Articles

Thermal Reactions of Chromium Aminocarbene Complexes with Alkynes. Synthesis of Bicyclo[3.1.0] Lactams

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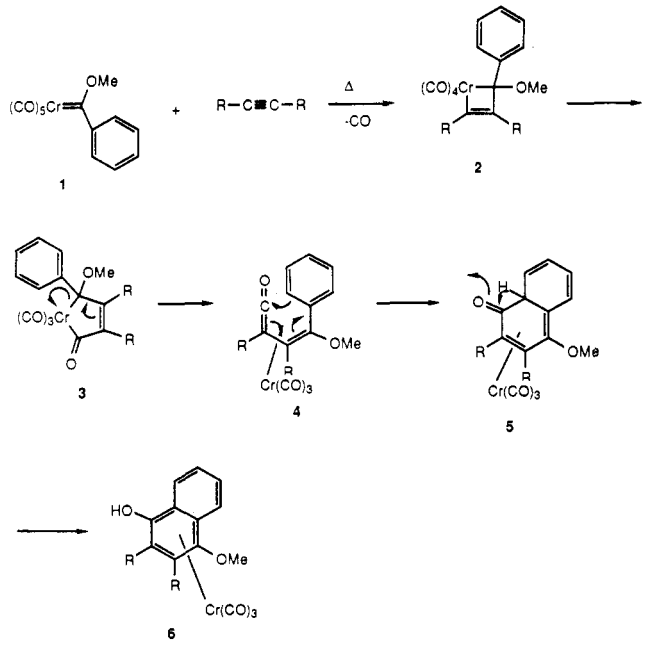
((Dimethylamino)methylene)chromium pentacarbonyl underwent thermal reaction with internal alkynes to produce coordinated enaminoketenes. In situ reaction of these with imines produced novel bicyclo[3.1.0] lactams rather than the expected [2 + 2] or [4 + 2] cycloaddition products.

Introduction

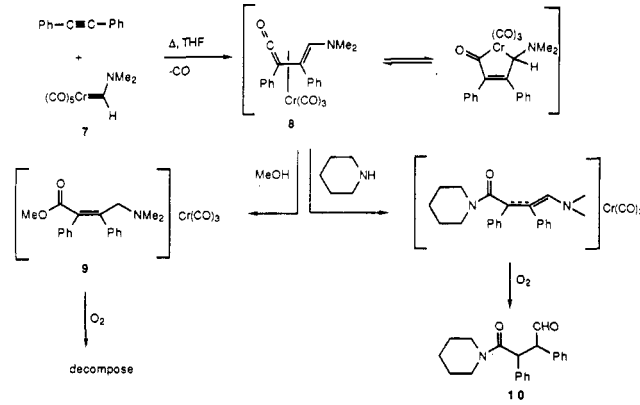
The use of the thermal reaction of alkynes with alkoxyaryl- and alkoxyvinylcarbene complexes of chromium to produce oxygenated aromatics has undergone a rapid growth in development and in application to organic synthesis.[1] Although not completely understood,[2] the reaction is thought to proceed as in Scheme I and to involve, as a key intermediate, a chromium-complexed vinyl ketene, 4. Cyclization of this vinyl ketene into the β-carbon of the unsaturated group on the (initial) carbene carbon leads to the observed products (6). This process is remarkably sensitive to reaction conditions and to the nature of the substituents on the carbene complex,[3] and furans, cyclobutenones, and indenes[4] can also be formed.

Photochemical reactions of chromium carbene complexes follow a somewhat different course. Photolysis of alkoxy- and aminocarbene complexes of chromium in the presence of imines produces β-lactams[5] by a process thought to involve photogeneration of a ketene–chromium complexes.[6] In the course of studies directed toward the synthesis of biologically active β-lactams by this photochemical procedure, an efficient general synthesis of ((dialkylamino)methylene) chromium pentacarbonyl complexes (e.g. 7) was developed in these laboratories.[7] The

