are concerned, we conclude paraphrasing Silvestre and Hoffmann: *the hydrido-acetylide channel is a dead end, as far as eventual vinylidene production is concerned.*[2]

**Acknowledgment.** We are grateful to Dr. C. Mealli for the helpful discussion and to Mr. P. Innocenti and Mr. A. Traversi for technical assistance. Part of this work was supported by a grant from the CNR program "Progetto Finalizzato". We wish to thank also Conselleria de Cultura of Generalitat Valenciana for a grant that made J.A.R.'s stay in Firenze possible.

**Supplementary Material Available:** Positional and thermal parameters for anisotropically refined atoms (Table S1), positional and thermal parameters for isotropically refined atoms (Table S2), and final positional parameters for hydrogen atoms for **3**·1.5 THF (Table S3) (5 pages); a listing of observed and calculated structure factors for **3**·1.5 THF (22 pages). Ordering information is given on any current masthead page.

# Synthesis and Properties of (*O*-Acyl imidato)carbene Complexes of Chromium, Molybdenum, and Tungsten

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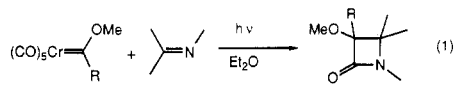
A number of (*O*-acyl imidato)carbene complexes of chromium, molybdenum, and tungsten were prepared by the acylation of aminocarbenes or by the reaction of acetoxycarbenes with amides. These relatively unstable complexes had unusual spectroscopic properties and underwent thermal reactions with imines to give low yields of 3-azetidinones. Two amido chromium carbene complexes were also prepared. These were quite unstable, resembling acetoxycarbenes, and readily decomposed. An (*N*-carbobenzoxyamino)carbene was also prepared. It was the most stable of these carbenes and underwent reactions typical of aminocarbene complexes.

Recently a novel photochemical reaction between imines and "Fischer" carbene complexes of chromium to produce β-lactams was developed in these laboratories (eq 1).[1] A



(1)

wide range of imines, including thiazines, benzothiazines, and thiazolines, as well as quinoline and dihydroisoquinolines underwent this reaction, producing β-lactams in excellent yield. Under similar conditions, azirines produced *N*-vinylimidates,[2] azobenzenes produced 1,2- and 1,3-diazetidinones,[3] and, with molybdenum carbene complexes, oxazoles and oxazolines produced β-lactams.[4] These studies utilized methoxymethyl- and methoxyphenylcarbene complexes since these were most readily accessible by classic Fischer methodology,[5] the reaction of an organolithium reagent with chromium hexacarbonyl, followed by treatment of the thus formed "ate" complex with trimethyloxonium tetrafluoroborate.[6] This resulted in the formation of β-lactams having methoxy and alkyl substituents α to the carbonyl group. However, most biologically active β-lactams have amide functionality at this position,[7] requiring the use of (*N*-acylamino)carbene complexes in the above synthesis.

Aminocarbene complexes are readily prepared by the reaction of alkoxycarbene complexes with amines,[8] a simple exchange process analogous to the conversion of organic esters to amides. However, amides do *not* undergo this exchange process with alkoxycarbene complexes, and amidocarbene complexes are not available by this route.[9] Acetoxycarbene complexes, prepared by O-acylation of acyl "ate" complexes, are similar to mixed anhydrides and are considerably more reactive toward weak nucleophiles than are the corresponding alkoxycarbenes.[10,11] The use of amides as nucleophiles would lead to the desired amidocarbene complexes, if successful (see below).

