on the heteroatom and the effect of antiaromaticity, but quantifying the energetic consequence of each is difficult (and arbitrary). Nonetheless, the difference for N is larger than for P, suggesting less antiaromaticity in the latter.

It should also be noted that cyclopropenyl anion does not have a transition structure that corresponds to direct inversion of the anionic carbon. Rather, this C_{2v} structure is a hilltop, pocessing two imaginary frequencies.[32] We have also noted this behavior for the inversion of diazirinyl anion.[33] These planar 4π-electron structures are apparently extremely unstable, most likely from their antiaromatic nature, and are decidedly different from **1pl**. The C_{2v} structure **1pl** is a true transition structure, implying that it is less antiaromatic than cyclopropyl anion or diazirinyl anion.

(32) Li, W.-K. *J. Chem. Res. Synop.* **1988**, 220.
(33) Kroeker, R. L.; Bachrach, S. M.; Kass, S. R. *J. Org. Chem.*, submitted.

Conclusions

1*H*-Phosphirene **1** is not antiaromatic. The P atom is pyramidal and two reasonable approaches to access the energy effect of the electron delocalization suggest no destabilization. The long P–C bonds coupled with the pyramidal P effectively reduce the interaction of the P lone pair with the π-electrons to nil. The inversion barrier of **1** is quite large, though only a small part of this can be attributed to antiaromaticity in the planar transition structure. Certainly, this planar transition structure is less antiaromatic that the planar form of 1*H*-azirine.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

Supplementary Material Available: Full geometries and energies of **1–3** (4 pages). Ordering information is given on any current masthead page.

Synthesis of α-Aminocyclobutanones by the Photolytic Reaction of Chromium–Aminocarbene Complexes with Olefins

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Photolysis of chromium–(*N*-phenylamino)carbene complexes in the presence of cyclohexadiene, cyclopentadiene, and dihydropyran produced bicyclic cyclobutanones in modest yields.

Introduction

Inter-[1] and intramolecular[2] [2+2] cycloaddition reactions of ketenes with olefins to produce cyclobutanones[3] have been extensively developed. Reactions of this type involving electron-rich alkoxy- or aminoketenes are considerably less common, and in the case of aminoketenes, the nitrogen atom was always substituted with an electron-withdrawing acyl group.[4] Recently Brady[5] reported the cycloaddition of a few *N*-(aryl/alkyl)amino)ketenes, generated from *N*-arylglycine salts and tosyl chloride, to cyclopentadiene and cyclooctene, to produce modest yields of α-aminocyclobutanones. Concurrent with this, work in our laboratories had shown that photolysis of chromium–alkoxy- and -aminocarbene complexes produced reactive intermediates having ketene-like reactivity[6] and that photolysis of chromium–alkoxycarbene complexes in the presence of olefins efficiently produced α-alkoxycyclobutanones.[7] The availability of a wide variety of chromium–aminocarbene complexes by the reaction of amides with $Cr(CO)_5^{2-}$[8] coupled with the ability to generate under very mild conditions (visible light irradiation through Pyrex, Et_2O solvent, no added base) species behaving like aminoketenes provided the opportunity to examine the photochemical reaction of these complexes with olefins to produce α-aminocyclobutanones. The results of these studies are presented below.

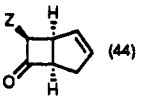
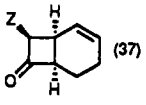
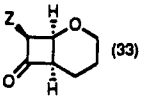
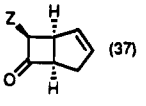
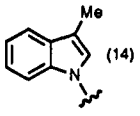
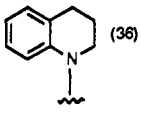
Results and Discussion

Photolysis of a variety of chromium–aminocarbene complexes with imines produces β-lactams[9] and with alcohols produces α-amino esters[10] in excellent yield, indicative of a ketene-like reactivity pattern of this class of reactions. In contrast, photolysis of (dimethylamino)-carbene complex **1** in the presence of an excess of cyclopentadiene resulted in no reaction. Starting carbene **1** was recovered unchanged after 48 h of irradiation, notwithstanding the fact that the same carbene converted to β-lactams in 12 h when photolyzed with imines[11] (eq 1). The inherent basicity of the dimethylamino group may seriously reduce the electrophilicity of the ketene carbonyl

