 (Ph*C*N), 74.5 (*C*H–OEt), 65.9 (OCH_2CH_3), 51.5 (CH_2), 14.6 (CH_3); IR (film) ν 1789 (CO) cm^{-1}; MS (EI) m/z 255 (M^+, 23%), 183 (M^+ – ethyl vinyl ether, 37%), 155 (PhCPyrrole, 100%). Anal. Calcd for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71; N, 5.48. Found: C, 75.29; H, 6.72; N, 5.44. Data for compound **12b′**: semisolid that melts at room temperature; R_f = 0.66 (hexane/EtOAc, 4/1); ^{1}H-NMR δ 7.35 (s, 5H, Ph), 6.78 (t, 2H, J = 2.3 Hz, pyrrole), 6.22 (t, 2H, J = 2.3 Hz, pyrrole), 5.14 (s, 1H), 5.05 (s, 1H); ^{13}C-NMR δ 146.3 (Ph*C*N), 136.9 (ipso), 129.0, 128.2, 127.8 (Ph), 121.0 (pyrrole), 109.2 (pyrrole), 103.1 (CH_2). When the reaction was performed at room temperature, olefin **12b′** was the major product (57% yield) and cyclobutanone **12b** was the minor product (6% yield).

Synthesis of Cyclobutanone 12c. Pentacarbonyl[(phenyl)(pyrrol-1-yl)carbene] chromium(0) **2a** (302 mg, 0.87 mmol, 1.5 equiv) and 3-vinyl-(*S*)-4-phenyl-2-oxazolidinone (109 mg, 0.58 mmol, 1 equiv) in CH_2Cl_2 (13 mL) were allowed to react according to the general procedure for 60 h. Flash chromatography (hexane/AcOEt, 7/3) of the crude product followed by radial chromatography (2 mm plate; hexane/AcOEt, 95/1, 70/1, 40/1, and 9/1) gave recovered ene–carbamate and a minor diastereoisomer of product as an inseparable mixture (5.5 mg, 0.015 mmol, 2.5%) and cyclobutanone **12c** (42 mg, 0.12 mmol, 20% yield) as a white solid. An analytical sample was recrystallized from hexane/AcOEt/CH_2Cl_2: mp 134–135 °C; $[\alpha]_D$ = +28.39 (c = 1, CH_2Cl_2); ^{1}H-NMR δ 7.45 (m, 2H, Ph), 7.32 (m, 2H, Ph), 7.18 (m, 4H, Ph), 6.99 (m, 12H, Ph), 6.19 (t, 2H, J = 2.2 Hz, pyrrole), 5.54 (t, 1H, J = 9.8 Hz), 3.96 (t, 1H, J = 8.5 Hz), 3.83 (dd, 1H, J = 8.5, 2.8 Hz), 3.52 (dd, 1H, J = 8.5, 2.8 Hz), 3.03 (dd, 1H, J = 18.8, J = 9.4 Hz), 2.94 (dd, 1H, J = 18.8, J = 9.9 Hz); ^{13}C-NMR δ 200.5 (cyclobutanone CO), 158.1 (carbamate CO), 139.8 (ipso), 135.8 (ipso), 129.5, 129.3, 129.0, 126.2, 125.3 (Ph), 119.9 (pyrrole), 109.1 (pyrrole), 87.2 (Ph*C*N), 70.6 (CH_2), 57.8 (CH), 49.2 (CH), 46.9 (CH_2); IR (film) ν 1796, 1750 cm^{-1}. Anal. Calcd for $C_{23}H_{20}N_2O_3$: C, 74.17; H, 5.41; N, 7.52. Found: C, 74.15; H, 5.63; N, 7.55. Data for the minor diastereoisomer: R_f = 0.37 (hexane/EtOAc, 7/3); ^{1}H-NMR δ 7.73 (m, 2H, Ph), 7.42–7.29 (m, 6H, Ph), 7.11 (m, 2H, Ph), 6.65 (t, 2H, J = 2.1 Hz, pyrrole), 6.29 (t, 2H, J = 2.1 Hz, pyrrole), 5.63 (t, 1H, J = 8.9 Hz), 4.20 (t, 1H, J = 8.5 Hz), 3.90 (dd, 1H, J = 8.3, 3.2 Hz), 3.51 (dd, 1H, J = 8.7, 3.2 Hz), 3.07 (dd, 1H, J = 19.3, J = 9.6 Hz), 2.99 (dd, 1H, J = 19.3, J = 8.4 Hz).

