Articles

Aminobenzannulation via Photocyclization Reactions of Chromium Dienyl(amino)carbene Complexes. Synthesis of *o*-Amino Aromatic Alcohols

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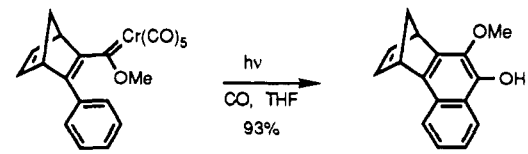
Photolysis of chromium dienyl(amino)carbene complexes is demonstrated to produce *o*-amino aromatic alcohols. The reaction is proposed to preceed via a chromium-complexed photogenerated dienylketene which undergoes subsequent electrocyclization and aromatization. These reactions are sensitive to the electronic nature of the amino substituent on the carbene carbon and can be tuned by variation in substituents. In particular, the ability to facilitate photolytic ketene generation by employing (acylamino)carbene complexes is illustrated. In addition, new methods of conversion of alkoxycarbene complexes to aminocarbene complexes are described.

Introduction

Though the first chromium carbene complexes were reported by Fischer in 1964,[1] the synthetic chemistry[2] of these species only truly blossomed after the report of facile benzannulation reactions of unsaturated carbene complexes by Dötz in 1975.[3] Recently, much attention has focused on the chemistry of aminocarbene complexes and how it contrasts with that of the more readily accessible alkoxycarbene complexes.[4] Of principle importance is the possibility of benzannulation reactions of aminocarbene complexes to yield *p*-amino aromatic alcohol products. The thermal reaction of alkynes with aryl(amino)carbene complexes, as first reported by Yamashita, produces indene products instead of the desired benzannulated products due to a failure of insertion of a CO unit.[5] The intermediate indene and indanone chromium tricarbonyl complexes have been isolated and characterized.[6,7] Dötz et al. have since demonstrated that carefully designed (acylamino)-carbene complexes can overcome the problem of CO insertion and produce the desired benzannulated products.[8]

Hegedus has employed aminocarbene complexes in photolytic reactions that generate transient aminoketenes complexed by chromium to prepare amino acids,[9] α-aminocyclobutanones,[10] β-lactams,[11] and γ-lactams.[12] Aminocarbene complexes have also been utilized by Rudler to obtain a variety of nitrogen heterocycles depending on carbene structure and the alkyne coreactant.[7,13] Recently, alkynyl(allylamino)carbene complexes have been shown to undergo extremely facile Pauson-Khand cyclization reactions to provide cyclopentenone carbene products.[14] Related to aminocarbene complexes, iminocarbene complexes have been used to prepare imidazoles, oxazolines, pyridines, and pyrroles.[15]

Recently, we reported a new type of benzannulation reaction that employs photolysis of chromium dienyl-(alkoxy)carbene complexes to produce ortho alkoxy aromatic alcohols (eq 1).[16] Photolysis converts the carbene complexes to chromium complexed dienylketenes, which then undergo thermal electrocyclization, tautomerization and demetalation to provide the product alcohols. We have since examined chromium aminocarbene complexes and report herein on photoinduced aminobenzannulation reactions of dienyl(amino)carbene complexes as a novel entry to ortho amino aromatic alcohols.



(1)

(1) Fischer, E. O.; Massböl, A. *Chem. Ber.* **1967**, *100*, 2445.
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(7) Alvarez, C.; Parlier, A.; Rudler, H.; Yefsah, R.; Daran, J. C.; Knobler, C. *Organometallics* **1989**, *8*, 2253.
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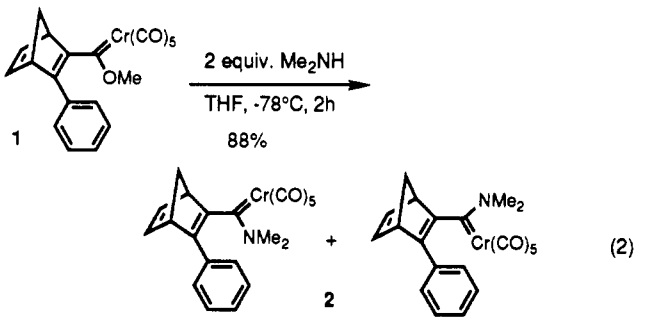
Results

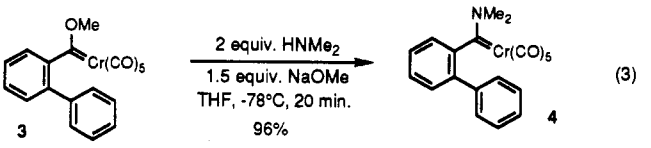
Preparation of Substrates. Aminocarbene complexes can be prepared by a number of synthetic routes. Typically they are prepared by aminolysis of alkoxycarbene complexes as developed by Fischer.[17] This method is, however, limited to sterically nonhindered amines. Use of activated substrates in the form of in situ prepared (acyloxy)carbene complexes has allowed for the preparation of sterically hindered aminocarbene complexes.[9b] Metathesis of aminoalkynes[18] and isonitriles[19] with alkoxycarbene complexes can also result in aminocarbene production. Finally, direct preparation of aminocarbene complexes is possible through reaction of the pentacarbonylchromium dianion with amides in the presence of trimethylsilyl chloride.[20] The aminocarbene complexes for this project were all prepared from the corresponding methoxycarbene complexes.[21]

Adapting reaction conditions from the aminolysis of phenyl(methoxy)carbene chromium complex,[17] the methoxy complex 1 was reacted with dimethylamine in ether. After 14 h at 5 °C, analytical TLC of the reaction mixture showed no sign of reaction; further stirring at room temperature for 2 days until disappearance of the starting carbene complex resulted only in the formation of pentacarbonylchromium dimethylamine complex, $(CO)_5Cr(HNMe_2)$, in about 30% yield. The sluggish aminolysis is attributable to the steric crowding of both the carbene and the amine. We then turned our attention to the sterically less hindered pyrrolidine. Pyrrolidine reacted rapidly with 1 at room temperature as indicated by a gradual color change from red to pale yellow and TLC confirmed that all starting carbene complex 1 had disappeared in about 1 h. However, after chromatographic separation and crystallization, the NMR spectra of the yellow crystals thus obtained were much more complex than anticipated and were undecipherable at that time. We were forced to return to the simpler dimethylamine. A close examination of the kinetic study on aminolysis reported by Fischer et al.[22] revealed that lower reaction temperatures and more basic solvents should expedite the aminolysis reaction. The reaction of 1 with dimethylamine did indeed proceed smoothly in THF at −78 °C, and with 2 equiv of the amine, the reaction was complete in 4 h. Again, the NMR spectra were complicated, however, it was clear this time that two isomeric materials had been produced. Pure single isomers were obtained by careful chromatographic separation of the mixture, and NMR spectra showed that both are the desired product 2 (eq 2). We rationalize that the isomeric phenomenon is due to hindered rotation about the single bond from the carbene carbon to the bicyclo[2.2.1] ring with the two isomers corresponding to the pentacarbonylchromium moiety exo and endo disposed in the bicyclic system. The aminolysis products obtained at various reaction temperatures always contained mixtures of isomers in roughly a 1:1 ratio. Further rate enhancement was observed at lower temperatures and this aminolysis was complete within 2 h at either −95 °C or −110 °C. Additionally, the use of dioxane or DMF as solvent gave a similar rate acceleration effect.



(2)

Direct aminolysis of 3 with excess dimethylamine under a number of conditions (e.g. Et_2O, −78 °C to 0 °C; THF, −78 °C or 0 °C) provided, at best, 25% of the aminocarbene complex 4. Recognizing again from the work of Fischer on the mechanism of aminolysis that the reaction might be facilitated by a proton acceptor,[22] we found that the presence of sodium methoxide greatly enhanced the rate of aminolysis of 3 and is particularly useful for aminolyses in general, when employing disubstituted amines as in eq 3.[23] Aminolysis of complex 3 with excess dimethylamine in the presence of catalytic amounts of sodium methoxide raised the yield to 75% and the use of 1.5 equivs of sodium methoxide in THF at −78 °C for 20 min resulted in a 96% yield of the (dimethylamino)carbene complex 4. Thus, this method provides a dramatic improvement over the direct aminolysis reaction.