(1) (a) Ghosez, L.; O'Donell, J. M. *Pericyclic Reactions*; Marchand, A., Lehr, R., Eds.; Academic Press: New York, 1977; Vol. II, pp 79–140. (b) Brady, W. T. *The Chemistry of Ketenes, Allenes, and Related Compounds*; Patai, S., Ed.; Interscience Publications: New York, 1980; pp 278–308. (c) Brady, W. T. *Tetrahedron* **1981**, *37*, 2949.
(2) Snider, B. B. *Chem. Rev.* **1988**, *88*, 793 and references therein.
(3) Bellus, D.; Ernst, B. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 797.
(4) Reichen, W. *Chem. Rev.* **1978**, *78*, 568 and references therein.
(5) Brady, W. T.; Gu, Y. Q. *J. Org. Chem.* **1989**, *54*, 2834.
(6) Hegedus, L. S.; deWeck, G.; D'Andrea, S. *J. Am. Chem. Soc.* **1988**, *110*, 2122.
(7) Söderberg, B. C.; Hegedus, L. S.; Sierra, M. *J. Am. Chem. Soc.* **1990**, *112*, 4364.
(8) (a) Imwinkelried, R.; Hegedus, L. S. *Organometallics* **1988**, *7*, 702; (b) Schwindt, M. A.; Lejon, T.; Hegedus, L. S. *Organometallics* **1990**, *9*, 2814.
(9) Hegedus, L. S.; Imwinkelried, R.; Alarid-Sargent, M.; Dvorak, D.; Satoh, Y. *J. Am. Chem. Soc.* **1990**, *112*, 1109.
(10) Hegedus, L. S.; Schwindt, M. A.; DeLombaert, S.; Imwinkelried, R. *J. Am. Chem. Soc.* **1990**, *112*, 2264.
(11) Borel, C.; Hegedus, L. S.; Krebs, J.; Satoh, Y. *J. Am. Chem. Soc.* **1987**, *109*, 1101.

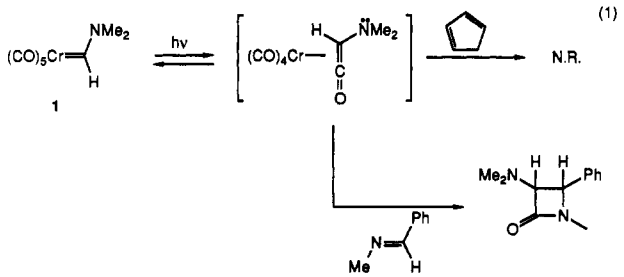
0022-3263/91/1956-2209$02.50/0

Table I. Syntheses of α-Aminocyclobutanones

$(CO)_5Cr{=}C(Z)H$ (%)[a]	alkene[b]	product (%)[a]
Me PhN— (63) 2		 (44) 3
2		 (37) 4
2		 (33) 5
Me pMeOPhN— (62) 6		 (37) 7
Ph_2N (47) 8		9 (45)
 10		11 (51)
 12		13 (44)
Me 2,6-Me_2PhN (61) 14		15 (38)[d]

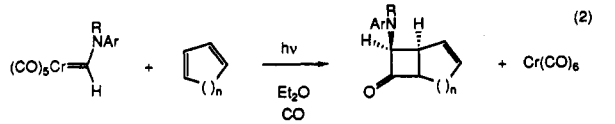
[a] Yield of pure, isolated complex. [b] A 10-fold excess of olefin was used. [c] Yield of pure product. Only *one* stereoisomer was observed. [d] An inseparable 36:19:8:4 mixture of isomers and/or rotamers was obtained.

carbon, limiting its reactivity to rather nucleophilic species such as imines, but not olefins.



(1)

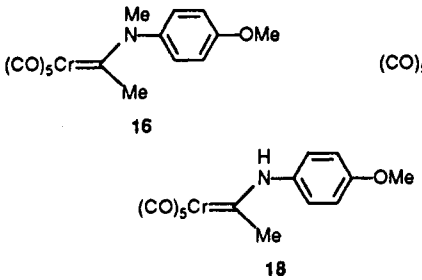
Replacement of an *N*-alkyl group by an *N*-aryl group substantially reduces (~10^6) the basicity of amines and should consequently *increase* the electrophilicity of aminoketenes. A number of (*N*-arylamino)chromium–carbene complexes were synthesized from the corresponding formamides[8] and were photolyzed in the presence of olefins (eq 2). The results are summarized in Table I.



(2)

(*N*-Phenyl-*N*-methylamino)carbene complex **2** underwent reaction with cyclopentadiene, cyclohexadiene, and dihydropyran to give modest yields of a single isomer of the bicyclic cyclobutanones **3–5**. Compound **3** is identical with that reported by Brady,[5] and the cis (endo) stereochemistry for **3, 4, 7, 9, 11,** and **13** was assigned on the basis of the coupling constants for the methine signal for the proton α to both the carbonyl group and nitrogen (J_{cis} = 9–10 Hz as observed vs J_{trans} = 5 Hz).[5,12] The cis (endo) stereochemistry of **5** was similarly assigned, but J_{cis} was much smaller (4.2 Hz) as previously reported[13] for this type of compound (here $J_{cis} \approx 5$ Hz, $J_{trans} \approx 1$ Hz). Other aromatic (aminocarbene)chromium complexes including the more electron rich methyl(*p*-methoxyphenyl)amino complex **6**, the diphenylamino complex **8**, the *N*-3-methyl-indolo complex **10**, and the *N*-tetrahydroquinolino complex **12** also underwent this cycloaddition reaction with cyclopentadiene, giving a single cis (endo) isomer in moderate yield. In contrast, the [*N*-methyl-*N*-(2,6-dimethylphenyl)amino]carbene complex **14** gave an inseparable 2:1 mixture of cis (δ 4.58, J_1 = 9 Hz) and trans (δ 4.18, J_1 = 6 Hz) isomers, contaminated with small amounts of other cyclobutanone isomers. (The reason for the lack of stereoselectivity is unclear.)