Scheme I



Scheme II



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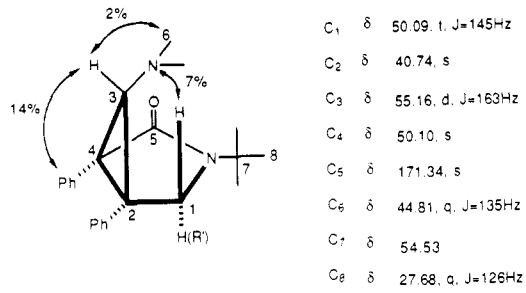


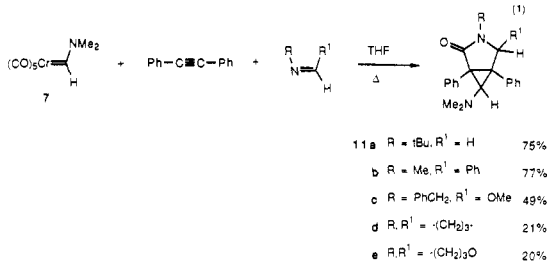
Figure 1. ^{13}C NMR spectral and NOE data for **11a**.

reactions of *this* type of carbene complex with alkynes could potentially produce a metal-bound enaminoketene, which, lacking appropriately situated sp^2 carbons to undergo cyclization as in Scheme I, might be trapped by external reagents. The results of studies addressing this question are presented below.

Results and Discussion

To assess the general reactivity of (dialkylamino)methylene complexes with alkynes, (dimethylamino)carbene complex **7** was heated with 1 equiv of diphenylacetylene in THF at 80 °C until no starting complex **7** remained (analytical TLC) (24 h). The resulting product appeared to be quite polar and did not elute from SiO_2 with nonpolar solvent systems. Elution with methanol/methylene chloride gave the arene chromium tricarbonyl complex **9** of the γ-amino ester. Oxidative removal of the chromium from this complex led to decomposition of the organic product. In contrast, treatment of the initial carbene/alkyne adduct with piperidine, followed by oxidative removal of the chromium residue, produced the fully characterized β-formyl amide **10**, resulting from hydrolysis of the enamine during oxidation. These transformations are summarized in Scheme II. They are best explained by formation of coordinated enaminoketene **8** followed by reaction of the ketene carbonyl group with the added external nucleophile. The enamine portion remained intact during this process.

In contrast to these simple alcohol or amine nucleophiles, imines have *two* potentially reactive sites, the nucleophilic nitrogen and the electrophilic carbon, in complement with the electrophilic carbonyl carbon and the nucleophilic enamine carbon of **8**. Heating a mixture of diphenylacetylene, ((dimethylamino)methylene)pentacarbonylchromium(I) complex **7** and an imine in THF at 80 °C (sealed tube) for 1–2 days produced bicylic lactams **11a–e** in modest yield (eq 1). (The same products were



obtained by heating diphenylacetylene and **7** together until no starting complex remained, as above, followed by addition of imine and continued heating. The yields of bicyclic lactam were somewhat lower with this procedure.) These were not expected products from the type of reaction, and the structural assignment requires comment.[8]

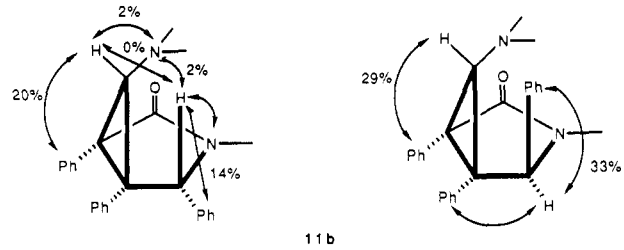
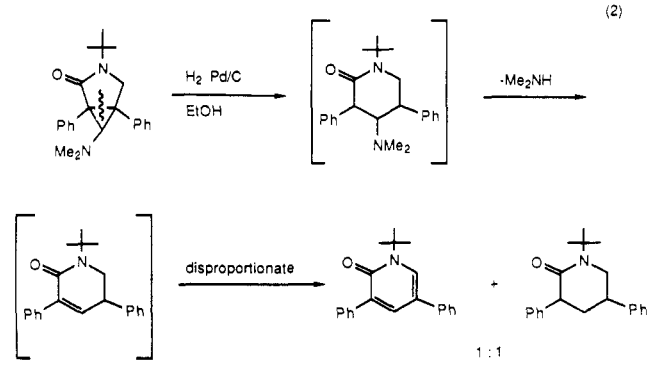


Figure 2.