Synthesis of Cyclobutanone 12d. Pentacarbonyl[(phenyl)(pyrrol-1-yl)carbene]chromium(0) **2a** (0.358 g, 1.03 mmol) and cyclopentadiene (0.58 mL, 7.10 mmol) in ether (12 mL) were allowed to react according to the general procedure for 60 h. Flash chromatography of the crude product (hexane/AcOEt, 9/1) followed by radial chromatography (2 mm plate; hexane/AcOEt, 40/1 and 9/1) yielded 144 mg (0.57 mmol, 58% yield) of **12d** as a white solid: mp 72–73 °C; ^{1}H-NMR δ 7.27, 7.01 (m 5H, Ph), 6.87 (t, 2H, J = 2.2 Hz, pyrrole), 6.24 (t, 2H, J = 2.2 Hz, pyrrole), 5.90 (m, 1H, =CH), 5.40 (m, 1H, =CH), 4.37 (m, 1H, C*H*–CH=), 4.18 (ddd, 1H, J = 9.1, 9.1, 1.3 Hz, CH_2), 2.86 (m, 1H, CH_2), 2.57 (dddd, 1H, J = 17.4, 9.1, 4.4, 4.3 Hz, CH_2); ^{13}C-NMR δ 206.9 (C=O), 137.0 (ipso), 135.4 (CH=), 129.2, 128.1, 128.0, 126.5 (Ph + CH=), 119.5, 109.4 (pyrrole), 86.7 (Ph*C*N), 59.7 (CH), 51.3 (CH), 35.0 (CH_2); IR (film) ν 1782 cm^{-1}. MS (EI) m/z 249 (M^+, 28%), 194 (M^+ – cyclopentadiene, 100%). Anal. Calcd for $C_{17}H_{15}NO$: C, 81.90; H, 6.06; N, 5.61. Found: C, 81.74, H, 6.04; N, 5.44.

Synthesis of Cyclobutanone 12e. Pentacarbonyl[(phenyl)(pyrrol-1-yl)carbene]chromium(0) **2a** (0.347 g, 1.00 mmol) and cyclohexadiene (47 mL, 5 mmol) in ether (12 mL) were allowed to react according to the general procedure for 60 h. Flash chromatography (hexane/AcOEt, 4/1) of the crude product followed by radial chromatography (2 mm plate; hexane/AcOEt, 50/1) gave 47 mg (0.18 mmol, 18%) of compound **12e′** as a white solid, followed by 63 mg (0.24 mmol, 24% yield) of cyclobutanone **12e** as a colorless oil. Data for cyclobutanone **12e**: ^{1}H-NMR δ 7.25 (m, 3H, Ph), 7.00 (m, 2H, Ph), 6.90 (t, 2H, J = 2.2 Hz, pyrrole), 6.25 (t, 2H, J = 2.2 Hz, pyrrole), 5.93 (m, 1H, =C*H*–CH_2), 5.48 (m, 1H, CH–C*H*=), 3.97 (m, 1H, C*H*–CH_2), 3.77 (m, 1H, C*H*–CH=), 2.19–2.03 (m, 3H), 1.65 (m, 1H); ^{13}C-NMR δ 204.6 (C=O), 136.6 (ipso), 131.3, 127.9, 127.8, 126.7, 124.6, 119.5 (pyrrole), 109.3 (pyrrole), 83.8 (ipso), 54.7 (CH), 36.8 (CH), 20.9 (CH_2), 18.3 (CH_2); IR (film)

ν 1778 (C=O) cm^{-1}. MS (EI) *m/z* 263 (M^+, 50%), 183 (M^+ − cyclohexadiene, 18%), 155 (PhCPyrrole, 100%). Anal. Calcd for $C_{18}H_{17}NO$: C, 82.09; H, 6.51; N, 5.31. Found: C, 81.96; H, 6.55; N, 5.22. Data for the [4 + 2] adduct **12e'** (this compound was identified by its X-ray structure): mp 85−86 °C (from hexane/CH_2Cl_2); ^{1}H-NMR δ 7.25 (m, 4H), 7.09 (m, 1H), 6.67 (t, 2H, J = 2.1 Hz), 6.49 (m, 2H), 6.28 (t, 2H, J = 2.1 Hz), 5.17 (m, 1H), 3.09 (m, 1H), 2.20 (m, 1H), 1.71 (m, 1H), 1.55 (m, 1H), 1.37 (m, 1H); ^{13}C-NMR δ 154.4, 137.1 (ipso), 133.3, 131.5, 127.9, 125.5, 125.4, 123.6, 112.0, 108.3, 71.5, 33.7, 25.8 (CH_2), 21.1 (CH_2); IR (film) ν 1636, 1613 cm^{-1}; MS (EI) *m/z* 263 (M^+, 45%), 155 (PhCPyrrole, 100%).