This reaction appears to be restricted to carbene complexes having hydrogen on the carbene carbon. Photolysis of complex **16** with cyclopentadiene produced an intractable mixture of products, none of which were cyclobutanones (by infrared spectroscopy), while complex **17** led primarily to photodegradation of the carbene complex to give the *N*,*N*-dimethylamide of *N*,*N*-dimethylalanine,[6] and complex **18** gave a low yield (30%) of the diketopiperazine resulting from dimerization of the aminoketene. Photolysis of the indole carbene **10** and the tetrahydroquinoline carbene **12** in the absence of an olefin in an attempt to effect intramolecular trapping of the ketene by the adjacent aryl group instead again led to an intractable mixture of products. Since each of these complexes reacts cleanly upon irradiation with methanol to give the α-amino acid ester, the ketene complex is clearly being formed but is unable to react cleanly with the alkene. (It should be noted that carbene complex **17** also fails to form β-lactams when irradiated in the presence of imines.[14]) However, the ability to produce unusual aminoketenes by photolysis of aminocarbene complexes is now well established,[9-11] and synthetic applications of these unusual intermediates are under investigation.



Experimental Section

Melting points are uncorrected. All NMR spectra were recorded in $CDCl_3$. Assignment of ^{13}C NMR spectra (broad band) and ^1H NMR spectra is based on comparison in the measured substance class and by homonuclear decoupling experiments (^1H). ^1H–^1H coupling constants are reported as calculated from spectra. Thus,

(12) DoMinh, T.; Strauss, O. P. *J. Am. Chem. Soc.* **1970**, *92*, 1766.
(13) Aben, R. W.; Scheeren, H. W. *J. Chem. Soc., Perkin Trans. 1* **1979**, 3132.
(14) Hafner, A.; Hegedus, L. S.; deWeck, G.; Hawkins, B.; Dötz, K. H. *J. Am. Chem. Soc.* **1988**, *110*, 8413.

a slight difference between $J_{a,b}$ and $J_{b,a}$ is usually obtained.

For the purification of crude reaction mixtures, radial-layer (Chromatotron Model 7924) and column chromatographic techniques were applied in all cases. Merck silica gel 60 PF (for radial-layer chromatography) and Merck silica gel (230–400 mesh, for column chromatography) were used as stationary phases. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

The following chemicals were prepared according to literature procedures: *N*-methyl-*N*-phenylformamide,[15] *N*-ethyl-*N*-phenylformamide,[16] *N*-(4-methoxyphenyl)-*N*-methylformamide,[16] *N*-(2,6-dimethylphenyl)-*N*-methylformamide,[17] 3-methylindoleformamide,[18] 1,2,3,4-tetrahydroquinolineformamide,[19] pentacarbonyl[[*N*-(4-methoxyphenyl)amino](methyl)carbene]chromium(0) (**18**),[20] pentacarbonyl[(*N*,*N*-diphenylamino)(hydrido)carbene]chromium(0) (**8**),[9] pentacarbonyl[(*N*,*N*-dimethylamino)(hydrido)carbene]chromium(0) (**1**),[8a] and pentacarbonyl[(*N*,*N*-dimethylamino)(methyl)carbene]chromium(0) (**17**).[8a] Carbene complexes **2**, **6**, **10**, **12**, and **14** were prepared from the corresponding amides and $K_2Cr(CO)_5$.[8b]

Pentacarbonyl[(hydrido)(*N*-methyl-*N*-phenylamino)carbene]chromium(0) (2). Reaction of 1.35 g (10.0 mmol) of *N*-methyl-*N*-phenylformamide gave, after chromatography (20 × 2.5 cm column, 100 mL of hexane followed by hexane–CH_2Cl_2, 1:1), 1.95 g (6.3 mmol, 63%) of **2** as yellow crystals: mp 63–65 °C (92:8 mixture of rotamers); ^{1}H NMR (major rotamer) δ 11.37 (s, 1 H, Cr=CH), 7.43 (m, 3 H, ArH), 7.17 (m, 2 H, ArH), 4.16 (s, 3 H, NMe); ^{13}C NMR (major rotamer) δ 272.16 (Cr=C), 224.11 (trans-CO), 217.29 (4 C, cis-CO), 150.95 (C_{ipso}), 129.67 (2 C), 128.58 (C_{para}), 121.59 (2 C), 47.36 (NMe); IR (CH_2Cl_2) ν 2057 (w), 1979 (w), 1932 (s) cm^{-1}; MS 312 (M + H$^+$), 137 (M – Cr(CO)$_5$ + NH$_4^+$), 136 (M$^+$ – Cr(CO)$_5$), 108 (H_2NMePh^+). Anal. Calcd for $C_{13}H_9CrNO_5$: C, 50.17; H, 2.92. Found: C, 50.12; H, 2.92.