(3)

For more sterically demanding secondary amines, improved results are obtained using a two-step sequence as reported by Hegedus.[9b] The dibenzylamino complexes 6 and 9 are readily formed by reaction of the corresponding methoxycarbene complexes 3 or 7 with benzylamine followed by deprotonation and alkylation to incorporate the second benzyl group (eqs 4 and 5).

The [(*tert*-butoxycarbonyl)alkylamino]carbene complexes 10, 12, 14, and 16 were prepared according a procedure reported by Dötz.[8b] Reaction of the (alkylamino)carbene complexes, made from the corresponding methoxy complexes, with 2 equiv of di-*tert*-butyl dicar-

(13) (a) Rudler, H.; Parlier, A.; Goumont, R.; Daran, J. C.; Vaissermann, J. *J. Chem. Soc., Chem. Commun.* **1991**, 1075. (b) Audouin, M.; Blandinieres, S.; Parlier, A.; Rudler, H. *J. Chem. Soc., Chem. Commun.* **1990**, 23. (c) Denise, B.; Goumont, R.; Parlier, A.; Rudler, H.; Daran, J. C.; Vaissermann, J. *J. Chem. Soc., Chem. Commun.* **1990**, 1238. (d) Denise, B.; Parlier, A.; Rudler, H.; Vaissermann, J.; Daran, J. C. *J. Chem. Soc., Chem. Commun.* **1988**, 1303. (e) Parlier, A.; Rudler, H.; Yefsah, R.; Daran, J. C.; Knobler, C. *J. Chem. Soc., Chem. Commun.* **1988**, 635.

(14) (a) Camps, F.; Moretó, J. M.; Ricart, S.; Viñas, J. M. *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1470. (b) Dötz, K. H.; Christoffers, J. *J. Organomet. Chem.* **1992**, *426*, C58.

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(16) Merlic, C. A.; Xu, D. *J. Am. Chem. Soc.* **1991**, *113*, 7418.

(17) (a) Conner, J. A.; Fischer, E. O. *J. Chem. Soc., A* **1969**, *104*, 578. (b) Fischer, E. O.; Kollmeier, H.-J. *Chem. Ber.* **1971**, *104*, 1339. (c) Fischer, E. O.; Leupold, M. *Chem. Ber.* **1972**, *105*, 599.

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(20) (a) Schwindt, M. A.; Lejon, T.; Hegedus, L. S. *Organometallics* **1990**, *9*, 2814. (b) Imwinkelried, R.; Hegedus, L. S. *Organometallics* **1988**, *7*, 702.

(21) Manuscript in preparation.

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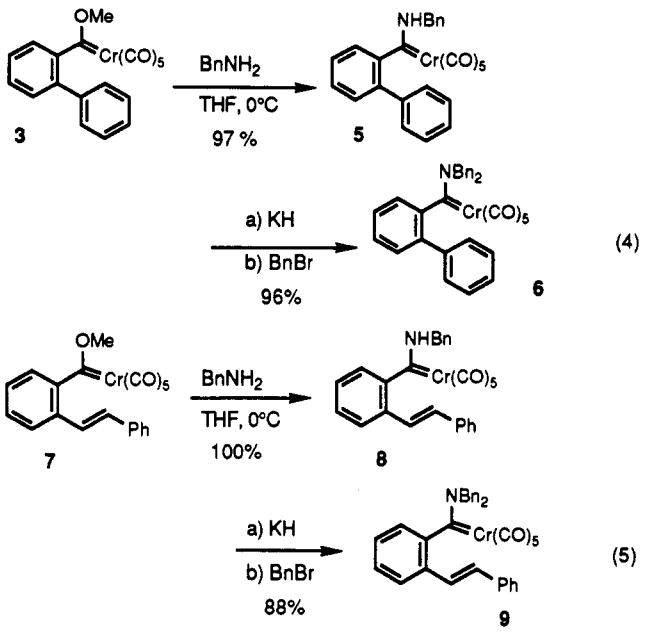
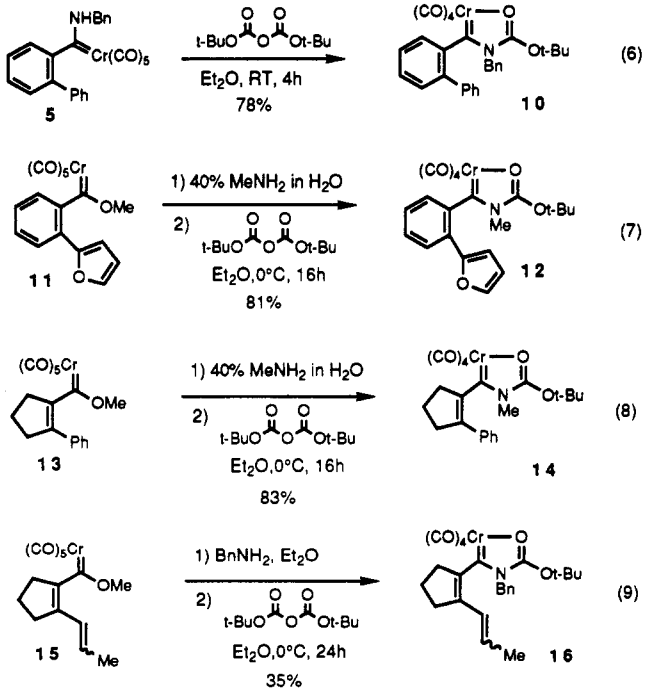
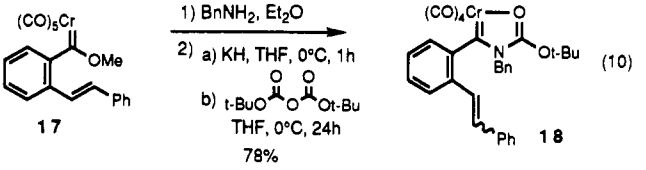
(23) Catalytic and stoichiometric use of sodium methoxide has been reported to promote ester aminolysis reactions. See: De Feo, R. J.; Strickler, P. D. *J. Org. Chem.* **1963**, *28*, 2915.



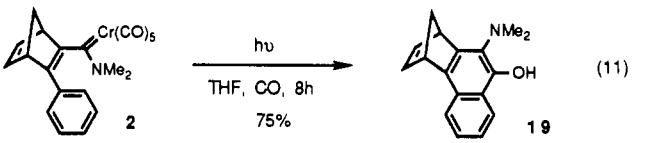
boxylate in the presence of DMAP catalyst gave the products in good yields (eqs 6–9). Displacement of a carbonyl ligand by the BOC carbonyl group readily occurs without heating such that only the BOC-coordinated tetracarbonyl complexes are isolated. It should be noted that aqueous methylamine solutions were used in preparations of complexes **12** and **14**. There has been no prior report on the aminolysis of Fischer carbene complexes in aqueous media, but as demonstrated by these results, such aminolyses can be conducted with excellent results.



Also of note is that the [(*tert*-butoxycarbonyl)amino]-carbene complexes can be obtained in comparable or higher yields by first treating the (alkylamino)carbene complexes with potassium hydride followed by reaction with di-*tert*-butyl dicarboxylate, as represented by the synthesis of complex **18** (eq 10). This route is especially useful when the substrates are thermally unstable. For example, the aminocarbene complex **16** was formed only in low yield using the Dötz method due to the instability of the methoxy complex **15**. However, using this new method, the even more unstable complex **17** gave the corresponding aminocarbene complex **18** in 78% yield. Another advantage of this pathway for the formation of [(*tert*-butoxycarbonyl)amino]carbene complexes is that it requires only 1 equiv of di-*tert*-butyl dicarboxylate.



Photoinduced Cyclization Reactions. Using a procedure analogous to our reported photoreaction of alkoxycarbene complexes,[16] complex **2** was photolyzed employing a 450-W Hanovia lamp with a Pyrex filter in THF solvent under 1 atm of carbon monoxide. This provided a 75% yield of the expected benzannulation product **19** as a white powder after purification (eq 11). The hydroxy group was not detected in the ^1H NMR spectrum in $CDCl_3$ solvent at room temperature probably due to the broadening effect from the *o*-amino group. The presence of the hydroxy group was easily identified in the IR spectrum, however, with a medium absorbance at 3291 cm^{-1} corresponding to the O–H stretch. Twelve distinct ^{13}C NMR signals between 120 and 147 ppm confirmed the formation of the expected *o*-aminonaphthol **19** (eq 11).