Synthesis of Cyclobutanone 12f. Pentacarbonyl[(phenyl)(pyrrol-1-yl)carbene]chromium(0) **2a** (0.175 g, 0.50 mmol) and 1,3-cycloheptadiene (0.27 mL, 2.52 mmol) in ether (13 mL) were allowed to react according to the general procedure for 72 h. The crude reaction product was purified by filtration through a short column on silica (hexane/AcOEt, 7/3) followed by radial chromatography (1 mm plate; hexane/AcOEt, 70/1, 40/1, and 9/1) to give 31 mg (0.108 mmol, 25% yield) of a mixture of products **12f** and **12f'** in a 46:54 ratio. With further purification by radial chromatography analytically pure samples of both isomers could be obtained. Data for cyclobutanone **12f**: white solid, mp 104−105 °C; ^{1}H-NMR δ 7.25 (m, 3H, Ph), 6.88−6.83 (m, 4H, Ph + pyrrole), 6.24 (t, 2H, pyrrole), 5.62−5.54 (m, 1H, =CH), 5.21 (bd, 1H, =CH), 4.26 (d, 1H, J = 11.3 Hz), 3.78 (dt, 1H, J = 11.2, 5.3 Hz, C*H*−CH_2), 2.23−1.94 (m, 4H), 1.67−1.52 (m, 2H); ^{13}C-NMR δ 207.4 (CO), 137.1 (ipso), 129.6, 128.3, 126.7, 125.7 (Ph + 2 =CH), 119.7 (pyrrole), 109.1 (pyrrole), 84.9 (Ph*C*N), 58.7 (CH), 42.5 (CH), 27.7 (CH_2), 23.6 (CH_2), 21.7 (CH_2); IR (film) ν 1777 (CO) cm^{-1}. Anal. Calcd for $C_{19}H_{19}NO$: C, 82.27; H, 6.90; N, 5.05. Found: C, 74.03; H, 7.04; N, 3.98. Data for the [4 + 2] adduct **12f'**: white solid, mp 78−79 °C; ^{1}H-NMR δ 7.31−7.19 (m, 4H, Ph), 7.11−7.05 (m, 1H, Ph), 6.63 (t, 2H, pyrrole), 6.29−6.14 (m, 4H, pyrrole + 2 =CH), 4.99 (m, 1H, CH), 2.91 (t, 1H, J = 6.8 Hz, CH), 1.82−1.53 (m, 6H); ^{13}C-NMR δ 156.6, 137.5 (ipso), 129.2, 129.2, 127.8, 125.9, 125.6 (Ph + 2 =CH), 123.7 (pyrrole), 112.9, 108.3 (pyrrole), 75.3 (CH), 35.0 (CH), 28.9 (CH_2), 28.8 (CH_2), 19.9 (CH_2); IR (film) ν 1627 cm^{-1}. High-resolution mass measurement (EI) calcd for $C_{19}H_{19}NO$: 277.1467. Found: 277.1474±0.0010.

Procedure for Hydrogenation of Cyclobutanone 12d. A pressure tube was sealed with a rubber septum, flame dried, evacuated, and filled with Ar. To the tube was added 10% Pd/C (27 mg), followed by a solution of cyclobutanone **12d** (0.103 g, 0.41 mmol) in EtOAc (5 mL). The tube was equipped with a pressure head and charged with H_2 (3 cycles to 45 psi). The reaction mixture was stirred for 30 min; H_2 was released, and the mixture was filtered through a bed of Celite. The filtrate was concentrated under reduced pressure to give the reduced cyclobutanone. This crude product was further purified by radial chromatography (2 mm plate; hexane/AcOEt, 50/1 and 95/5) to give 91.5 mg (0.36 mmol, 88% yield) of compound **13d** as a white solid. An analytical sample was recrystallized from hexane/CH_2Cl_2: mp 112−113 °C; ^{1}H-NMR δ 7.29 (m, 5H, Ph), 6.85 (t, J = 2.2 Hz, 2H, pyrrole), 6.18 (t, 2H, J = 2.2 Hz, pyrrole), 3.95 (dd, 1H, J = 8.2, 8.1 Hz), 3.72 (ddd, 1H, J = 8.6, 8.2, 1.6 Hz), 2.20 (m, 1H), 2.03−1.59 (m, 4H), 1.38−1.25 (m, 1H); ^{13}C-NMR δ 208.6 (CO), 136.0 (ipso), 128.4 (ipso), 128.0, 126.6 (Ph), 119.0 (pyrrole), 109.1 (pyrrole), 83.3 (Ph*C*N), 62.7 (CH), 43.1 (CH), 29.6 (CH_2), 29.3 (CH_2), 26.3 (CH_2); IR (film) ν 1772 (CO) cm^{-1}. Anal. Calcd for $C_{17}H_{17}NO$: C, 81.24; H, 6.82; N, 5.57. Found: C, 81.14; H, 6.76; N, 5.62.