Because of extensive delocalization of the nitrogen lone pair of electrons into the electron-deficient chromium system,[12] direct acylation of aminocarbene complexes was not feasible. However, aminocarbene complexes have been *alkylated* by deprotonation at nitrogen with a strong base (e.g., $CH_3Li$, LDA) followed by N-alkylation with active alkylating agents (e.g., $CH_3I$, $Me_3OBF_4$).[13,14] The use of acyl halides or anhydrides as electrophiles would again result in formation of the desired amidocarbene complexes

(1) Hegedus, L. S.; McGuire, M. A.; Schultze, L. M.; Yijun, C.; Anderson, O. P. *J. Am. Chem. Soc.* **1984**, *106*, 2680.
(2) Hegedus, L. S.; Kramer, A.; Yijun, C. *Organometallics* **1985**, *4*, 1747.
(3) Hegedus, L. S.; Kramer, A. *Organometallics* **1984**, *3*, 1263.
(4) Hegedus, L. S.; Schultze, L. M.; Toro, J.; Yijun, C. *Tetrahedron* **1985**, *41*, 5833.
(5) Aumann, R.; Fischer, E. O. *Chem. Ber.* **1960**, *101*, 954.
(6) We have recently developed efficient syntheses of $(CO)_5Cr{=}C(NR_2)H$ complexes. See: Borel, C.; Hegedus, L. S.; Krebs, J.; Satoh, Y. *J. Am. Chem. Soc.* **1987**, *109*, 1101. Imwinkelried, R.; Hegedus, L. S. *Organometallics* **1988**, *7*, 702.
(7) Durkheimer, W.; Blumbach, J.; Lattrell, R.; Scheunemann, K. H. *J. Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 180.
(8) (a) Heckl, B.; Werner, H.; Fischer, E. O. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 817. (b) Werner, H.; Fischer, E. O.; Heckl, B.; Kreiter, C. G. *J. Organomet. Chem.* **1971**, *28*, 367.
(9) Connor, J. A.; Fischer, E. O. *J. Chem. Soc. A* **1969**, 578.
(10) Connor, J. A.; Jones, E. M. *J. Chem. Soc. A* **1971**, 3368.
(11) Semmelhack, M. F.; Bozell, J. J.; Sato, T.; Wulff, W.; Spiess, E.; Zask, A. *J. Am. Chem. Soc.* **1982**, *104*, 5850.
(12) Connor, J. A.; Mills, O. S. *J. Chem. Soc. A* **1969**, 334.
(13) Moser, E.; Fischer, E. O. *J. Organomet. Chem.* **1968**, *15*, 147.
(14) Casey, C. P.; Vollendorf, N. W.; Haller, K. J. *J. Am. Chem. Soc.* **1984**, *106*, 3755.

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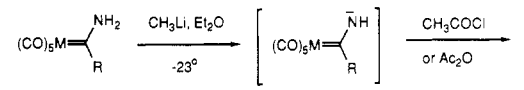
**Table I. $^{13}C$ and IR Spectral Data for Complexes 1a, 2a, 2b, 5, 6, and 7**

| complex | δ(M=*C*) | δ(RC(=O)–O) | δ(R–C=N) | δ(RC(=O)–N) | ν<sub>CO</sub>(RC(=O)–) |
|---|---|---|---|---|---|
| 1 | 291.0 | | | | |
| **2a** | 252.6 | 166.2 | 130.0 | | 1775 |
| **2b** | 249.6 | 166.1 | 129.1 | | 1771 |
| **5** | 285.8 | | | 174.7 | 1730 |
| **6** | 316.9 | | | 183.2 | 1620 |
| | | | | | 1688 |
| **7** | 327.6 | | | 144.9 | 1779 |
| | | | | | 1715 |

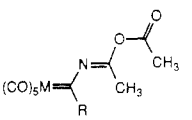
if successful. The results of studies of both of these approaches are presented below.

## Results and Discussion

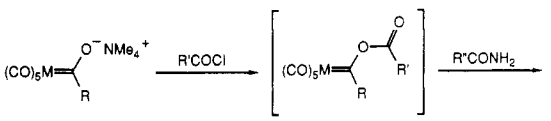
Treatment of unsubstituted aminocarbene complexes of chromium, molybdenum, or tungsten with methyllithium followed by acylation with acetic anhydride or acetyl chloride resulted in exclusive *diacylation*, producing the unusual (*O*-acyl imidato)carbene complexes **2a–d** as orange-red oils (eq 2). This same class of compounds resulted from the reaction of acyloxycarbene complexes with primary amides (eq 3).