Compared with the photoreaction of the corresponding alkoxycarbene complex **1**, the formation of **19** was very slow as TLC testing of the reaction mixture showed that about 7–9 h of photolysis was required for complete conversion. This is understandable since the more electron-rich nature of the aminocarbene complex **2** as compared to the corresponding alkoxy complex **1** hinders the reaction. As will be shown in the discussion section, the key step of CO insertion to form intermediate ketene complexes is always slower for more electron-rich substrates. Nevertheless, this initial result demonstrated the feasibility of using photoinduced benzannulation reactions for the formation of *o*-amino aromatic alcohols.

Following this initial success, the biphenylaminocarbene complex **4** was submitted to the same photoconditions. The expected benzannulation reaction, however, never occurred. Changes in irradiation conditions (quartz filter, Vycor filter) and solvents (Et_2O, THF, CH_2Cl_2) proved successful. In one instance, photolysis of **4** in methylene chloride with a pyrex filter yielded 2-phenylbenzaldehyde as the only identifiable organic product (45%). According to Hegedus,[24] the CO insertion process occurs more readily under photolytic conditions for (benzylamino)carbene complexes than for simpler (dimethylamino)carbene complexes. Thus, the dibenzylamino complex **6** was prepared and tested. To our dismay, photolysis resulted in extensive decomposition of the starting material, with no detectable

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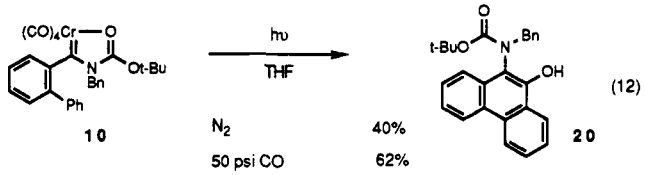
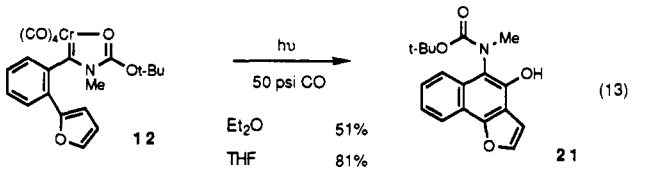
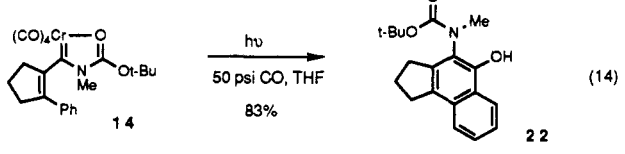
benzannulation product being formed. Quite possibly, the ketene complex was actually formed, however the desired benzannulation reaction failed due to the high activation energy required for destruction of two aromatic rings en route to the final product. To test this idea, the stilbenyl complex **9** was subjected to photolysis since it was known from our previous study of the photolyses of alkoxycarbene complexes that destruction of one aromatic system does not pose any obstacle for the benzannulation process. Failure to generate the desired benzannulation product from substrate **9** reflected a general difficulty of CO insertion in these (dialkylamino)carbene systems.

Prompted by the successful thermal alkyne plus carbene benzannulation reactions using acetyl protected/activated aminocarbene complexes as reported by Dötz,[8] we performed the photolysis on the relatively electron-poor (*tert*-butoxycarbonyl)amino complex **10** and successfully obtained the desired benzannulation product **20** in moderate yield (eq 12). The product existed as two rotamers about the amide linkage at room temperature as ^{1}H NMR showed two broad signals for the *tert*-butyl group at 1.26 and 1.46 ppm which coalesced to 1.31 ppm at 50 °C. The hydroxy group was not located in the ^{1}H NMR spectrum at room temperature, but appeared as a very broad peak centered at 5.72 ppm at 50 °C. The hydroxy group was further confirmed by the characteristic absorption at 3516 cm^{-1} in the IR spectrum. As observed in the alkoxycarbene complex benzannulation,[16] addition of CO enhanced the benzannulation reaction of this aminocarbene complex. The yield of **20** was substantially increased when the reaction was run under 50 psi of CO (eq 12).



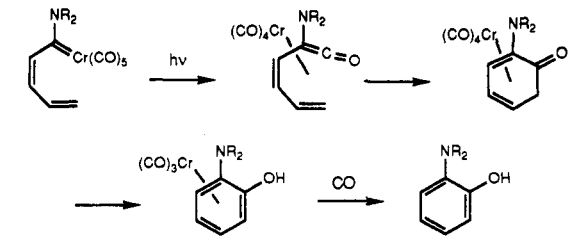
Using the same conditions of photolysis under 50 psi CO, amino aromatic alcohols **21** and **22** were also obtained in good yields from substrates **12** and **14**, respectively (eqs 13 and 14). A remarkable solvent effect was noticed for the photoreaction of complex **12**. As shown in eq 13, the yield of the benzannulation product **21** was increased from 51 to 81% when the solvent was changed from ether to THF. We have observed a similar, but less pronounced, solvent effect in photoinduced benzannulation reactions of alkoxycarbene complexes.

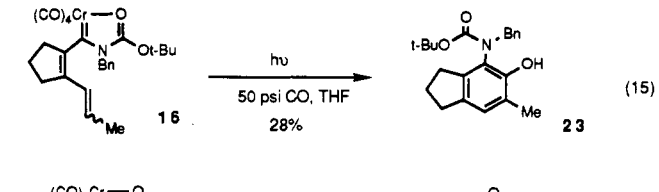


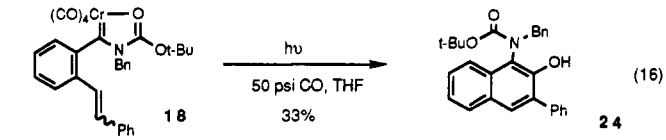


Substrates **16** and **18** gave benzannulation products **23** and **24**, respectively, in moderate yields under photolytic conditions (eqs 15 and 16). The moderate yields for these reactions are probably due to the instability of these substrates under the reaction conditions. While an average time of 2 days was needed for the complete photolysis of other substrates, substrates **16** and **18** were completely consumed within 10 h under identical reaction conditions. Analytical TLC testing of the reaction mixtures indicated a number of side products, reflecting the existence of nonproductive competing pathways. In general, photolysis of aminocarbene complexes offers high yields of the final benzannulation products, if the substrates are stable to the reaction conditions.

Scheme I







Discussion

A proposed mechanism for these photochemical benzannulation reactions is shown in Scheme I. Photoactivation promotes CO insertion to the ketene complex as demonstrated by Hegedus, and then subsequent thermal electrocyclization[25,26] of the dienylketene[27] and tautomerization provides a chromium arene complex. In the presence of excess CO, this complex is readily demetalated to provide the free arene product and chromium hexacarbonyl.

The increased efficiency of the benzannulation reaction under CO pressure is noteworthy. While the presence of CO has been shown to inhibit the Dötz benzannulation reaction,[28] Hegedus has found that CO facilitates photochemical reactions of chromium carbene complexes.[9,11] Presumably, CO traps tetracarbonyl carbene complexes formed by thermal or photoinduced[29] CO loss. Such tetracarbonyl complexes would not be expected to undergo

(25) Quinkert, G.; Kleiner, E.; Freitag, B.-J.; Glenneberg, J.; Billhardt, U.-M.; Cech, F.; Schmieder, K. R.; Schudok, C.; Steinmetzer, H.-C.; Bats, J. W.; Zimmermann, G.; Dürner, G.; Rehm, D.; Paulus, E. F. *Helv. Chim. Acta* **1986**, *69*, 469.

(26) For recent applications of electrocyclizations of dienylketenes, see: Danheiser, R. L.; Brisbois, R. G.; Kowalczyk, J. J.; Miller, R. F. *J. Am. Chem. Soc.* **1990**, *112*, 3093 and references therein.

(27) For reviews, see: (a) Tidwell, T. T. *Acc. Chem. Res.* **1990**, *23*, 273. (b) Brady, W. T. *Tetrahedron* **1981**, *37*, 2949. (c) Patai, S., Ed. *The Chemistry of Ketenes, Allenes and Related Compounds*; Wiley: New York, 1980; Parts 1 and 2.

(28) (a) Dötz, K. H.; Dietz, R. *Chem. Ber.* **1977**, *110*, 1555. (b) Fischer, H.; Mühlemeier, J.; Märkl, R.; Dötz, K. H. *Ibid.* **1982**, *115*, 1355.