General Procedure for the Ozonolysis of Cyclobutanones. Cyclobutanones **12a** and **13d** were ozonized following the same procedure described for cyclopropanes **3**. ^{1}H-NMR spectra of the crude reaction products for these reactions revealed that the α-formamidocyclobutanones existed in two conformeric structures (~95/5). The crude products were quite clean and could be used in the next step without purification. However, for characterization purposes, the compounds were chromatographed on silica or purified by radial chromatography, and the major conformers were isolated and characterized.

Synthesis of Compound 14a. Ozonolysis of compound **12a** (138 mg, 0.52 mmol) in CH_2Cl_2 (22 mL) followed by treatment with thiourea (40 mg, 0.52 mmol) in MeOH (3 mL) and workup as described above gave 111 mg (0.45 mmol, 88% yield) of pure α-formamidocyclobutanone as a mixture of two conformers (~95/5). Data for the major conformer after purification by radial chromatography (hexane/AcOEt, 4/1 and 1/1): white solid, mp 133−134 °C; ^{1}H-NMR δ 8.85 (s, 2H), 7.65, 7.35 (m, 5H, Ph), 4.95 (d, 1H, J = 6.5 Hz), 3.78 (m, 1H), 3.65 (m, 1H), 3.30 (m, 1H), 2.18 (m, 1H), 1.8−1.5 (m, 3H), 1.40 (m, 1H); ^{13}C-NMR δ 162.8 (CO, NHCHO), 132.4 (ipso), 129.5, 128.5, 127.9 (Ph), 81.8 (Ph*C*N), 68.9 (CH), 64.9 (CH_2), 54.8 (CH), 20.6 (CH_2), 18.1 (CH_2). IR (film) ν 1780 (CO), 1679 (NHCHO) cm^{-1}. MS (EI) *m/z* 245 (M^+, 16%), 216 (M^+ − HCO, 7%), 104 (PhCNH, 100%).

Synthesis of Compound 14d. Ozonolysis of compound **13d** (52 mg, 0.21 mmol) in CH_2Cl_2 (7 mL) followed by treatment with thiourea (18 mg, 0.24 mmol) in MeOH (1.5 mL) and workup of the reaction as described above gave 34 mg (0.15 mmol, 72% crude yield) of compound **14d** as an oil (92:8), which was chromatographed on silica (hexane/AcOEt, 1/1) to give 31 mg (0.14 mmol, 66% yield) of a white solid. An analytical sample was recrystallized from hexane/CH_2Cl_2. Data for the major conformer: mp 92−93 °C: ^{1}H-NMR δ 9.0 (bs, 2H, NHCHO), 7.52−7.20 (m, 5H, Ph), 3.98 (ddd, 1H, J = 9.4, 9.3, 2.2 Hz), 3.78 (m, 1H), 2.12−1.92 (m, 2H), 1.78−1.52 (m, 3H), 1.25 (m, 1H); ^{13}C-NMR δ 163.1 (CO, NHCHO), 134.7 (ipso), 128.6, 128.3 (Ph), 80.5 (Ph*C*NHCHO), 63.1 (CH), 41.5 (CH), 30.2 (CH_2), 28.3 (CH_2), 26.9 (CH_2); IR (film) ν 1774 (CO), 1681 (NHCHO) cm^{-1}. MS (EI) *m/z* 229 (M^+, 9%), 200 (M^+ − HCO, 100%). High-resolution mass measurement (EI) calcd for $C_{14}H_{15}NO_2$: 229.1103. Found: 229.1103.