Pentacarbonyl[(hydrido)[*N*-(4-methoxyphenyl)-*N*-methylamino]carbene]chromium(0) (6). Reaction of 1.65 g (10.0 mmol) of *N*-(4-methoxyphenyl)-*N*-methylformamide gave, after chromatography (16 × 2 cm column, hexane–CH_2Cl_2, 7:3), 2.12 g (6.2 mmol, 62%) of **6** as yellow crystals as a 70:30 mixture of rotamers. mp 80–84 °C; ^{1}H NMR (major rotamer) δ 11.24 (s, 1 H, Cr=CH), 7.09 (d, 2 H, *J* = 8.8 Hz, ArH), 6.90 (d, 2 H, *J* = 8.8 Hz, ArH), 4.12 (s, 3 H, Me), 3.83 (s, 3 H, Me) (minor rotamer) δ 11.39 (s, 1 H, Cr=CH), 7.25 (d, 2 H, *J* = 8.6 Hz, ArH), 7.02 (d, 2 H, *J* = 8.6 Hz, ArH), 3.85 (s, 3 H, Me), 3.80 (s, 3 H, Me); ^{13}C NMR (major rotamer) δ 270.42 (Cr=C), 224.12 (trans-CO), 217.37 (4 C, cis-CO), 159.34 (C_{ipso}), 144.55 (C_{para}), 122.76 (2 C), 114.51 (2 C), 55.64 (OMe), 47.62 (NMe) (minor rotamer) δ 271.54 (Cr=C), 224.1 (trans-CO), 217.04 (4 C, cis-CO), 159.97 (C_{ipso}), 140.5 (C_{para}), 126.68 (2 C), 115.17 (2 C), 58.22 (OMe), 55.64 (NMe); IR(CH_2Cl_2) ν 2056 (w), 1977 (w), 1939 (s) cm^{-1}; MS 166 (M$^+$ – Cr(CO)$_5$ + NH$_3$), 138 ($H_2NMepMeOPh^+$). Anal. Calcd for $C_{14}H_{11}CrNO_6$: C, 49.27; H, 3.25. Found: C, 49.11; H, 3.31.

Pentacarbonyl[(hydrido)(3-methylindol-1-yl)carbene]chromium(0) (10). Reaction of 3-methylindole-1-formamide (1.59 g, 10.0 mmol) gave, after chromatography (20 × 2.5 cm column, 100 mL of hexane followed by 100 mL of hexane–CH_2Cl_2, 9:1, and hexane–CH_2Cl_2, 8:2), **10** (0.49 g, 1.5 mmol, 15%) as red crystals. Some impurities still remained but could not be removed by repeated chromatography; thus, it was not possible to obtain an analytically pure sample. The product decomposed slowly in solution and as crystals. Some data could not be unambiguously assigned to the desired product: mp 148 °C dec; ^{1}H NMR (partial) δ 13.04 (s, 1 H, Cr=CH), 2.60 (s, 3 H, Me); ^{13}C NMR (partial) δ 277.15 (Cr=C), 224.80 (trans-CO), 216.53 (4 C, cis-CO), 128.89, 126.76, 125.94, 119.53, 111.51, 32.45 (Me); IR (CH_2Cl_2) ν 2060 (w), 1944 (s) cm^{-1}.

Pentacarbonyl[(hydrido)(1,2,3,4-tetrahydroquinolin-1-yl)carbene]chromium(0) (12). Reaction of 1,2,3,4-tetrahydroquinolineformamide (1.61 g, 10.0 mmol) gave, after chromatography on a 22 × 2 cm column eluting with first 150 mL of hexane and then hexane–CH_2Cl_2 (2:1), 1.22 g (3.6 mmol, 36%) of **12** as yellow crystals: mp 113–116 °C; ^{1}H NMR δ 11.67 (s, 1 H, Cr=CH), 7.23 (m, 3 H, ArH), 7.07 (m, 1 H, ArH), 4.58 (t, 2 H, $J_{2,3}$ = 5.8 Hz, H-2), 3.02 (t, 2 H, $J_{4,3}$ = 6.8 Hz, H-4), 2.30 (quintet, 2 H, *J* = 6.3 Hz, H-3); ^{13}C NMR δ 265.48 (Cr=C), 224.30 (trans-CO), 217.27 (4 C, cis-CO), 143.73 (C8a), 129.60, 128.78 (C4a), 128.05, 127.48, 120.22, 55.59 (C2), 26.29 (C4), 23.88 (C3); IR (CH_2Cl_2) ν 2056 (w), 1932 (s) cm^{-1}; MS 162 (M$^+$ – Cr(CO)$_5$ + NH$_3$), 134 (1,2,3,4-tetrahyroquinoline + H$^+$). Anal. Calcd for $C_{15}H_{11}CrNO_5$: C, 53.42; H, 3.29. Found: C, 53.44; H, 3.41.