(29) It has been reported that photoinduced CO loss is the primary photoreaction of carbene complexes, even with the use of Pyrex filters: Foley, H. C.; Strubinger, L. M.; Targos, T. S.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1983**, *105*, 3064.

CO insertion, due to enhanced π-backbonding from the central metal to the *cis*-carbonyl ligands, and would lead to side products. Thus, the particular benefit of CO pressure is evident here, since the BOC-coordinated substrates are converted under these conditions to the more reactive pentacarbonyl complexes. An added benefit of performing the reaction in the presence of CO is that $Cr(CO)_6$ can often be recovered at the end of reaction.

Two conceivable mechanisms may account for the solvent effect operating in the benzannulation reaction. First, because ketene formation proceeds primarily from the nonchelated pentacarbonyl carbene complex, and THF facilitates the reformation of a nonchelated pentacarbonyl complex more than ether, photolysis of the chelated carbene complexes is expected to be more facile and cleaner in THF than in ether. Secondly, a solvent of stronger coordinating ability such as THF may stabilize coordinatively unsaturated intermediate complexes, formed during photolysis, more efficiently than a solvent of weaker coordinating ability such as ether. Thus, the chemical yields of the photolytic reactions in more coordinating solvents are expected to be higher than those in less coordinating solvents. This stabilizing effect from solvents is especially pronounced in cases where long reaction times are needed.

While all alkoxycarbene complexes are subject to facile CO insertion under photolytic conditions, the formation of the ketene intermediates from the corresponding aminocarbene complexes is generally slow and, in some cases, unseen. This observation has also been reported by Hegedus.[9,11,30] Difficulty in ketene formation from aminocarbene complexes results from a substantial increase in the energy of the LUMO when the stabilizing atom is changed from oxygen to nitrogen.[31] Thus, only a small portion of the radiation light which passes through a Pyrex filter will have sufficient energy to generate the requisite carbene excited state. Therefore, the quantum yield under these conditions is expected to be very low. Light of much shorter wavelength has been shown to be ineffective in promoting benzannulation reactions and, instead, promotes extensive decomposition of starting carbene complexes due to photolytic CO extrusion and formation of unstable intermediates.[16]

It is not yet clear why a small structural change in the amino substituent of the substrate can turn an aminocarbene complex from one which effectively undergoes ketene formation to one which is inactive to this process under the same photolytic conditions. Hegedus has attempted to correlate the photolytic reactivity of aminocarbene complexes to the line width of resonances of ^{53}Cr nuclei in the NMR spectra after failing to find any correlation with IR, ^{13}C NMR, and electronic spectra. It was indicated that the broader the ^{53}Cr NMR line width an aminocarbene complex possesses, the more photolytically reactive it is.[24] However, it appears that most alkoxycarbene complexes have more narrow line widths, yet are much more reactive than the corresponding aminocarbene complexes. Furthermore, some of the aminocarbene substrates with narrow ^{53}Cr NMR line widths originally reported not to form the ketene derived products, were later shown to effectively undergo reactions involving ketene-like intermediates. For example, the phenyl(diethylamino)carbene chromium complex, which has a line width of 230 Hz (well below the 1000-Hz mark which can be considered to be the lower limit for reactive aminocarbenes),[24] gave an excellent yield of the ester as the trapping product of the intermediate ketene complex upon photolysis in methanol.[9b]

According to Fenske's molecular orbital calculations,[31] the ground state of the carbene carbon in an aminocarbene ligand is more electron rich than that in the corresponding methoxycarbene ligand. Thus, the aminocarbene carbon should in theory be more nucleophilic and therefore undergo a more facile ketene formation than the analogous methoxycarbene carbon. However, just the opposite results are observed. Also, according to the calculations, an aminocarbene ligand is a better σ-electron donor and poorer π-electron acceptor compared to the analogous methoxycarbene ligand. As a result of this perturbation, the CO ligands must accept more electron density via backbonding from the central metal rendering them less electrophilic, thus hindering the ketene formation process. This speculation, coupled with the general trends observed in the traditional Dötz reactions,[2] suggests that *ketene formation depends more on the electrophilicity of the cis-carbonyl ligands than on the nucleophilicity of the carbene carbons.* This conclusion is supported by the fact that all facile ketene formations are associated with electron deficient systems.[2] Any change on the substrates that will reduce the overall electron density on the central metal, and thus increase the electrophilicity of the carbonyl ligands, will be beneficial to the formation of the ketene intermediates. This argument is in accord with the observations that the alkoxycarbene complexes are more reactive than the analogous aminocarbene complexes and that the (acylamino)carbene complexes are more reactive than the corresponding (dialkylamino)carbene complexes in transformations involving photolytic ketene formation.

In particular, this proposal explains the failure of complexes **4**, **6**, and **9** to yield benzannulated products and the successful reaction of complexes **10** and **18**. Note that Dötz has also reported that α,β-unsaturated (acylamino)carbene complexes undergo benzannulation reactions, which require thermal CO insertions, as alkoxycarbene complexes do, but not (dialkylamino)carbene complexes which, due to their electron-rich nature, instead give indene products when reacted with alkynes.[5-7] However, the facilitation of photochemical ketene formation by acylating aminocarbene complexes, as opposed to using sterically more demanding alkyl substituents,[24] has not been emphasized before.

Conclusion

In summary, we have demonstrated photochemical benzannulation reactions of chromium aminocarbene complexes that promise to have application to the synthesis of novel *o*-amino aromatic alcohols. We have also noted some improved procedures for the preparation of chromium aminocarbene complexes. Current experiments are exploring a range of substituent effects on the benzannulation substrates and potential applications to synthetic targets.

Experimental Section

General. All reactions were carried out under nitrogen by standard Schlenk-tube techniques, unless noted otherwise.

(30) (a) Hegedus, L. S.; deWeck, G.; D'Andrea, S. *J. Am. Chem. Soc.* 1988, *110*, 2122. (b) Söderberg, B. C.; Hegedus, L. S.; Sierra, M. A. *J. Am. Chem. Soc.* 1990, *112*, 4364.

(31) (a) Block, T. F.; Fenske, R. F. *J. Organomet. Chem.* 1977, *139*, 235. (b) Sheridan, J. B.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* 1986, *5*, 1514.

Diethyl ether and tetrahydrofuran were distilled from sodium benzophenone ketyl under nitrogen. Dichloromethane and hexane were distilled from calcium hydride. All other reagents were used as received. Flash chromatography was performed on Merck silica gel 60 (230–400 mesh). Infrared spectra were recorded on a Perkin-Elmer 1600 FT-infrared spectrometer. ^1H and ^{13}C NMR spectra were recorded on Bruker AF 200 and AM 360 and 500 spectrometers. Chemical shifts are reported in ppm with Me_4Si or $CDCl_3$ as internal standards. Mass spectra were recorded at 70 eV on an AEI MS902 instrument. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

[(3-Phenylnorbornadien-2-yl)(dimethylamino)methylene]pentacarbonylchromium (2). Anhydrous dimethylamine (66 μL, 1.0 mmol) was added to a solution of [(3-phenylnorbornadien-2-yl)methoxymethylene]pentacarbonylchromium (1) (0.202 g, 0.50 mmol) in THF (10 mL) at −78 °C and stirred for 4 h. Volatile materials were removed in vacuo, and the resulting yellow oil was purified by flash chromatography (95:5 hexane/ethyl acetate) to yield 80 mg (38.5%) of one isomer of the product (**2a**) and 103 mg (49.5%) of the other isomer (**2b**). Both isomers were obtained as yellow oils and were crystallized from hexane and diethyl ether as yellow crystals. ^1H NMR of isomer **2a** ($CDCl_3$, 360 MHz) δ: 2.00 (1 H, d, J = 6.5 Hz), 2.16 (1 H, d, J = 6.5 Hz), 3.41 (3 H, s), 3.60 (1 H, s, br), 3.97 (3 H, s), 4.09 (1 H, s, br), 6.80–7.34 (7 H, m). ^1H NMR of isomer **2b** ($CDCl_3$, 360 MHz) δ: 2.20 (1 H, d, J = 6.5 Hz), 2.62 (1 H, d, J = 6.5 Hz), 2.84 (3 H, s), 3.87 (3 H, s), 3.92 (1 H, s, br), 4.15 (1 H, s, br), 6.79–7.34 (7 H, m). ^{13}C NMR ($CDCl_3$, 50 MHz) δ: (**2b** only) 46.1, 51.1, 53.3, 55.7, 66.6, 126.0, 126.7, 128.7, 132.7, 135.6, 140.4, 141.6, 156.2, 217.3, 222.9, 273.6. IR of isomer **2b** (hexane) CO stretching only: 2054 (sh, m), 1974 (w), 1936 (s), 1929 (vs) cm^{-1}. HRMS of isomer **2a**: calcd for $C_{21}H_{17}CrNO_5$: 415.0512; found: 415.0544. MS: 415 (15, M^+), 387 (15, M^+ − CO), 359 (100, M^+ − 2CO), 331 (93, M^+ − 3CO), 303 (99, M^+ − 4CO). Anal. Calcd for $C_{21}H_{17}CrNO_5$ (mixture of two isomers): C 60.73; H 4.13; found: C 60.38, H 4.26.