General Procedure for the Hydrolysis of α-Formamidocyclobutanones.[14] The formamido group in α-formamidocyclobutanones was hydrolyzed by heating at reflux temperature a solution of the compound in HCl/MeOH (0.5−1 N) for 1−2.5 h. After cooling to room temperature, the solvent was evaporated under reduced pressure and the residue was diluted with water and four drops of concentrated hydrochloric acid. The solution was washed with CH_2Cl_2, and the aqueous layer was basified with NaOH (3 N aqueous solution) until pH 10−11 and extracted with CH_2Cl_2 (×2). The organic layer was washed with 5% $NaHCO_3$ aqueous solution (×2), water, and brine (×2), dried over $MgSO_4$, and concentrated on a rotary evaporator to give pure α-aminocyclobutanones.

Synthesis of Compound 15a. α-Formamidocyclobutanone **14a** (60 mg, 0.25 mmol) was dissolved in 15 mL of 1 N HCl/MeOH, and the solution was heated at reflux temperature for 1 h. Evaporation of the solvents and treatment of the residue according to the general procedure afforded 34 mg (0.16 mmol, 61% yield) of pure α-aminocyclobutanone **15a** as a colorless oil. This material was filtered through a small plug of silica before characterization: R_f = 0.29 (hexane/EtOAc, 1/2); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.50−7.46 (m, 2H, Ph), 7.37−7.25 (m, 3H, Ph), 4.25 (d, 2H, J = 5.9 Hz, CH(O)), 3.88 (ddd, 1H, J = 7.9, 5.9, 2.0 Hz CH(CO)), 3.70 (d, 1H, J = 11.4 Hz, H-3), 3.25 (ddd, 1H, J = 11.2, 8.6, 2.6 Hz, H-3'), 2.14 (m, 1H, H-5), 1.90 (s, 2H, NH_2), 1.67−1.75 (m, 1H, H-5'), 1.57−1.24 (m, 2H, H4, 4'); ^{13}C-NMR δ 209.6 (CO), 138.6 (ipso), 128.0, 127.4, 127.0 (Ph), 79.4 (Ph*C*N), 73.1 (HCO), 64.7 (CH_2(O)), 53.5 (CH), 21.9 (CH_2), 18.6 (CH_2); IR (film) ν 3372, 3310 (NH_2), 1776 (CO) cm^{-1}. This material was used without further purification.

Synthesis of Compound 15d. α-Formamidocyclobutanone **14d** (55 mg, 0.24 mmol) was dissolved in 10 mL of 0.5 N HCl/MeOH, and the solution was heated at reflux temperature for 2.5 h. Evaporation of the solvents and treatment of the residue according to the general procedure afforded 29 mg

(0.14 mmol, 60% yield) of pure α-aminocyclobutanone **15d** as a colorless oil that became a white solid upon refrigeration overnight: mp 36–37 °C; ^{1}H-NMR δ 7.38–7.22 (m, 5H, Ph), 3.84 (t, 1H, J = 8.3 Hz), 2.80 (dd, 1H, J = 7.9, 6.7 Hz), 2.08 (dd, 1H, J = 12.9, 7.3 Hz), 2.00 (bs, 2H, NH_2), 1.69–1.45 (m, 4H), 1.22–1.07 (m, 1H); ^{13}C-NMR δ 216.8 (CO), 138.6 (ipso), 128.2, 127.5, 126.8 (Ph), 78.0 (PhCN), 60.9 (CH), 46.6 (CH), 29.6 (CH_2), 29.5 (CH_2), 26.0 (CH_2); IR (film) ν 3360 (NH_2), 3290 (NH_2), 1766 (CO) cm^{-1}. This was used without further purification.

Preparation of α-(*tert*-Butoxycarbonylamino)cyclobutanone 16a. α-Aminocyclobutanone **15a** (11 mg, 0.05 mmol) was dissolved in *t*-BuOH (10 mL) under Ar, and di-*tert*-butyl dicarbonate (34 mg, 0.16 mmol) and Et_3N (22 μL, 0.16 mmol) were added to the solution. The reaction mixture was heated at 60 °C for 8.5 h. After removal of the solvent on a rotary evaporator, the residue was purified by flash chromatography on silica (hex/AcOEt, 1/1) followed by radial chromatography (hex/AcOEt, 95/5 and 9/1) to afford 6 mg (0.02 mmol, 38% yield) of compound **16a** as a white solid: mp 120–121 °C; ^{1}H-NMR δ 7.68 (s, 1H), 7.27 (m, 5H, Ph), 5.95 (bd, 1H, J = 7.5 Hz), 5.71 (d, 1H, J = 7.7 Hz), 4.00 (m, 2H), 2.28 (dt, 1H, J = 16.8, 6.4 Hz), 2.13 (dt, 1H, J = 16.8, 6.4 Hz), 1.79 (m, 2H), 1.38 (s, 9H), 1.23 (bs, 1H); ^{13}C-NMR δ 194.3 (CO), 158.8 (CH), 154.9 ($NHCO_2$), 138.8 (ipso), 128.9, 127.9, 127.5 (Ph), 114.0 (PhCN), 79.6 ($C(CH_3)$), 67.1 (CH_2), 58.0 (CH), 28.2 (CH_3), 20.7 (CH_2), 18.3 (CH_2); IR (film) ν 3421, 3364 (NH), 1711 (CO), 1656, 1616 ($NHCO_2$) cm^{-1}. Anal. Calcd for $C_{18}H_{23}NO_4$: C, 68.11; H, 7.30; N, 4.41. Found: C, 67.93; H, 7.49; N, 4.13.