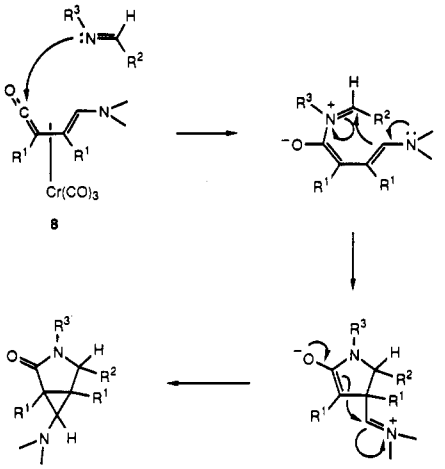
All compounds had parent ions in the mass spectra consistent with the assigned constitution and elemental composition, and all had acceptable elemental analyses or high-resolution, exact mass measurements. The presence of a 5-membered lactam was indicated by infrared absorptions between 1675 and 1695 cm^{-1} (6-membered lactams appear at ~1640 cm^{-1}) as well as a signal in the ^{13}C NMR spectrum between δ 169 and 172 ppm, characteristic of a lactam carbonyl carbon. The most conclusive proof of structure came from the gated decoupled ^{13}C NMR spectra, shown for **11a** in Figure 1. All ^{13}C chemical shifts and C–H coupling constants are consistent with the assigned structure. Most informative was the signal observed for C_3, which appeared as a doublet, J = 163 Hz, at δ 55.16. This coupling constant and chemical shift was *only* consistent with a cyclopropyl methine. Chemical confirmation of structure was obtained by hydrogenolysis (H_2, Pd/C, EtOH) of the cyclopropyl ring. Exclusive cleavage of the ring junction cyclopropyl bond occurred, followed by loss of dimethylamine and disproportionation of the α,β-unsaturated lactam (eq 2).



With the exception of **11b**, a single stereoisomer of the bicyclic lactams was obtained. Detailed NOE measurements established the stereochemistry to be that shown in Figure 1, a structure that entails the least steric crowding of the substituents. For **11b**, two isomers were obtained, in roughly equal amounts. For compounds **11a,c–e** and one isomer of **11b**, the cyclopropyl methine appeared at δ 2.85–3.10 and the dimethylamine group at δ 2.5–2.6 as a sharp singlet. For the other isomer of **11b**, however, while the cyclopropyl methine appeared at δ 2.96, the dimethylamino group appeared as two broadened peaks at δ 1.8 and 2.35, which, upon warming to 381 K, coalesced to a single sharp peak at δ 2.18. This indicates a lack of free rotation by the dimethylamino group, indicating that the stereochemistry for this isomer is that shown in Figure 2, in which the phenyl group and the dimethylamino group

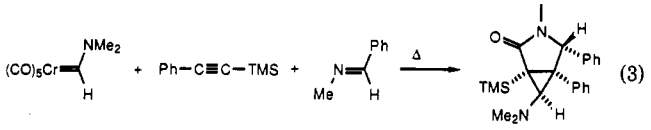
(8) Related bicyclo[3.1.0]hexanones have been reported from the reaction of vinylketenes resulting from the reaction of bis(trimethylsilyl)acetylene with (methoxy)(phenyl)pentacarbonylchromium. See: Dötz, K. H.; Trenkle, B.; Schubert, U. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 287. Dötz, K. H.; Mühlemeier, J.; Trenkle, B. *J. Organomet. Chem.* **1985**, *289*, 257. No mechanism was proposed, but it is likely that reaction similar to those presented in Scheme III are involved.

Scheme III



are cis to each other and sterically interact across the ring. Again, NOE measurements were entirely consistent with this assignment.

Phenyl(trimethylsilyl)acetylene also underwent this unusual cyclization reaction to produce bicyclic lactam **12** (eq 3). In contrast, both 5-decyne and methylphenyl-



(3)

acetylene failed to produce bicyclic lactams when treated with the carbene complex and an imine, although the carbene complex was consumed. When these same acetylenes were treated with carbene **7** and methanol, complexed γ-amino esters corresponding to **9** were produced, indicating that the enaminoketene had formed but had failed to react productively with the imine. Terminal alkynes underwent reaction but gave an intractable mixture of products.