{[(1,1′-Biphenyl)-2-yl](dimethylamino)methylene}pentacarbonylchromium (4). A solution of {[(1,1′-biphenyl)-2-yl]methoxymethylene}pentacarbonylchromium (**3**) (1.50 g, 3.86 mmol) in THF (10 mL) was cooled to −78 °C in a dry ice–acetone bath. Dimethylamine (0.73 mL, 11.0 mmol) was added via a precooled syringe. Sodium methoxide (0.27 g, 5.0 mmol) was added to the above mixture all at once. After 20 min, the reaction was quenched with a saturated aqueous solution of $NaHCO_3$ (20 mL). The mixture was warmed to room temperature and extracted twice with Et_2O (50 mL + 20 mL). The combined organic layers were dried ($MgSO_4$) and filtered through a plug of silica gel. The solvents were removed in vacuo. The resulting yellow oil was crystallized from Et_2O at −20 °C to provide 1.22 g of yellow crystals. The mother liquor was purified via silica gel chromatography (85:15 hexane/ethyl acetate) to give a further 0.262 g of the aminocarbene product for a total combined yield of 96%. ^1H NMR ($CDCl_3$, 200 MHz) δ: 3.13 (3 H, s), 3.85 (3 H, s), 6.85 (1 H, d, J = 7.3 Hz), 7.23–7.42 (8 H, m). ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 46.7, 51.2, 120.5, 126.8, 127.4, 127.6, 128.3, 128.8, 131.0, 131.6, 140.1, 150.9, 216.8, 223.6, 277.1. IR ($CDCl_3$) CO only: 2054 (sh, m), 1974 (w), 1926 (vs) cm^{-1}. HRMS: calcd for $C_{20}H_{15}CrNO_5$: 401.0355; found: 401.0358. MS: 401 (10, M^+), 373 (9, M^+ − CO), 345 (22, M^+ − 2CO), 317 (58, M^+ − 3CO), 289 (54, M^+ − 4CO), 261 (100, M^+ − 5CO), 233 (30), 231 (48), 225 (16), 218 (53), 208 (45), 205 (59).

{[(1,1′-Biphenyl)-2-yl](benzylamino)methylene}pentacarbonylchromium (5). Benzylamine (1.09 mL, 10.0 mmol) was added to a solution of {[(1,1′-biphenyl)-2-yl]-methoxymethylene}pentacarbonylchromium (**3**) (1.94 g, 5.0 mmol) in THF (15 mL) at 0 °C and the mixture stirred for 1 h. About 2 cm^3 of silica gel was added to the above yellow solution, and the solvent was removed in vacuo. The crude product was deposited on the silica gel and purified by flash chromatography (90:10 hexane/ethyl acetate) to yield 2.255 g (97%) of (benzylamino)carbene complex **5** as a yellow powder. NMR spectra showed the presence of two isomers in a ratio of 1:1 due to the hindered rotation about the $N–C_{carbene}$ bond. ^1H NMR ($CDCl_3$, 200 MHz) mixture of two isomers in a ratio of 1:1 δ: 4.22 (0.5 H, dd, J = 15.0, 4.3 Hz), 4.58 (0.5 H, dd, J = 14.9, 6.8 Hz), 4.94 (1 H, d, J = 4.8), 6.83 (0.5 H, d, J = 7.3 Hz), 6.94 (1 H, d, J = 3.6 Hz), 7.14–7.31 (8 H, m), 8.37 (0.5 H, s, br), 9.05 (0.5 H, s, br). ^{13}C NMR ($CDCl_3$, 50 MHz) δ: (mixture of two isomers in a ratio of 1:1) 55.9, 58.3, 119.9, 123.6, 127.4, 127.6, 127.7, 127.9, 128.0, 128.6, 128.7, 128.9, 128.99, 129.04, 129.4, 129.5, 129.8, 131.1, 131.3, 133.5, 133.6, 134.0, 134.2, 139.96, 140.08, 147.6, 153.0, 216.5, 217.0, 222.8, 223.3, 280.3, 283.9. IR (hexane) CO only: 2056 (m, sh), 1975 (vw), 1940 (vs), 1934 (vs) cm^{-1}. HRMS: calcd for $C_{25}H_{17}CrNO_5$: 463.0512; found: 463.0480. FABMS (25 °C, 5 kV): 463 (100, M^+), 435 (38, M^+ − CO). MS (90 °C, 16 eV): 463 (2, M^+), 379 (47, M^+ − 3CO), 323 (100, M^+ − 5CO), 296 (8), 270 (85), 231 (57), 205 (75), 91 (26).

{[(1,1′-Biphenyl)-2-yl](dibenzylamino)methylene}pentacarbonylchromium (6). A solution of the (benzylamino)-carbene complex **5** (0.417 g, 0.90 mmol) in THF (10 mL) was added dropwise into a THF (5 mL) suspension of potassium hydride (freshly washed with hexane and THF, 40 mg, 1.00 mmol) at −78 °C and stirred at −78 °C for 1 h and at 0 °C for 30 min. It was then recooled to −78 °C. Benzyl bromide (0.131 mL, 1.10 mmol) was added and the mixture was stirred at 0 °C for 1 h. Solvents were removed in vacuo and the residue was purified by flash chromatography (90:10 hexane/ethyl acetate) to yield 0.479 g (96%) of the product **6** as a yellow oil. It was crystallized from hexane and ether as yellow crystals. ^1H NMR ($CDCl_3$, 360 MHz) δ: 3.92 (1 H, d, J = 14.8 Hz), 4.72 (1 H, d, J = 14.1 Hz), 5.03 (1 H, d, J = 14.8 Hz), 6.02 (1 H, d, J = 14.1 Hz), 6.72 (2 H, d, J = 7.1 Hz), 6.97 (2 H, d, J = 6.7 Hz), 7.15 (1 H, d, J = 7.7 Hz), 7.23–7.46 (14 H, m). ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 57.9, 64.2, 120.5, 126.6, 127.3, 127.5, 127.7, 128.3, 128.6, 128.7, 128.9, 129.0, 129.2, 131.4, 131.6, 133.3, 133.4, 140.5, 151.0, 216.7, 223.5, 280.9. IR (hexane) CO stretching region only: 2054 (sh, m), 1973 (vw), 1933 (vs) cm^{-1}. HRMS for M^+ − 5CO: calcd for $C_{27}H_{23}CrNO_5$: 413.1210; found: 413.1186. MS (140 °C, 16 eV): 469 (17, M^+ − 3CO), 413 (17, M^+ − 5CO), 361 (49), 322 (52), 270 (98), 231 (17). FABMS (25 °C, 5 kV): 553 (2, M^+), 525 (8, M^+ − CO), 469 (100, M^+ − 3CO), 413 (92, M^+ − 5CO).

{[2-(2-Phenylethenyl)phenyl](dibenzylamino)methylene}pentacarbonylchromium (9). Following the procedure used for the formation of **6**, reaction of {[2-(2-phenylethenyl)phenyl]-methoxymethylene}pentacarbonylchromium (**7**) (1.63 g, 3.9 mmol) and benzylamine (0.877 mL, 8.0 mmol) yielded, after chromatography purification, 1.902 g (100%) of {[2-(2-phenylethenyl)phenyl]benzylmethylene}pentacarbonylchromium **8** as a yellow oil. Reaction of the thus formed (benzylamino)carbene complex **8** (0.415 g, 0.85 mmol), potassium hydride (34 mg, 0.85 mmol), and benzyl bromide (0.119 mL, 1.00 mmol) provided, after flash chromatography (90:10 hexane/ethyl acetate) separation, 0.432 g (88%) of the product **9** as a yellow oil.