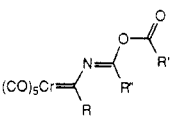



**1a** M = Cr; R = Ph
**1b** M = Cr; R = $CH_3$
**1c** M = Mo; R = Ph
**1d** M = W; R = Ph




**2a** 45%
**2b** 27%
**2c** 26%
**2d** 30%

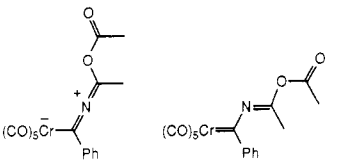



**2a** R = Ph; R', R" = Me 39%
**2b** R = R; = R" = Me 27%
**2e** R = Ph; R' = Me; R" = Et 34%
**2f** R = Ph; R' = Et; R" = Me 36%

The constitution and structure of these unusual complexes are supported by all available physical data, including $^1H$ and $^{13}C$ NMR spectroscopy, infrared and UV–visible spectroscopy, mass spectrometry, and elemental analysis of the more stable members. They have a number of unusual spectroscopic properties (see Table I for illustrative data) which argue for the assigned *O*-acyl imidato structure rather than the possible alternative bis(acylamino) (e.g. (Cr=C(R)($NAc_2$)) structure. The [(*O*-acyl imidato)carbene]chromium complex **2a** is typical. The $^1H$ NMR spectrum shows two distinct three-proton singlets, at δ 2.21 and 2.35, respectively, due to the two different acetyl-derived methyl groups. Similarly, there are two acetyl-derived methyl groups in the $^{13}C$ NMR spectrum, at δ 19.1 and 20.6, respectively. The signal from the carbene carbon appears at unexpectedly high field, δ 252.6! For comparison, the carbene carbon absorption for $(CO)_5Cr$=C(Ph)OMe appears at δ 354.5, for the starting $(CO)_5Cr$=C(Ph)$NH_2$ at δ 291.0. Thus, bis acylation caused a ~40 ppm *upfield* shift, indicating more shielding by the *O*-acyl imidato group than by either the $NH_2$ or the OMe group (see below). This trend holds for all complexes **2a–f** each of which has a $^{13}C$ carbene carbon signal ~50 ppm upfield from that of the starting complex. The $^{13}C$ chemical shifts of the two carbonyl carbons introduced by acylation are also unusual, appearing at δ 166.2 and 130.0, somewhat upfield from those of simple imides or amides (170–180 ppm). The unusually high field absorption for one of the carbonyl carbons is *not* due to an interaction with the adjacent phenyl group in **2a**, since the methyl compound **2b** has very similar chemical shift values for these "carbonyl" carbons (δ 166.1, 129.1). The δ 166 peak is the range of normal acid anhydrides (160–170 ppm) while the δ ~130 peak is too high a field to be *any* amidic carbonyl carbon. This peak is assigned to the $sp^2$ carbon of the imidate, –N=*C*(OAc)R. This also correlates well to the chemical shift (δ 134) of the $sp^2$ carbon of the imidate –N*C*(OR')R in the recently reported (*O*-methyl imidato)carbene complexes.[15,16] In the infrared spectrum, the acetyl group absorbs at 1775 $cm^{-1}$, about 100 $cm^{-1}$ above normal imides or amides, but well within the range for vinyl esters. No band assignable to the C=N is apparent. The elemental analysis (C, H, N, Cr) confirms the assigned constitution, and the mass spectrum has a weak parent ion (*m/e* 381). The visible spectrum has $\lambda_{max}$ = 445 nm (ε = 3.6 × $10^4$).