Although the mechanism of this process has not been studied and is not understood, many of its features are consistent with the intermediacy of chromium-coordinated enaminoketene complex **8**. Scheme III details a reasonable series of steps leading from starting materials to products. The strained and sterically congested nature of the product in addition to the general requirement of a nucleophilic nitrogen and electrophilic carbon accounts for the limited range of imines (those derived from aldehydes), which successfully undergo this reaction. Thus ketone imines (steric), *N*-phenylimines (nucleophilicity), and oxazolines and thiazolines (electrophilicity) failed to undergo reaction and were recovered unchanged. Enamines and enamides also failed to undergo reaction, while indole and *N*-methylindole were consumed but were converted to an intractable mixture of products, many of which appeared to contain more than one molecule of indole. Thus this process appears to be delicately balanced and to have stringent requirements for productive reactions with nucleophiles.

Exploration of the unusual chemistry of these metal-bound enaminoketenes continues.

Experimental Section

General Procedures. Melting points were taken on a Mel-Temp apparatus and are uncorrected. IBM 200, 270, and 500 NMR spectrometers were used for the 200-, 270-, and 500-MHz ^{1}H NMR spectra, respectively. IR spectra were recorded either on a Beckman 4240 or a Beckman Acculab 3 spectrophotometer. Radial layer chromatographic technique was used for the purification in most cases, by using Chromatotron Model 7924 with Merck silica gel 60PF as the stationary phase. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

Materials. Tetrahydrofuran (Fisher, reagent grade) was distilled from benzophenone ketyl under a nitrogen atmosphere just prior to use. Hexane was distilled at atmospheric pressure and stored over Molecular Sieve 4A. Methylene chloride (Fisher) and ethyl acetate (Fisher) were distilled over CaH_2 and stored over Molecular Sieve 4A.

Chromium hexacarbonyl (Pressure Chemical Co.), diphenylacetylene (Aldrich), piperidine (Aldrich), 5% palladium on charcoal (Aldrich), and methanol (Fisher) were obtained from commercial supplies and used without further purification.

The following chemicals were prepared according to the literature procedures: methyl *N*-benzylformimidate,[9] 5,6-dihydro-4*H*-1,3-oxazine,[10] and 1-pyrroline.[11]

γ-Amino Ester (9). The carbene complex **7** (249 mg, 1.0 mmol) and diphenylacetylene (178 mg, 1.0 mmol) were placed in an acylation tube under a stream of Ar. Freshly distilled THF (3 mL) was placed in the tube, which was quickly sealed and heated at 85 °C for 24 h. Material was eluted on preparative TLC with 8:2 CH_2Cl_2–MeOH. The γ-amino ester $Cr(CO)_3$ complex **9** was recovered in 18.6% yield (80 mg) as an orange oil: ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.20 (s, 6 H, NMe_2), 3.30 (s, 2 H, CH_2), 3.87 (s, 3 H, OMe), 4.91 (m, 2 H, Ar H), 5.2–5.4 (m, 4 H, Ar H), 7.0–7.3 (m, 5 H, Ar H); ^{13}C NMR ($CDCl_3$) δ 232.0 ($Cr(CO)_3$), 168.0 (CO), 143.8, 138.7, 130.0, 128.9, 128.4, 127.8 (Ar and olefinic), 102.5, 96.6, 94.2, 88.0 (Ph·$Cr(CO)_3$), 63.7 (CH_2), 51.7 (OMe), 45.1 (NMe_2); IR ($CDCl_3$) ν 3080–3010, 2980–2770, 1940 (Cr(CO)), 1900 (Cr(CO)), 1720 (CO) cm^{-1}; mass spectrum (NH_3CI), *m/e* 432 (parent), 296 (P − $Cr(CO)_3$), 281, 264, 250.