Spectroscopic Data for 8. ^1H NMR ($CDCl_3$, 360 MHz) mixture of two isomers in a ratio of 1:1 δ: 4.19 (0.5 H, dd, J = 14.8, 3.9 Hz), 4.25 (0.5 H, dd, J = 14.6, 5.0 Hz), 4.35 (0.5 H, dd, J = 14.6, 6.1 Hz), 4.47 (0.5 H, dd, J = 14.8, 7.0 Hz), 6.37 (0.5 H, d, J = 12.4 Hz), 6.63 (0.5 H, d, J = 12.4 Hz), 6.70–7.73 (15 H, m), 9.20 (0.5 H, s, br), 9.25 (0.5 H, s, br).

Spectroscopic Data for 9. ^1H NMR ($CDCl_3$, 500 MHz) mixture of two isomers in a ratio of 1:1 δ: 3.97 (0.5 H, d, J = 14.7 Hz), 4.10 (0.5 H, d, J = 14.9 Hz), 4.55 (0.5 H, d, J = 14.9 Hz), 4.89 (0.5 H, d, J = 14.7 Hz), 4.91 (0.5 H, d, J = 14.6 Hz), 5.08 (0.5 H, d, J = 14.6 Hz), 6.03 (0.5 H, d, J = 14.6 Hz), 6.11 (0.5 H, d, J = 14.6 Hz), 6.50 (0.5 H, d, J = 12.3 Hz), 6.71 (0.5 H, d, J = 12.3 Hz), 6.90–7.64 (20 H, m). MS: 523 (15, M^+ − 2CO), 495 (76, M^+ − 3CO), 467 (27, M^+ − 4CO), 439 (100, M^+ − 5CO).

{[(1,1′-Biphenyl)-2-yl][(*tert*-butoxycarbonyl)benzylamino]methylene}tetracarbonylchromium (10). A solution of {[(1,1′-biphenyl)-2-yl](benzylamino)methylene}pentacarbonylchromium (**5**) (0.463 g, 1.00 mmol), di-*tert*-butyl dicarbonate (0.458 g, 2.10 mmol) and (dimethylamino)pyridine (12.2 mg, 0.10 mmol) in ether (3 mL) was stirred at room temperature for 3 h. Solvents were removed in high vacuum and the resulting dark oil was purified by flash chromatography (80:20 hexane/ethyl acetate) to yield 0.386 g (78%) of the product as a dark brown powder. ^1H NMR ($CDCl_3$, 360 MHz) δ: 1.34 (9 H, s), 4.87 (1 H, d, J = 15.8 Hz), 5.17 (1 H, d, J = 15.8 Hz), 7.07 (2 H, d, J = 7.3 Hz), 7.25–7.48 (12 H, m). ^{13}C NMR ($CDCl_3$, 90 MHz) δ: 9.5, 27.6, 54.6, 90.0, 122.8, 127.2, 127.7, 128.4, 128.5, 129.09, 129.12, 129.6, 130.0, 131.5, 136.4, 137.2, 141.5, 147.2, 161.2, 324.8 (4 CO carbons

were not located). IR ($CDCl_3$) CO only: 2016, 1941, 1917, 1858, 1656 cm^{-1}. Anal. Calcd for $C_{29}H_{25}NO_6Cr$: C 65.04, H 4.71; found: C 64.75, H 4.76.

{[2-(2'-Furyl)phenyl][(*tert*-butoxycarbonyl)methylamino]methylene}tetracarbonylchromium (12). An aqueous solution of methylamine (40%, 0.26 mL, 3.0 mmol) was added to a solution of {[2-(2'-furyl)phenyl]methoxymethylene}pentacarbonylchromium (11) in ether (0.580 g, 1.53 mmol) at −20 °C and stirred until it turned pale yellow. A saturated aqueous solution of sodium bicarbonate (20 mL) was added. The product was extracted with ether and dried ($MgSO_4$) and the solvent was removed in vacuo to give 0.557 g (97%) of the (methylamino)carbene complex as a yellow microcrystalline solid. It was used directly for the following acylation without further purification. A solution of the thus formed (methylamino)carbene complex (0.557 g, 1.478 mmol), di-*tert*-butyl dicarbonate (0.677 g, 3.10 mmol) and (dimethylamino)pyridine (15 mg, 0.12 mmol) in ether (4 mL) was stirred at 0 °C for 24 h. The solvent was removed in vacuo and dried further under high vacuum. The resulting dark oil was purified by flash chromatography (80:20 hexane/ethyl acetate) to yield 0.519 g (83%) of the product 12 as a dark brown powder. ^1H NMR ($CDCl_3$, 360 MHz) δ: 1.60 (9 H, s), 3.05 (3 H, s), 6.45 (1 H, s), 6.52 (1 H, s), 7.20–7.35 (4 H, m), 7.70 (1 H, s). ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 28.0, 36.4, 88.4, 108.0, 111.9, 121.8, 123.5, 126.8, 127.4, 127.6, 142.8, 144.8, 153.0, 160.0, 325.0 (four resonances for CO ligands were not located in the spectrum). IR (hexane) CO only: 2018 (w), 1938 (s), 1920 (s), 1880 (m), 1660 (m) cm^{-1}. HRMS: calcd for $C_{21}H_{19}CrNO_7$: 449.0567; found: 449.0545. MS: 449 (8, M^+), 368 (19, M^+ − 3CO), 337 (99), 281 (100, M^+ − 5CO), 236 (22), 185 (14), 144 (22), 131 (11).

{(2-Phenylcyclopenten-1-yl)[(*tert*-butoxycarbonyl)methylamino]methylene}tetracarbonylchromium (14). An aqueous solution of methylamine (40%, 0.26 mL, 3.0 mmol) was added to a solution of [(2-phenylcyclopenten-1-yl)methoxymethylene]pentacarbonylchromium (13) in ether (0.576 g, 1.50 mmol) at −20 °C and stirred at this temperature until it turned pale yellow. A saturated aqueous solution of sodium bicarbonate (20 mL) was added. The product was extracted with ether and dried ($MgSO_4$) and the solvent was removed in vacuo to give the (methylamino)carbene complex as a yellow oil. A solution of the thus formed crude (methylamino)carbene complex, di-*tert*-butyl dicarbonate (0.655 g, 3.00 mmol), and (dimethylamino)pyridine (15 mg, 0.12 mmol) in ether (5 mL) was maintained at 5 °C for 24 h. The solvent was removed in vacuo and dried further under high vacuum. The resulting dark oil was purified by flash chromatography (85:15 hexane/ethyl acetate) to yield 0.556 g (83%) of the product 14 as a dark brown powder which was further purified by crystallization from hexane and ethyl acetate to give the pure product as brown crystals. ^1H NMR ($CDCl_3$, 200 MHz) δ: 1.57 (9 H, s), 2.00–2.14 (1 H, m), 2.22–2.28 (1 H, m), 2.60–2.70 (1 H, m), 2.85–2.95 (1 H, m), 3.10–3.40 (2 H, m), 2.24 (3 H, s), 7.15–7.29 (5 H, m). ^{13}C NMR (CD_2Cl_2, 50 MHz) δ: 23.8, 28.0, 36.8, 37.4, 40.5, 89.3, 127.2, 128.0, 128.6, 132.3, 137.0, 145.9, 160.4, 217.0, 217.7, 232.3, 234.3, 324.9. IR (hexane) CO only: 2018 (m), 1951 (m), 1926 (s), 1875 (s), 1651 (w) cm^{-1}. Anal. Calcd for $C_{22}H_{23}CrNO_6$: C 58.80, H 5.16; found C 58.50, H 5.25.