Pentacarbonyl[[*N*-(2,6-dimethylphenyl)-*N*-methylamino](hydrido)carbene]chromium(0) (14). Reaction of *N*-(2,6-dimethylphenyl)-*N*-methylformamide (1.53 g, 10.0 mmol) gave, after flash chromatography (16 × 2 cm column, hexane–CH_2Cl_2, 7:3), compound **14** (2.10 g, 6.2 mmol, 62%) as yellow crystals as a 63:27 rotamer mixture: mp 101–104 °C; ^{1}H NMR (major rotamer) δ 10.97 (s, 1 H, Cr=CH), 7.17 (m, 3 H, ArH), 3.94 (s, 3 H, NMe), 2.20 (s, 6 H, ArMe), (minor rotamer) δ 11.59 (s, 1 H, Cr=CH), 7.17 (m, 3 H, ArH), 3.68 (s, 3 H, NMe), 2.31 (s, 6 H, ArMe); ^{13}C NMR (major rotamer) δ 272.00 (Cr=C), 224.16 (trans-CO), 217.41 (4 C, cis-CO), 150.11 (C_{ipso}), 130.83 (C_{para}), 129.10 (2 C), 128.50 (2 C), 46.34 (NMe), 17.34 (2 C, Ar*Me*), (minor rotamer) δ 272.62 (Cr=C), 223.79 (trans-CO), 216.53 (4 C, cis-CO), 144.47 (C_{ipso}), 132.92 (C_{para}), 129.43 (2 C), 129.00 (2 C), 55.17 (NMe), 17.34 (2 C, ArMe); IR (CH_2Cl_2) ν 2060 (w), 1944 (s) cm^{-1}; MS 165 (M – Cr(CO)$_5$ + NH$_4^+$), 164 (M$^+$ – Cr(CO)$_5$ + NH$_3$), 136 (H_2NMe – 2,6-Me_2Ph^+). Anal. Calcd for $C_{15}H_{13}CrNO_5$: C, 53.10; H, 3.86. Found: C, 52.94; H, 3.75.

Pentacarbonyl[[*N*-(4-methoxyphenyl)-*N*-methylamino](methyl)carbene]chromium(0) (16). To a slurry of 53 mg (2.20 mmol) of NaH in 20 mL of THF was added 682 mg (2.00 mmol) of pentacarbonyl[[*N*-(4-methoxyphenyl)amino](methyl)carbene]chromium(0), in THF (10 mL) by syringe. The mixture was stirred for 20 min until no more H_2 evolved. To the anion was added 187 μL (3.00 mmol) of MeI by syringe followed by stirring for 5 h. The solvent was removed on a rotary evaporator to give a yellow semisolid. The crude product was chromatographed on a 3 × 1 cm column, eluting with hexane–CH_2Cl_2 (1:1) to give, after solvent removal, 703 mg (1.98 mmol, 99%) of **16** as pale yellow crystals, mp 72–76 °C. By ^{1}H NMR a 78:22 mixture of rotamers was obtained: ^{1}H NMR (major rotamer) δ 6.96 (s, 4 H, Ar), 4.09 (s, 3 H, NMe), 3.84 (s, 3 H, OMe), 2.46 (s, 3 H, Cr=C*Me*), (minor isomer) δ 7.17 (d, 2 H, J = 8.4 Hz, ArH), 6.96 (2 H, ArH), 3.84 (s, 3 H, OMe), 3.58 (s, 3 H, NMe), 2.94 (s, 3 H, Cr=C*Me*); ^{13}C NMR (major rotamer) δ 278.50 (Cr=C), 223.52 (trans-CO), 217.89 (4 C, cis-CO), 159.28 (C_{para}), 139.15 (C_{ipso}), 125.14 (2 C, C_{ortho}), 115.23 (2 C, C_{meta}), 55.44 (OMe), 53.90 (NMe), 42.42 (Cr=C*Me*), (minor rotamer) δ 281.09 (Cr=C), 223.93 (trans-CO), 217.47 (4 C, cis-CO), 159.28 (C_{para}), 145.51 (C_{ipso}), 126.88 (2 C, C_{ortho}), 114.91 (2 C, C_{meta}), 55.44 (OMe), 46.07 (NMe), 40.90 (Cr=C*Me*); IR (CH_2Cl_2) ν 2054 (w), 1924 (s) cm^{-1}; MS 180 (M$^+$ – Cr(CO)$_5$ + NH$_3$), 164 (M – Cr(CO)$_5$ – H$^+$), 138 ($H_2NMepMeOPh^+$). Anal. Calcd for $C_{15}H_{13}CrNO_6$: C, 50.71; H, 3.67. Found: C, 50.39; H, 3.83.

General Procedure for Preparation of Aminocyclobutanones. To a solution of 1.0 mmol of the carbene in 10 mL of ether (0.1 M) in a 20-mL Fischer Porter pressure tube was added 10.0 mmol of alkene. The solution was saturated with CO (three cycles to 90 psi of CO) and irradiated (450-W Conrad-Hanovia 7825 medium-pressure mercury lamp, Pyrex well) under 90 psi of CO overnight. The resulting brown-yellow suspension was filtered through a Celite pad, and the Celite was washed with Et_2O to give a pale yellow solution. The solvent was removed on a rotary evaporator to give a yellow to orange semisolid. The crude material was purified by either radial-layer chromatography or flash chromatography to give pure products. The isomer ratio was determined by ^{1}H NMR. The cyclobutanones decomposed slowly, even at −20 °C, and thus analytically pure samples for elemental analysis could not be obtained.