β-Formyl Amide (10). The carbene complex **7** (100 mg, 0.40 mmol) and diphenylacetylene (81 mg, 0.45 mmol) were placed in an acylation tube under a stream of Ar. THF was transferred to the tube via syringe, and then piperidine (51 mg, 0.60 mmol) was introduced by syringe into the tube. The tube was quickly sealed and heated to 80 °C for 1.5 days. The reaction was followed by TLC until no carbene could be detected. The mixture was then air-oxidized in sunlight or under Vitalite, filtered through Celite, and purified by Chromatotron (5:1 hexane–ethyl acetate) to yield the aldehyde as a white solid (mp 113–116 °C) in 40% yield (51 mg): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.30–1.60 (m, 6 H, CH_2), 3.38 (m, 3 H, CH_2), 3.69 (m, 1 H, CH), 4.37 (d, *J* = 2.0 Hz, 1 H, =CH), 4.56 (d, *J* = 2.0 Hz, 1 H, =CH), 6.90–7.20 (m, 10 H, Ar H), 9.89 (s, 1 H, CHO); ^{13}C NMR ($CDCl_3$) δ 199.3 (CHO), 170.1 (C(O)N), 137.1, 133.2, 130.0, 128.5, 128.3, 127.8, 127.4, 126.8 (Ar), 62.9 (J_1 = 138 Hz, J_2 = 22 Hz, *C*HCHO), 51.4 (*C*HC(O)N), 46.7, 43.5 (CH_2N), 25.6, 25.5, 24.5 (CH_2); IR ($CDCl_3$) ν 3080–2800, 1715 (CHO), 1620 (CO–N), 1450 cm^{-1}. Anal. Calcd for $C_{21}H_{23}NO_2$: C, 78.47; H, 7.21; N, 4.36. Found: C, 78.63; H, 7.09; N, 4.33.

Bicyclic Lactam (11a). Via the above procedure using 100 mg (0.40 mmol) of carbene complex **7**, 81 mg (0.45 mmol) of diphenylacetylene, and 38 mg (0.45 mmol) of *N*-*tert*-butylimine, the lactam was obtained as a white solid, mp 115–117 °C, in 75% yield (104 mg): ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.45 (s, 9 H, *t*-Bu), 2.50 (s, 6 H, NMe_2), 2.85 (s, 1 H, cyclopropyl H), 3.68 (d, *J* = 10.6 Hz, 1 H, CH_2), 3.78 (d, *J* = 10.6 Hz, 1 H, CH_2), 7.05–7.25 (m, 10 H, Ar H); ^{13}C NMR ($CDCl_3$) δ 171.3 (C(O)N), 138.2, 134.8, 129.6, 128.9, 128.3, 127.9, 126.9, 126.8 (Ar), 55.2 (d, *J* = 163 Hz, =*C*H-(NMe_2)), 54.5 (*C*Me_3), 50.1 (t, *J* = 145 Hz, CH_2), 50.1 (C(O)*C*H-(Ph)), 44.8 (q, *J* = 135 Hz, NMe_2), 40.7 (s, *C*Ph), 27.7 (q of sept, J_1 = 126 Hz, J_3 = 4.4 Hz, *C*CH_3); IR ($CDCl_3$) ν 3100–2780, 1680 (C(O)N), 1600, 1500, 1470, 1450 cm^{-1}. Anal. Calcd for $C_{23}H_{28}N_2O$: C, 79.27; H, 8.10; N, 8.04. Found: C, 78.96; H, 7.91; N, 7.82.

Bicyclic Lactams (11b). Via the above procedure using 125 mg (0.50 mmol) of carbene complex **7**, 108 mg (0.60 mmol) of diphenylacetylene, and 123 μL (1.0 mmol) of *N*-methylphenyl-

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(10) Wenker, H. *J. Am. Chem. Soc.* **1935**, *57*, 1079.
(11) Nomura, Y.; Ogawa, K.; Takeuchi, Y.; Tomoda, S. *Chem. Lett.* **1977**, 693.