[(2-Propenylcyclopenten-1-yl)[(*tert*-butoxycarbonyl)benzylamino]methylene]tetracarbonylchromium (16). Benzylamine (0.55 mL, 5.0 mmol) was added to a solution of [(2-(1'-propenyl)cyclopenten-1-yl)methoxymethylene]pentacarbonylchromium (15) (0.790 g, 2.30 mmol) in THF (5 mL) at 0 °C and the mixture stirred at this temperature until it turned pale yellow. A saturated aqueous solution of sodium bicarbonate (20 mL) was added. The product was extracted with ether and dried ($MgSO_4$) and the solvent was removed in vacuo. The resulting yellow oil was purified by chromatography (90:10 hexane/ethyl acetate) to give 0.836 g (87%) of the (benzylamino)carbene complex as a yellow oil. A solution of the thus formed crude (benzylamino)carbene complex, di-*tert*-butyl dicarbonate (0.917 g, 4.2 mmol), and (dimethylamino)pyridine (12 mg, 0.10 mmol) in ether (5 mL) was stirred at 0 °C for 24 h. The solvent was removed in vacuo and dried further under high vacuum. The resulting dark oil was purified by flash chromatography (90:10 hexane/ethyl acetate) to yield 0.342 g (35%) of the product 16 as a dark brown oil which was crystallized from hexane and ether to give light brown crystals. ^1H NMR ($CDCl_3$, 360 MHz) δ: 1.37 (9 H, s), 1.78–1.86 (1 H, m), 1.89 (3 H, d, J = 7.2 Hz), 2.12–2.27 (2 H, m), 2.84–2.99 (2 H, m), 3.26 (1 H, dt, J = 16.0, 7.8 Hz), 4.72 (1 H, d, J = 15.4 Hz), 5.11 (1 H, d, J = 15.4 Hz), 5.54 (1 H, dt, J = 11.8, 7.2 Hz), 6.97 (2 H, d, J = 7.0 Hz), 7.25–7.35 (3 H, m). ^{13}C NMR ($CDCl_3$, 90 MHz) δ: 15.9, 25.1, 28.5, 37.4, 39.1, 53.2, 89.3, 125.0, 126.9, 128.0, 128.4, 129.6, 137.2, 149.5, 160.3, 325.1 (four CO carbons were not located). IR ($CDCl_3$) CO only: 2018, 1940, 1925, 1874, 1652 cm^{-1}. HRMS: calcd for $C_{25}H_{27}CrNO_6$: 489.1243; found: 489.1261. FABMS: 489 (9, M^+), 405 (14, M^+ − 3CO), 377 (100, M^+ − 4CO), 321 (50), 270 (54), 226 (22), 185 (13).

{[2-(2-Phenylethenyl)phenyl][(*tert*-butoxycarbonyl)benzylamino]methylene}tetracarbonylchromium (18). A solution of {[2-(2-phenylethenyl)phenyl](benzylamino)methylene}pentacarbonylchromium (8) (0.60 g, 1.37 mmol) in THF (10 mL) was added dropwise into a THF (5 mL) suspension of potassium hydride (freshly washed with hexane and THF, 60 mg, 1.50 mmol) at −78 °C and stirred at −78 °C for 30 min and at 0 °C for 1 h. A solution of di-*tert*-butyl dicarbonate (0.33 g, 1.50 mmol) in THF (2 mL) was added and the reaction was stirred for 24 h at 0 °C. Solvents were removed in vacuo and the residue was purified by flash chromatography (85:15 hexane/ethyl acetate) to yield 0.543 g (78%) of the product 18 as a brown oil which was crystallized from hexane and ethyl acetate to give brown crystals. ^1H NMR ($CDCl_3$, 360 MHz) mixture of cis and trans isomers in a ratio of 1:1 δ: 1.34 (4.5 H, s), 1.37 (4.5 H, s), 4.53 (0.5 H, d, J = 15.4 Hz), 4.58 (0.5 H, d, J = 15.4 Hz), 4.79 (0.5 H, d, J = 15.4 Hz), 5.00 (0.5 H, d, J = 15.4 Hz), 6.35 (0.5 H, d, J = 12.2 Hz), 6.63 (0.5 H, d, J = 12.3 Hz), 6.86–6.95 (2 H, m), 7.05–7.11 (1 H, m), 7.18–7.38 (10.5 H, m), 7.42–7.45 (1 H, m), 7.68–7.70 (0.5 H, m). ^{13}C NMR ($CDCl_3$, 90 MHz) δ: (two isomers in a ratio of 1:1) 27.66, 27.71, 52.85, 88.77, 88.91, 123.87, 123.94, 125.31, 125.49, 126.23, 126.36, 126.81, 127.22, 127.35, 127.42, 127.65, 127.70, 127.74, 127.86, 127.91, 127.94, 128.33, 128.39, 128.60, 128.65, 128.68, 128.70, 128.86, 129.31, 130.69, 131.69, 135.89, 136.08, 136.49, 137.19, 146.76, 147.30, 160.02, 160.22, 324.81, 325.35 (four CO carbons were not located). IR ($CDCl_3$) CO only: 2018, 1980, 1919, 1862, 1655 cm^{-1}. HRMS: calcd for $C_{31}H_{27}CrNO_6$: 561.1243; found: 561.1225. FABMS: 561 (8, M^+), 477 (13, M^+ − 3CO), 449 (100, M^+ − 4CO), 393 (52), 348 (12), 296 (12), 257 (22), 154 (26).

1,4-Dihydro-10-(dimethylamino)-9-hydroxy-1,4-methanophenanthrene (19). A solution of the (dimethylamino)carbene complex 2 (0.415 g, 1.00 mmol) in THF (250 mL) was photolyzed for 7 h with a 450-W medium pressure mercury lamp with a Pyrex filter while slowly sparging with CO. The yellow solution was allowed to stand overnight under 1 atm of CO to effect decomplexation of the product from its tricarbonylchromium complex. The resulting solution was concentrated in vacuo and the residue was purified by flash chromatography on silica gel to yield 0.181 g (72%) of the product 19 as a white waxy solid and 0.120 g (55%) of chromium hexacarbonyl. ^1H NMR ($CDCl_3$, 360 MHz) δ: 2.34 (1 H, d, br, J = 6.7 Hz), 2.41 (1 H, dt, J = 6.7, 1.7 Hz), 2.85 (6 H, s), 4.39–4.42 (2 H, m), 6.85–6.88 (1 H, m), 6.94–6.97 (1 H, m), 7.26–7.31 (1 H, m), 7.34–7.39 (1 H, m), 7.78 (1 H, d, br, J = 8.4 Hz), 8.11 (1 H, d, br, J = 8.4 Hz) (OH is not located). ^{13}C NMR ($CDCl_3$, 90 MHz) δ: 45.1, 47.0, 50.2, 70.9, 120.0, 122.6, 123.3, 123.5, 125.5, 127.7, 130.0, 139.6, 142.8, 144.6, 145.5, 146.6. IR ($CDCl_3$): 3291 (O–H) 3068, 2974, 2939, 2872, 2795, 1628, 1590, 1566, 1446, 1377, 1321, 1235, 1195, 1035 cm^{-1}. Anal. Calcd for $C_{17}H_{17}NO$: C 81.24, H 6.82; found: C 81.24, H 6.98. HRMS: calcd for $C_{17}H_{17}NO$ 251.1310; found: 251.1304. MS: 251 (100, M^+), 236 (97), 221 (6), 210 (24), 193 (5), 178 (17), 165 (20), 152 (18), 151 (11), 115 (6), 102 (3).

9-[(*tert*-Butoxycarbonyl)benzylamino]-10-hydroxyphenanthrene (20). A solution of the aminocarbene complex 10 (0.40 g, 0.747 mmol) in THF (45 mL) in a Pyrex pressure tube was degassed by two cycles of the freeze–thaw method and pressurized to 50 psi with CO. It was photolyzed with a 450-W medium pressure mercury lamp for 36 h at room temperature. The solvent was removed in vacuo and the residue was purified by flash chromatography (85:15 hexane/ethyl acetate) to yield 0.185 g (62%) of the product as white crystals (from hexane). When the photolysis was run under one atmosphere of CO (CO sparging), a 40% yield of the product was isolated. ^1H NMR ($CDCl_3$, 360 MHz) δ (at 50 °CO): 1.32 (9 H, s), 4.19 (1 H, d, J = 14.2 Hz), 5.42 (1 H, d, J = 14.2 Hz), 5.72 (1 H, s, br), 7.23–7.30 (5 H, m), 7.46–7.65 (5 H, m), 8.23 (1 H, d, J = 7.6 Hz), 8.60 (2

H, d, J = 8.2 Hz). ^{13}C NMR ($CDCl_3$, 90 MHz) δ (at 50 °C): 28.1, 53.6, 81.2, 117.9, 122.0, 122.4, 123.1, 123.6, 124.3, 125.5, 126.5, 127.2, 127.3, 127.4, 128.0, 128.8, 128.9, 129.8, 130.8, 138.5, 146.8, 156.1. IR ($CDCl_3$): 3516 (O–H), 3067, 2981, 2933, 1693 (C=O), 1630, 1606, 1498, 1454, 1385, 1368, 1323, 1300, 1246, 1215, 1157 cm^{-1}. HRMS: calcd for $C_{26}H_{25}NO_3$: 399.1834; found: 399.1850. MS: 399 (7, M^+), 343 (19), 298 (29), 234 (13), 208 (100), 180 (58), 165 (42), 152 (23). Anal. Calcd for $C_{26}H_{25}NO_3$: C 78.17, H 6.31; found C 78.32, H 6.50.