7-(*N*-Methyl-*N*-phenylamino)bicyclo[3.2.0]hept-2-en-6-one (3). A pressure tube containing 311 mg (1.00 mmol) of **2** and 660 mg (10.00 mmol) of cyclopentadiene in 10 mL of Et_2O was irradiated for 18 h as described above. The solution was diluted with 10 mL of hexane and air-oxidized in a light box (six 20-W Vitalite fluorescent bulbs) for 22 h.[21] The brown precipitate was removed

(15) Roberts, R. M.; Vogt, P. J. *J. Am. Chem. Soc.* **1956**, *78*, 4778.
(16) Prepared according to the general procedure in footnote 15, but not reported in that reference.
(17) Walter, W.; Becher, R. F. *Liebigs, Ann. Chem.* **1972**, *755*, 145.
(18) Kashimura, M.; Kikugawa, Y. *Chem. Pharm. Bull.* **1983**, *31*, 2892.
(19) Kost, A. N.; Yudin, L. G. *Zh. Obshch. Khim.* **1955**, *25*, 1947.
(20) Connor, J. A.; Fischer, E. O. *J. Chem. Soc. A* **1969**, 578.

by filtration, and the solvent was removed to give a yellow semisolid. Radial-layer chromatography (2-mm plate) eluting with hexane–CH_2Cl_2 (3:7) gave, after solvent removal, 93 mg (0.44 mmol, 44%) of **3** as a pale yellow oil. Spectra data were in complete accordance with literature values.[5] Only the endo isomer was observed (endo:exo > 20:1).

8-(*N*-Methyl-*N*-phenylamino)bicyclo[4.2.0]oct-2-en-7-one (4). A pressure tube containing 311 mg (1.00 mmol) of **2** and 950 μL (10.00 mmol) of 1,3-cyclohexadiene in 10 mL of Et_2O was irradiated as described above. The suspension was filtered through Celite, the solvent was removed, and the yellow semisolid residue was purified by flash chromatography (16 × 2 cm column, hexane–CH_2Cl_2, 1:1) to give 74 mg (0.33 mmol, 33%, endo:exo > 20:1) of **4** as a colorless oil: ^{1}H NMR δ 7.25 (m, 2 H, ArH), 6.75 (m, 3 H, ArH), 5.87 (m, 1 H, H-3), 5.71 (m, 1 H, J = 10.4 Hz, H-2), 4.95 (dd, 1 H, $J_{8,1}$ = 8.4, $J_{8,6}$ = 2.8 Hz, H-8), 3.33 (m, 2 H, H-1, H-6), 2.99 (s, 3 H, NMe), 2.20–2.01 (m, 3 H, H-4, H-5), 1.69–1.56 (m, 1 H, H-5′); ^{13}C NMR δ 207.71 (CO), 148.44 (C_{ipso}), 130.09, 129.17, 125.15, 117.29, 111.94, 73.55 (C8), 50.17 (C6), 35.09 (C1), 30.60 (NMe), 21.28 (C4), 18.06 (C5); IR (film) ν 1775 (CO) cm^{-1}; MS 228 (M + H$^+$), 108 (H_2NMePh^+).

A similar reaction of 311 mg (1.00 mmol) of **2** in 4 mL of 1,3-cyclohexadiene as solvent gave, after 18 h of irradiation and identical workup, 84 mg (0.37 mmol, 37%) of **4** with a >20:1 endo:exo ratio.

8-(*N*-Methyl-*N*-phenylamino)-2-oxabicyclo[4.2.0]octan-7-one (5). Irradiation of a solution of 311 mg (1.00 mmol) of **2** and 910 μL (10.00 mmol) of 2,3-dihydropyran in 10 mL of Et_2O for 25 h gave, after filtration and solvent removal, a yellow oil with some solid particles. The crude material was purified by radial-layer chromatography (2-mm plate), eluting with hexane–CH_2Cl_2 (1:1) to give, after solvent removal, 77 mg (0.33 mmol, 33%) of **5** as a pale yellow oil: ^{1}H NMR δ 7.23 (m, 2 H, ArH), 6.75 (m, 3 H, ArH), 4.82 (t, 1 H, J = 4.2 Hz, H-8), 4.62 (t, 1 H, J = 5.1 Hz, H-1), 3.85 (m, 1 H, J = 11.4 Hz, H-3), 3.25 (m, 1 H, H-3′), 3.11 (s, 3 H, NMe), 2.95 (m, 1 H, H-6), 2.19 (m, 1 H), 1.73–1.48 (m, 3 H); ^{13}C NMR δ 204.97 (CO), 148.70 (C_{ipso}), 129.11 (2 C), 117.52 (C_{para}), 112.30 (2 C), 74.56 (C8), 67.94 (C1), 64.69 (C3), 49.63 (C6), 35.77 (NMe), 22.05 (C5), 18.33 (C4); IR (film) ν 1781 (CO) cm^{-1}; MS 232 (M + H$^+$), 108 (MeH_2NPh^+).