imine, the lactam was obtained as white solids in two isomeric forms. More polar isomer: 40%; mp 194–203 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.80 and 2.35 (br) sharpened at 381 K to 2.18 (s, 6 H, NMe_2), 2.96 (s, 1 H, cyclopropyl H), 3.05 (s, 3 H, NMe), 5.07 (s, 1 H, C(Ph)H), 7.0–7.25 (m, 15 H, Ar H); ^{13}C NMR ($CDCl_3$) δ 172.4 (C(O)N), 137.7, 135.8, 134.5, 130.6, 129.2, 128.4, 128.3, 128.0, 127.5, 127.4, 127.2, 126.9 (Ar), 70.7 (CHPh), 58.3, 49.5, 47.3, 46.2, 29.7 (C(O)NCH_3); IR ($CDCl_3$) ν 3100–2780, 1680 (C(O)–N), 1600, 1500, 1460, 1450 cm^{-1}. Anal. Calcd for $C_{26}H_{26}N_2O$: C, 81.64; H, 6.85; N, 7.32. Found: C, 81.41; H, 6.78; N, 7.12. Less polar isomer: 37%; mp 52–55 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.61 (s, 6 H, NMe_2), 2.83 (s, 3 H, NMe), 2.96 (s, 1 H, cyclopropyl H), 4.55 (s, 1 H, C(Ph)H), 6.65–7.30 (m, 15 H, Ar H); ^{13}C NMR ($CDCl_3$) δ 172.9 (C(O)N), 137.5, 135.4, 134.2, 131.3, 129.1, 128.3, 128.2, 127.7, 127.5, 127.3, 127.0, 126.5 (Ar), 66.6 (CHPh), 57.2, 48.7, 47.2, 45.4, 28.7 (C(O)NCH_3); IR ($CDCl_3$) ν 3100–2770, 1675 (C(O) N), 1600, 1500, 1450 cm^{-1}. Anal. Calcd for $C_{26}H_{26}N_2O$: C, 81.64; H, 6.85; N, 7.32. Found: C, 81.38; H, 6.64; N, 7.05.

Bicyclic Lactam (11c). Via the above procedure using 100 mg (0.40 mmol) of carbene complex **7**, 81 mg (0.45 mmol) of diphenylacetylene, and 67 mg (0.45 mmol) of methyl *N*-benzylformimidate, the lactam was obtained as a white solid; mp 137–140 °C, in 49% yield (81 mg): ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.59 (s, 6 H, NMe_2), 3.11 (s, 1 H, cyclopropyl H), 3.12 (s, 3 H, OMe), 4.17 (d, J = 15 Hz, 1 H, CH_2Ph), 4.97 (s, 1 H, =CH), 5.16 (d, J = 15 Hz, 1 H, CH_2Ph), 7.07–7.40 (m, 15 H, Ar H); ^{13}C NMR ($CDCl_3$) δ 169.7 (C(O)N), 137.6, 137.1, 133.5, 129.7, 129.0, 128.5, 128.4, 128.2, 128.1, 127.3, 127.2, 127.0 (Ar), 95.4 (CHOMe), 59.3, 58.0, 48.5, 46.8, 45.8, 43.8; IR ($CDCl_3$) ν 3100–2770, 1695 (C(O)–N), 1600, 1500, 1450 cm^{-1}. Anal. Calcd for $C_{27}H_{28}N_2O_2$: C, 78.61; H, 6.84; N, 6.79. Found: C, 78.40; H, 6.94; N, 6.55.

Bicyclic Lactam (11d). Via the above procedure using 100 mg (0.40 mmol) of carbene complex **7**, 81 mg (0.45 mmol) of diphenylacetylene, and 138 mg (2.0 mmol) of pyrroline, the lactam was obtained as a colorless oil in 21% yield (28 mg): ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.70 (ddd, 1 H, J = 2.6, 6.3, 6.6 Hz, CH_2), 1.95 (m, 1 H, CH_2), 2.06 (m, 1 H, CH_2), 2.15 (m, 1 H, CH_2), 2.52 (s, 6 H, NMe_2), 2.99 (s, 1 H, cyclopropyl H), 3.16 (ddd, J = 3.4, 8.3, 11.2 Hz, 1 H, CH_2), 3.47 (ddd, J = 8.2, 8.2, 10.8 Hz, 1 H, CH_2), 4.34 (dd, J = 6.5, 9.3 Hz, 1 H, =CH), 7.01–7.20 (m, 10 H, Ar H); ^{13}C NMR ($CDCl_3$) δ 171.9 (C(O)N), 138.5, 129.5, 128.8, 128.4, 128.2, 127.1, 127.0 (Ar), 68.4, 58.9, 52.7, 46.2, 44.0, 41.9, 29.6, 27.9, 25.0. IR ($CDCl_3$) ν 3100–2770, 1685 (C(O)–N), 1600, 1500, 1445 cm^{-1}; high-resolution mass spectrum calcd for $C_{22}H_{24}N_2O$ 332.1890, found 332.1883.