Preparation of α-(*tert*-Butoxycarbonylamino)cyclobutanone 16d. α-Aminocyclobutanone **15d** (28 mg, 0.14 mmol) was dissolved in *t*-BuOH (10 mL) under Ar, and di-*tert*-butyl dicarbonate (67 mg, 0.31 mmol) and Et_3N (43 μL, 0.31 mmol) were added to the solution. The reaction mixture was stirred at room temperature for 48 h and at 60 °C for 6 h. After removal of the solvents on a rotary evaporator, the residue was purified by flash chromatography on silica (hexane/AcOEt, 1/1) followed by radial chromatography (hexane/AcOEt, 95/5 and 9/1) to afford 31 mg (0.10 mmol, 73% yield) of compound **16d** as a colorless oil, which became a white solid upon refrigeration: mp 58–59 °C; ^{1}H-NMR δ 7.33–7.27 (m, 5H, Ph), 4.93 (bs, 1H, NH), 3.97 (t, 1H, J = 8.9 Hz), 3.45 (bs, 1H), 1.97 (dd, 1H, J = 13.3, 7.4 Hz), 1.68–1.44 (m, 3H), 1.36 (s, 10H, ^{t}Bu + CH), 0.94–0.83 (m, 1H); ^{13}C-NMR δ 154.1 (CO, $NHCO_2$), 136.1 (ipso), 128.6, 128.1, 127.1 (Ph), 80.3, 78.3, 62.4 (CH), 45.7 (CH), 29.9 (CH_2), 28.7 (CH_2), 28.1 (CH_3), 26.4 (CH_2); IR (film) ν 3348, 3262 (NH), 1778 (CO), 1694 ($NHCO_2$) cm^{-1}. Anal. Calcd for $C_{18}H_{23}NO_3$: C, 71.73; H, 7.69; N, 4.65. Found: C, 71.59; H, 7.63; N, 4.61.

General Procedure for the Synthesis of β-Lactams 17. An Ace pressure tube was sealed with a rubber septum, flame dried, evacuated, and filled with Ar. Carbene **2a** was added into the tube, followed by dry degassed acetonitrile (10–15 mL) and 0.9–1.1 equiv of the corresponding imine to produce a deep brown solution. Glass beads were added to the solution, and the tube was sealed with a pressure cap and irradiated (450 W Conrad-Hanovia 7825 medium-pressure Hg lamp, Pyrex well) until the brown solution turned bright yellow (9–15 h), which indicated complete consumption of the carbene. The yellow solution was filtered through Celite and concentrated under reduced pressure to give a solid residue, which was taken up in EtOAc. Air was bubbled into the solution, and the resulting suspension was filtered through Celite. The yellow filtrate was diluted 1:1 by volume with hexane and air oxidized either on the rooftop in sunlight or in a light box (6 × 20 W Vitalite fluorescent bulbs). After 2–3 h, the resulting brown suspension was filtered through Celite and the filtrate was air oxidized again. These operations were successively repeated until a clear colorless solution was obtained (12–36 h). Solvent removal on a rotary evaporator gave the crude β-lactam that was purified by column or radial chromatography.