7-[*N*-(4-Methoxyphenyl)-*N*-methylamino]bicyclo[3.2.0]-hept-2-en-6-one (7). Irradiation of a solution of 341 mg (1.00 mmol) of **6** and 660 mg (10.00 mmol) of 1,3-cyclopentadiene in 10 mL of Et_2O gave, after flash chromatography (16 × 2 cm column, hexane–Et_2O, 7:3), 91 mg (0.37 mmol, 37%) of **7** as a colorless oil: ^{1}H NMR δ 6.85 (d, 2 H, J = 9.2 Hz, ArH), 6.74 (d, 2 H, J = 9.2 Hz, ArH), 5.84 (dd, 1 H, $J_{2,3}$ = 5.6, $J_{2,1}$ = 1.7 Hz, H-2), 5.70 (m, 1 H, H-3), 5.04 (dd, 1 H, $J_{7,1}$ = 8.3 Hz, $J_{7,5}$ = 2.7 Hz, H-7), 3.94 (m, 1 H, H-5), 3.76 (s, 3 H, OMe), 3.57 (m, 1 H, H-1), 2.87 (s, 3 H, NMe), 2.76 (m, 1 H, $J_{4,4'}$ = 17.0 Hz, H-4), 2.52 (qdd, 1 H, $J_{4',4}$ = 17.1, $J_{4',3}$ = 9.0, J = 2.1 Hz, H-4′); ^{13}C NMR δ 210.04 (CO), 152.36 (C_{para}), 143.17 (C_{ipso}), 134.16, 129.80, 114.70 (2 C), 114.60 (2 C), 78.35 (C7), 55.67, 54.77, 47.06 (NMe), 36.55, 34.67; IR (film) ν 1775 (CO) cm^{-1}; MS 244 (M + H$^+$), 138.

7-(*N*,*N*-Diphenylamino)bicyclo[3.2.0]hept-2-en-6-one (9). A mixture of 157 mg (0.40 mmol) of pentacarbonyl[(hydrido)-(*N*,*N*-diphenylamino)carbene]chromium(0) (**8**) and 264 mg (4.00 mmol) of 1,3-cyclohexadiene in 5 mL of Et_2O was irradiated for 18 h. Radial-layer chromatography (1-mm plate) eluting with, in sequence, hexane (50 mL), hexane–CH_2Cl_2 (9:1, 75 mL), and hexane–CH_2Cl_2 (7:3) gave 21 mg (0.12 mmol, 31%) of diphenylamine followed by 52 mg (0.18 mmol, 45%) of **9** as a pale yellow oil: ^{1}H NMR δ 7.23 (m, 4 H, ArH), 7.07–6.92 (m, 6 H, ArH), 5.66 (dd, 1 H, $J_{2,3}$ = 5.6, $J_{2,1}$ = 1.7 Hz, H-2), 5.47 (m, 1 H, H-3), 5.27 (dd, 1 H, $J_{7,1}$ = 8.1, $J_{7,5}$ = 2.8 Hz, H-7), 4.05 (m, 1 H, H-5), 3.58 (m, 1 H, H-1), 2.59 (m, 1 H, $J_{4,4'}$ = 17.2 Hz, H-4), 2.44 (qdd, 1 H, $J_{4',4}$ = 17.1, J = 8.9, J = 2.1 Hz, H-4′); ^{13}C NMR δ 208.13 (CO), 146.60 (C_{ipso}), 133.99, 129.79, 129.00 (4 C), 122.59 (6C), 77.19 (C7), 55.21 (C5), 47.51 (C1), 34.64 (C3); IR (film) ν 1781 (CO) cm^{-1}; MS 276 (M + H$^+$), 170 ($H_2NPh_2^+$).

7-(3′-Methylindol-1′-yl)bicyclo[3.2.0]hept-2-en-6-one (11). Irradiation of 315 mg (0.94 mmol) of **10** and 594 mg (9.00 mmol) of 1,3-cyclopentadiene in 15 mL of Et_2O–CH_2Cl_2 (2:1)[23] for 17 h gave, after radial-layer chromatography (1-mm plate, hexane–EtOAc, 9:1), 113 mg (0.48 mmol, 51%) of **11** as a pale yellow oil: ^{1}H NMR δ 7.54 (d, 1 H, J = 7.6 Hz, ArH), 7.27–7.10 (m, 3 H, ArH), 6.83 (s, 1 H, NC*H*=C), 5.94 (dd, 1 H, $J_{2,3}$ = 5.7, $J_{2,1}$ = 1.7 Hz, H-2), 5.83 (dd, 1 H, $J_{7,1}$ = 8.5, $J_{7,5}$ = 2.3 Hz, H-7), 5.34 (m, 1 H, H-3), 4.06 (m, 1 H, H-5), 3.80 (m, 1 H, H-1), 2.86 (m, 1 H, $J_{4,4'}$ = 17.2 Hz, H-4), 2.56 (qdd, 1 H, $J_{4',4}$ = 17.2, J = 8.7, J = 2.2 Hz, H-4′), 2.26 (s, 3 H, Me); ^{13}C NMR ($CDCl_3$ + three drops of C_6D_6) δ 207.17 (CO), 135.82, 135.65, 128.66, 128.58, 123.85, 121.58, 119.38, 118.97, 111.13, 108.70, 71.18 (C7), 56.64, 46.72, 34.95, 9.51 (Me); IR (film) ν 1782 cm^{-1}; MS 238 (M + H$^+$), 132 (3-methylindole + H$^+$).