Bicyclic Lactam (11e). Via the procedure above using 100 mg (0.40 mmol) of carbene **7**, 81 mg (0.45 mmol) of diphenylacetylene, and 43 mg (0.50 mmol) of 1,3-oxazine, the lactam was obtained in 20% yield (28 mg): ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.56 (m, 1 H, CH_2), 2.00 (m, 1 H, CH_2), 2.51 (s, 6 H, NMe_2), 3.02 (s, 1 H, cyclopropyl H), 3.11 (ddd, J = 13, 13, 4 Hz, 1 H, CH_2), 3.71 (ddd, J = 12, 12, 2 Hz, 1 H, CH_2), 4.16 (ddd, J = 11, 4, 4 Hz, 1 H, CH_2), 4.29 (ddd, J = 13, 4, 4 Hz, 1 H, CH_2), 4.72 (s, 1 H, CHNO), 7.15 (m, 10 H, Ar H); ^{13}C NMR ($CDCl_3$) δ 168.9 (C(O)N), 133.7, 133.1, 132.0, 131.6, 129.6, 128.1, 127.6, 127.5, 127.2 (Ar), 86.2 (OCHN), 67.9, 58.2, 47.1, 47.0, 45.4, 38.1, 25.5; IR ($CDCl_3$) ν 3080–2760, 1690 (C(O)–N), 1500, 1445 cm^{-1}. Anal. Calcd for $C_{22}H_{24}N_2O_2$: C, 75.83; H, 6.94; N, 8.04. Found: C, 76.09; H, 6.85; N, 7.81.

Hydrogenolysis of 11a. The bicyclic lactam **11a** (200 mg, 0.57 mmol) was placed in a Fisher Porter tube and dissolved in 30 mL of absolute EtOH with 10 mol % of 5% Pd/C. The vessel was charged with 60 psi of H_2, and the reaction mixture was stirred for 2.5 days. The solution was filtered through Celite, and the crude material was separated by Chromatotron (1-mm plate, 5:1 hexane–EtOAc) giving two products.

Unsaturated lactam: 26% yield (44 mg); ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.73 (s, 9 H, *N*-*t*-Bu), 7.20 (m, 8 H), 7.70 (m, 4 H, Ar H); IR ($CDCl_3$) ν 3100–2800, 1645 (C(O)–N), 1600, 1550, 1450 cm^{-1}; mass spectrum (NH_3CI), m/e 304 (M + 1).

Saturated lactam: 28% yield (48 mg); ^{1}H NMR (500 MHz, COSY, $CDCl_3$) δ 1.46 (s, 9 H, *N*-*t*-Bu), 2.18 (ddd, $J_{1-2} = J_{1-3} = J_{1-6}$ = 12.5 Hz, 1 H, $PhCH^1Ph$), 2.29 (dddd, J_{2-5} = 2.3, J_{2-3} = 3.5, J_{2-6} = 6.7, J_{2-1} = 12.5 Hz, 1 H, $PhCH^2Ph$), 3.10 (dddd, J_{3-2} = 3, J_{3-5} = 5, J_{3-4} = 11.5, J_{3-1} = 12.5 Hz, 1 H, $PhCH^3CH_2$), 3.37 (dd, $J_{4-3} = J_{4-5}$ = 11.5 Hz, 1 H, CH^4N), 3.65 (ddd, J_{5-2} = 2.3, J_{5-3} = 5, J_{5-4} = 12 Hz, 1 H, CH^5N), 3.70 (dd, J_{6-2} = 6.7, J_{6-1} = 12 Hz, 1 H, CH^6CO), 7.19–7.38 (m, 10 H, Ar H); ^{13}C NMR ($CDCl_3$) δ 171.8 (C(O)N), 142.7, 142.4, 128.7, 128.5, 128.4, 128.1, 127.1, 127.0, 126.5 (Ar), 57.7 (s, $C(CH_3)_3$), 51.9 (t, CH_2N), 41.5 (d, C(O)CH(Ph)), 37.6 (t, C(Ph)CH_2C(Ph)), 28.5 (d, CH_2CH(Ph)CH_2), 28.3 (q, $C(CH_3)_3$); IR ($CDCl_3$) ν 3100–2800, 1638 (C(O)–N) cm^{-1}; mass spectrum (NH_3CI), m/e 308 (M + 1).