5-[(*tert*-Butoxycarbonyl)methylamino]-4-hydroxynaphtho[1,2-*b*]furan (21). Photolysis in Et_2O. Following the procedure used above for the formation of **19**, photolysis of a solution of {[2-(2′-furyl)phenyl][(*tert*-butoxycarbonyl)methylamino]methylene]tetracarbonylchromium, **12**, (0.100 g, 0.244 mmol) in Et_2O (40 mL) for 14 h in a pressure tube yielded 34.2 mg (51%) of the product **21** as a pale yellow oil.

Photolysis in THF. Following the same procedure above, photolysis of a solution of **12** (0.300 g, 0.733 mmol) in THF (40 mL) in the pressure tube for 2.5 days yielded 0.169 g (81%) of the product **21** as a white powder which was crystallized from hexane to give **21** as white crystals. ^{1}H NMR ($CDCl_3$, 360 MHz) δ (at 50 °C): 1.19 (9 H, s), 3.27 (3 H, s), 6.29 (1 H, s, br), 6.94 (1 H, s, br), 7.40–7.51 (2 H, m), 7.61 (2 H, d, J = 8.2 Hz), 8.21 (1 H, J = 7.9 Hz). ^{13}C NMR ($CDCl_3$, 90 MHz) δ (at 50 °C): 28.2, 37.1, 80.9, 105.5, 118.0, 120.7, 122.0, 123.7, 126.1, 128.7, 143.7, 144.7, 150.9, 156.7. IR ($CDCl_3$): 3521 (O–H), 3226 (br, O–H···O), 2981, 2933, 1682 (C=O) 1590, 1509, 1469, 1443, 1394, 1369, 1352, 1250, 1219, 1151 cm^{-1}. HRMS: calcd for $C_{18}H_{19}NO_4$: 313.1314; found: 313.1288. MS: 313 (14, M^+), 257 (99), 213 (100), 198 (29), 161 (18), 106 (9). Anal. Calcd for $C_{18}H_{19}NO_4$: C 69.00, H 6.11; found: C 68.88, H 6.15.

4-[(*tert*-Butoxycarbonyl)methylamino]-5-hydroxybenzo[*g*]indan (22). Following the procedure above, photolysis of a solution of **14** (0.225 g, 0.50 mmol) in THF (40 mL) for 30 h under 50 psi of CO yielded 0.129 g (83%) of the product **22** as a white powder which was crystallized from hexane to give **22** as white crystals. ^{1}H NMR ($CDCl_3$, 360 MHz) δ (at 50 °C): 1.44 (9 H, s, br), 2.18–2.28 (2 H, m), 2.97 (2 H, t, J = 7.5 Hz), 3.17 (3 H, s), 3.19 (2 H, t, J = 7.4 Hz), 6.01 (1 H, s, br), 7.40 (1 H, t, J = 7.0 Hz), 7.46 (1 H, t, J = 7.1 Hz), 7.68 (1 H, d, J = 8.1 Hz), 8.24 (1 H, d, J = 8.1 Hz). ^{13}C NMR ($CDCl_3$, 90 MHz) δ (at 50 °C): 24.5, 28.3, 31.0, 32.0, 36.7, 80.9, 122.5 (br), 123.3, 124.0, 1234.2, 124.7 (br), 130.1, 132.1 (br), 138.3, 146.0, 155.9. IR ($CDCl_3$): 3535 (O–H), 3062, 2979, 2848, 1697 (C=O), 1593, 1579, 1478, 1454, 1406, 1388, 1369, 1209, 1149 cm^{-1}. HRMS: calcd for $C_{19}H_{23}NO_3$: 313.1678; found: 313.1659. MS: 313 (83, M^+), 258 (16), 257 (80), 213 (100), 200 (13), 171 (5), 152 (6), 141 (7), 115 (5). Anal. Calcd for $C_{19}H_{23}NO_3$: C 72.82, H 7.40; found: C 72.85, H 7.39.

4-[(*tert*-Butoxycarbonyl)benzylamino]-5-hydroxy-6-methylindan (23). Following the procedure above, photolysis of a solution of **16** (0.190 g, 0.388 mmol) in THF (40 mL) for 18 h at 50 psi of CO yielded 38.6 mg (28%) of the product **23** as a pale yellow oil, which was crystallized from hexane to give faint yellow crystals. ^{1}H NMR ($CDCl_3$, 360 MHz) δ (at 50 °C): 1.38 (9 H, s), 1.91 (2 H, quintet, J = 6.6 Hz), 2.01 (3 H, s), 2.35 (1 H, s, br), 2.50–2.64 (1 H, m), 2.61 (2 H, t, J = 7.5 Hz), 4.50 (1 H, d, J = 14.4 Hz), 4.72 (1 H, d, J = 14.4 Hz), 5.25 (1 H, s, br), 6.88 (1 H, s), 7.20–7.28 (5 H, m). ^{13}C NMR ($CDCl_3$, 90 MHz) δ (at 50 °C): 16.0, 25.8, 28.2, 31.3, 32.6, 53.3, 80.9, 123.8, 125.3, 125.8, 127.6, 128.5, 128.6, 136.0, 138.3, 139.5, 148.5, 148.3, 155.3. IR ($CDCl_3$): 3535 (O–H), 2978, 2932, 2848, 1691 (C=O), 1469, 1454, 1392, 1368, 1254, 1159 cm^{-1}. HRMS: calcd for $C_{22}H_{27}NO_3$: 353.1991; found: 353.1994. MS: 353 (38, M^+), 297 (58), 280 (14), 252 (100), 216 (9), 188 (15), 174 (11), 163 (58), 162 (49), 132 (12), 117 (12), 104 (17). Anal. Calcd for $C_{22}H_{27}NO_3$: C 74.76, H 7.70; found: C, 74.77, H 7.82.

1-[(*tert*-Butoxycarbonyl)benzylamino]-2-hydroxy-3-phenylnaphthalene (24). Following the procedure above, photolysis of a solution of **18** (0.290 g, 0.51 mmol) in THF (45 mL) for 24 h at 50 psi of CO yielded 71.5 mg (33%) of the product **24** as a pale yellow oil. ^{1}H NMR ($CDCl_3$, 360 MHz) δ (at 50 °C): 1.34 (9 H, s), 4.37 (1 H, d, J = 14.2 Hz), 5.29 (1 H, d, J = 14.2 Hz), 5.56 (1 H, s, br), 7.21–7.35 (7 H, m), 7.38–7.46 (3 H, m), 7.49–7.52 (2 H, m), 7.57 (1 H, d, J = 8.4 Hz), 7.70 (1 H, s), 7.77 (1 H, d, J = 8.6 Hz). ^{13}C NMR ($CDCl_3$, 90 MHz) δ (at 50 °C): 28.14, 53.76, 81.02, 121.54, 122.29, 123.80, 126.83, 127.54, 127.85, 128.31, 128.50, 128.59, 128.64, 128.90, 129.28, 129.39, 130.52, 131.04, 137.76, 138.15, 148.30, 155.89. IR ($CDCl_3$): 3513 (O–H), 3065, 3032, 2980, 2932, 1694 (C=O), 1497, 1456, 1435, 1393, 1368, 1322, 1255, 1161 cm^{-1}. HRMS: calcd for $C_{28}H_{27}NO_3$: 425.1991; found: 425.1986. MS: (CI/NH_3) 426 (17, $[MH]^+$), 425 (13, M^+), 370 (100), 325 (48), 234 (55).

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Supplementary Material Available: ^{1}H NMR spectra for compounds **4–6**, **9**, **12**, **16**, **18**, and **24** and a ^{13}C NMR spectrum for **12** (9 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.