Synthesis of β-Lactam 17a. Pentacarbonyl[(phenyl)(pyrrol-1-yl)carbene]chromium(0) **2a** (0.215 g, 0.62 mmol) and methyl *N*-benzylformimidate (89 mg, 0.60 mmol) were photolyzed in CH_3CN (14 mL) for 9 h according to the general procedure. Air oxidation of the reaction mixture as described above gave a crude product, which was purified by flash chromatography (hexane/AcOEt, 4/1) to afford 102 mg of β-lactam **17a** (0.31 mmol, 51% yield) in a 98:2 ratio of diastereomers as a white solid: mp 110–111 °C; ^{1}H-NMR δ 7.37–7.23 (m, 8H, Ph), 7.07–7.03 (m, 2H, Ph), 6.90 (t, 2H, J = 2.2 Hz, pyrrole), 6.27 (t, 2H, J = 2.2 Hz, pyrrole), 5.09 (s, 1H), 4.78 (d, 2H, J = 15.1 Hz, CH_2Ph), 4.33 (d, 2H, J = 15.1 Hz, CH_2Ph), 3.11 (s, 3H, OCH_3); ^{13}C-NMR δ 164.1 (C=O), 134.4 (ipso), 133.9 (ipso), 128.9, 128.5, 128.2, 128.1, 127.9, 126.9 (2Ph), 120.2, 109.2 (pyrrole), 91.1 (HC(OMe)), 80.1 (PhCN), 56.1 (OCH_3), 44.3 (CH_2); IR (film) ν 1772 cm^{-1}. Anal. Calcd for $C_{21}H_{20}N_2O_2$: C, 75.88; H, 6.06; N, 8.42. Found: C, 76.03; H, 5.89; N, 8.30.

Synthesis of β-Lactam 17b. Pentacarbonyl[(phenyl)(pyrrol-1-yl)carbene]chromium(0) **2a** (0.243 g, 0.70 mmol) and *N*-methylbenzaldimine (91 mg, 0.77 mmol) were photolyzed in CH_3CN (13 mL) for 14 h according to the general procedure. Air oxidation of the reaction mixture as described above gave a crude product, which was purified by radial chromatography (2 mm plate; hexane/AcOEt, 95/5 and 9/1) to afford 103 mg (0.34 mmol, 49% yield) of β-lactam **17b** in a 72:27 ratio of diastereomers as a white solid: mp 109–110 °C; ^{1}H-NMR δ 7.46–7.03 (m, 10H, Ph), 7.02 (b), 6.48 (a) (t, 2H, pyrrole), 6.24 (b), 5.85 (a) (t, 2H, pyrrole), 5.31 (b), 5.30 (a) (s, 1H), 2.92 (b), 2.91 (a) (s, 3H, CH_3). ^{13}C-NMR δ 166.0 (CO), 165.6 (CO), 137.4 (ipso), 134.1 (ipso), 133.2 (ipso), 133.0 (ipso), 128.8, 128.5, 128.4, 128.3, 128.0, 127.8, 127.6, 127.4, 126.9, 126.5 (Ph), 119.8 (pyrrole), 119.6 (pyrrole), 109.0 (pyrrole), 108.1 (pyrrole), 81.1 (PhCN), 80.4 (PhCN), 69.9 (CH), 69.0 (CH), 27.1 (CH_3), 26.9 (CH_3); IR (film) ν 1760 (CO) cm^{-1}. Anal. Calcd for $C_{20}H_{18}N_2O$: C, 79.44; H, 5.99; N, 9.26. Found: C, 77.80; H, 5.89; N, 9.16.

Ozonolysis of β-Lactams. β-Lactams **17a** and **17b** were ozonized following the same procedure described for cyclopropanes **3**. As in the case of cyclobutanones, the α-formamido-β-lactams were obtained in two rotameric forms (~95:5 ratio) and the crude reaction materials could be used in the next step without further purification; however, in some reactions these crude products were purified by chromatography prior to characterization.

Synthesis of Compound 18a. Ozonolysis of compound **15a** (67 mg, 0.20 mmol) in CH_2Cl_2 (8 mL) followed by treatment with thiourea (15 mg, 0.2 mmol) in MeOH (2 mL) and workup of the reaction as described above gave 54 mg (0.17 mmol, 86% yield) of α-formamido-β-lactam **18a** as a mixture of two rotamers (91:9 ratio). Data for the major conformer after separation by column chromatography (hexane/AcOEt, 1/1): R_f = 0.56 (hexane/EtOAc, 1/1); ^{1}H-NMR δ 9.33 (bs, 2H, NHCHO), 7.41–7.25 (m, 10H, Ph), 5.16 (s, 1H), 4.76 (d, 1H, J = 14.9 Hz, CH_2), 4.25 (d, 1H, J = 14.9 Hz, CH_2), 3.28 (s, 3H, OCH_3); ^{13}C-NMR δ 162.4 (NCO, NHCHO), 133.8 (ipso), 133.2, 129.0, 128.9, 128.5, 128.4, 128.2, 127.3 (Ph), 87.7 (CH), 76.4 (PhCNHCHO), 57.3 (OCH_3), 44.1 (CH_2); IR (film) ν 1768, 1734, 1699 cm^{-1}. High-resolution mass measurement (FAB, M + 1) calcd for $C_{18}H_{19}N_2O_3$: 311.1396. Found: 311.1398±0.0010.