Bicyclic Lactam (12). Via the above procedure using 100 mg (0.40 mmol) of carbene complex **7**, 78 mg (0.45 mmol) of (trimethylsilyl)phenylacetylene, and 55 μL (0.45 mmol) of *N*-methylphenylimine, the lactam was obtained as a white solid in 34% yield (52 mg): ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.59 (s, 9 H, $Si(CH_3)_3$), 2.44 (s, 1 H, $HCSiMe_3$), 2.49 (s, 6 H, $N(CH_3)_2$), 2.59 (s, 3 H, NCH_3), 4.18 (s, 1 H, $HCPh$), 7.20–7.55 (m, 10 H, Ar H); ^{13}C NMR ($CDCl_3$) δ 172.8 (C(O)N), 139.5, 136.5, 130.4, 129.7, 129.2, 128.5, 128.3, 128.2, 127.5 (Ar), 65.1, 55.9, 48.8, 45.6, 31.9, 27.9, –1.03 ($SiCH_3$); IR ($CDCl_3$) ν 3100–2760, 1690 (C(O)–N), 1600, 1500, 1455 cm^{-1}; mass spectrum (NH_3CI), m/e 378 (parent). Anal. Calcd for $C_{23}H_{30}SiN_2O$: C, 72.97; H, 7.99; N, 7.40. Found: C, 72.82; H, 7.87; N, 7.19.

γ-Amino Ester of 5-Decyne. The carbene complex **7** (125 mg, 0.5 mmol) and 5-decyne (83 mg, 0.6 mmol) were placed in an acylation tube under a stream of Ar. Freshly distilled MeOH (5 mL) was placed in the tube, which was quickly sealed and heated at 85 °C for 48 h. The reaction mixture was filtered through Celite, and the solvent removed in vacuo to produce the ester as a yellow-green oil (414 mg). As above, this material contained the $Cr(CO)_3$ fragment, removal of which led to decomposition: ^{1}H NMR ($CDCl_3$) δ 0.92 and 1.35 (m, 18 H, C_4H_{18}), 2.14 (s, 6 H, $N(CH_3)_2$), 2.90 (s, 2 H, CH_2N), 3.71 (s, 3 H, OMe); IR ($CDCl_3$) ν 3000–2840, 1930 (M – CO), 1720 (C(O)–C) cm^{-1}; mass spectrum (NH_3CI), m/e 392 (parent), 257 (P – $Cr(CO)_3$).

γ-Amino Ester of 1-Phenyl-1-propyne. The carbene complex **7** (125 mg, 0.50 mmol) and 1-phenyl-1-propyne (75 μL, 0.60 mmol) were placed in an acylation tube under a stream of Ar. Freshly distilled MeOH (5 mL) was placed in the tube, which was quickly sealed and heated to 85 °C for 3 days. The reaction mixture was filtered through Celite, and the solvent was removed in vacuo to produce the ester as a yellow oil (107 mg). This material contained the $Cr(CO)_3$ fragment, removal of which led to decomposition: ^{1}H NMR ($CDCl_3$) δ 1.72 (s, 3 H, =CMe), 2.24 (s, 6 H, NMe_2), 3.12 (s, 2 H, CH_2), 3.67 (s, 3 H, OMe), 7.50–7.10 (m, Ar H); IR ($CDCl_3$) ν 3100–2750, 1930 (M – CO), 1730 (C(O)–O), 1600, 1450 cm^{-1}; mass spectrum (NH_3CI), m/e 370 (parent), 235 (P – $Cr(CO)_3$).

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