7-(1′,2′,3′,4′-Tetrahydroquinolin-1′-yl)bicyclo[3.2.0]hept-2-en-6-one (13). Photolysis of 337 mg (1.00 mmol) of **12** in 10 mL of Et_2O in the presence of 660 mg (10.00 mmol) of 1,3-cyclopentadiene for 15 h followed by air oxidation[21] for 24 h in a light box gave a clear solution plus some brown precipitate. The precipitate was removed by filtration through Celite, and the crude product was purified by flash chromatography (14 × 2 cm column, hexane–CH_2Cl_2, 1:1) to give 104 mg (0.44 mmol, 44%, endo:exo > 20:1) of **13** as a pale yellow oil: ^{1}H NMR δ 7.07 (m, 1 H, ArH), 6.96 (d, 1 H, J = 6.4 Hz, ArH), 6.62 (m, 2 H, ArH), 5.84 (m, 1 H, H-2), 5.74 (m, 1 H, H-3), 5.08 (dd, 1 H, $J_{7,1}$ = 8.1, $J_{7,5}$ = 2.8 Hz, H-7), 3.97 (m, 1 H, H-5), 3.60–3.47 (m, 2 H), 3.13 (m, 1 H), 2.74 (m, 1 H, H-4), 2.71 (m, 2 H), 2.54 (m, 1 H, H-4′), 1.92–1.77 (m, 2 H); ^{13}C NMR δ 209.45 (CO), 143.80, 134.27, 129.84, 129.43, 126.93, 122.84, 116.74, 110.56, 76.43 (C7), 54.98, 46.57, 46.10, 34.93, 27.71, 22.14; IR (film) ν 1774 (CO) cm^{-1}; MS 240 (M + H$^+$), 134 (1,2,3,4-tetrahydroquinoline + H$^+$).

7-[*N*-(2,6-Dimethylphenyl)-*N*-methylamino]bicyclo-[3.2.0]hept-2-en-6-one (15). Irradiation of 331 mg (0.98 mmol) of **14** and 660 mg (10.00 mmol) of 1,3-cyclopentadiene in 10 mL of Et_2O for 48 h gave, after radial-layer chromatography (2-mm plate, 100 mL of hexane–CH_2Cl_2, 9:1, followed by 100 mL of hexane–CH_2Cl_2, 1:1, and MeOH), three products: 35 mg (0.10 mmol, 11%) of starting carbene **14** as yellow crystals; 85 mg (0.39 mmol, 39%, 36:19:8:4 mixture of endo rotamer–exo rotamer–endo rotamer 2–exo rotamer 2) of **15**[22] as a pale yellow oil; 70 mg (0.46 mmol, 47%) of *N*-(2,6-dimethylphenyl)-*N*-methylformamide as a yellow oil: ^{1}H NMR (selected peaks from the mixture) δ 7.00 (m, ArH), 6.40 (dd, J = 5.6, 3.0 Hz), 6.20 (dd, J = 5.6, 3.1 Hz), 5.99 (m), 5.90 (dd, J = 5.5, 2.3 Hz), 5.86 (m), 5.78 (m), 5.68 (m), 4.58 (dd, J = 9.0, 2.3 Hz), 4.18 (dd, J = 6.0, 3.1 Hz), 2.86 (NMe), 2.80 (NMe), 2.78 (NMe), 2.75 (NMe), 2.38 (Me), 2.35 (Me), 2.34 (Me), 2.33 (Me), 2.32 (Me), 2.31 (Me), 2.30 (Me), 2.27 (Me); IR (film) ν 1770 (CO) cm^{-1}; MS 136 (MeH_2N – 2,6-Me_2Ph^+).

A similar reaction of 331 mg (0.98 mmol) of **14** in 10 mL of 1,3-cyclopentadiene without Et_2O gave, after 72 h of irradiation followed by chromatography, 90 mg (0.27 mmol, 27%) of starting carbene **14** and 44 mg (0.20 mmol, 20%) of **15**. The isomeric ratio of cyclobutanones was the same as above.

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Supplementary Material Available: NMR spectra of compounds **4**, **5**, **7**, **9**, **11**, **13**, and **15** (15 pages). Ordering information is given on any current masthead page.

(21) Oxidation was required to remove the $Cr(CO)_3$ fragment that had coordinated to the aryl group.

(22) Isomers and rotamers were tentatively assigned from ^{1}H NMR spectra.

(23) The carbene complex was not soluble in Et_2O.