Synthesis of Compound 18b. Ozonolysis of compound **17b** (97 mg, 0.32 mmol) in CH_2Cl_2 (10 mL) followed by treatment with thiourea (27 mg, 0.35 mmol) in MeOH (3 mL) and workup of the reaction as described above gave 57 mg (0.20 mmol, 63% yield) of α-formamido-β-lactam **18b** as a mixture of two diastereoisomers (79:21 ratio) and in two rotamers (91/9). During purification by radial chromatography the two rotamers underwent interconversion, and the initially minor product was isolated as the major product (2:1 ratio of a/b) (2 mm plate; hexane/AcOEt, 4/1, 1/1, and 1/2): mp 108–109 °C (hex/CH_2Cl_2); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.08 (a), 7.70 (b) (d, 1H, J = 11.9 Hz, HCO), 7.64–7.26 (m, 10H, Ph), 6.31

(b) (s, 1H, NH), 5.77 (a) (d, 1H, NH), 5.13 (b), 4.86 (a) (s, 1H, CH), 2.95 (a), 2.89 (b) (s, 3H, CH_3); ^{13}C-NMR δ 166.3 (NCO), 165.9 (NCO), 163.3 (NHCHO), 159.2 (NHCHO), 137.6 (ipso), 136.6 (ipso), 133.2 (ipso), 132.1 (ipso), 129.7, 129.6, 129.3, 128.9, 128.7, 128.7, 128.4, 128.1, 127.3, 126.6, 126.2 (Ph), 74.3 (Ph*C*N), 73.8 (Ph*C*N), 70.3 (CH), 69.4 (CH), 27.1 (CH_3), 27.0 (CH_3); IR (film) ν 3263 (NH), 1759 (NCO), 1693 (NHCHO) cm^{-1}. High-resolution mass measurement (FAB M + 1) calcd for $C_{17}H_{17}N_2O_2$: 281.1290. Found: 281.1291±0.0006.

Preparation of α-Amino-β-lactam 19a. α-Formamido-β-lactam **18a** (70 mg, 0.23 mmol) was dissolved in MeOH (3 mL) under Ar, and the solution was cooled to 0 °C. PBr_3 (70 μL, 0.74 mmol) was added dropwise via syringe, and the reaction mixture was stirred for 40 min at 0 °C and for 3.5 h at room temperature. Elimination of the solvent on a rotary evaporator gave a residue, which was taken up in THF (3 mL). Et_3N (0.18 mL, 1.29 mmol) was added to the solution at 0 °C, and a white solid was immediately produced. After stirring the reaction mixture for an additional 1 h, the solid was filtered through Celite and the filtrate was concentrated under reduced pressure. The crude material was purified by column chromatography (hexane/AcOEt, 1/4) to give 29 mg (0.10 mmol, 45% yield) of α-amino-β-lactam **19a** as a colorless oil, which became a white solid upon refrigeration: mp 46–47 °C; ^{1}H-NMR δ 7.52 (m, 2H, Ph), 7.38–7.26 (m, 8H, Ph), 4.76 (d, 1H, J = 15.0 Hz, CH_2), 4.51 (s, 1H), 4.22 (d, 1H, J = 15.0 Hz, CH_2), 3.04 (s, 3H, OCH_3), 1.89 (bs, 2H, NH_2); ^{13}C-NMR δ 170.4 (CO), 135.7 (ipso), 135.2 (ipso), 128.8, 128.2, 128.1, 127.8, 127.0 (Ph), 93.6 (CH), 76.3 (Ph*C*N), 56.2 (OCH_3), 44.1 (CH_2); IR (film) ν 3363 (NH_2), 3299 (NH_2), 1755 (CO) cm^{-1}. MS (EI) m/z 282 (M^+, 2%), 150 (M^+ − $PhCH_2NCO$, 100%), 134 (M^+ − methyl *N*-benzylformimidate, 42%). High-resolution mass measurement calcd for $C_{17}H_{18}N_2O_2$: 282.1368. Found: 282.1359±0.000 66 (n = 7).

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