(*O*-Acyl imidato)carbenes can be represented by two extreme structures, **2a** and **2a'**. Structure **2a'** is likely to



**2a'** **2a**

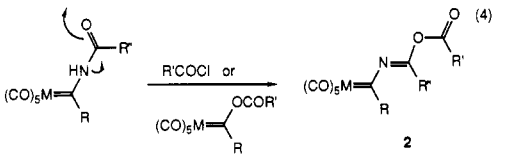
be important for several reasons. The only source of stabilization for the carbene is overlap with the lone pair on nitrogen, and the degree to which this happens determines the importance of **2a'** versus **2a**. In closely related (*O-alkyl* imidato)carbene complexes[15] the C–N–C bond angle varies from 153 to 174°, indicating extensive interaction of the nitrogen with the carbene carbon and hence the importance of structures such as **2a'**. Support for the importance of **2a'** also comes from the $^1H$ NMR spectrum of **2e**. As the *O*-acyl imidato ligand approaches linearity,

(15) Yang, D. C.; Dragisch, V.; Wulff, W. D.; Huffman, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 307.

(16) Related *O*-acyl imidatocarbene complexes have recently been characterized by X-ray crystallography by Professor W. D. Wulff. The spectroscopic parameters for these complexes correlate well with those reported in this manuscript. We thank him for making his data available prior to publication. After submission of this paper, preparation of *O*-acyl imidatocarbenes from the reaction of aminocarbenes, acid chlorides, and tertiary amines was reported: Aumann, R.; Hinterding, P. *Chem. Ber.* **1989**, *122*, 365.

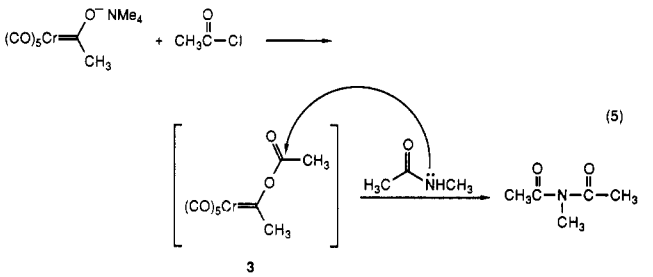
it approaches the structure of a 2-azaallenyl cation, which has a plane of chirality.[17] Methylene groups directly attached to this linear moiety become diastereotopic, and, indeed, the $CH_2$ group of the $CH_3CH_2C{=}N$ moiety in **2e** is diastereotopic, appearing as two dq's at $\delta$ 2.64 and 2.73 with $J$'s = 18.9 (gem) and 7.4 (vic).

Formation of O-acyl imidates in these reactions resulted because the initially formed monoacylamidocarbene complexes were highly reactive toward further O-acylation (eq 4). (This occurred even when inverse addition procedures



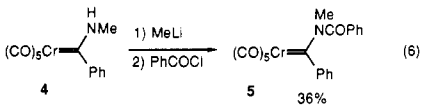

(4)

were used.) Attempts to produce amidocarbene complexes by treatment of acetoxycarbene complex **3** with *N*-methylacetamide led instead to N-acylation of the amide (eq 5).



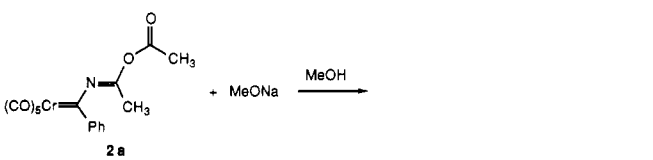

(5)

(*N*-methylamino)carbene complex **4** was deprotonated with methyllithium and acylated with acid halides (eq 6).

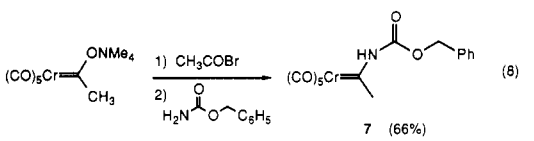



(6)

With acetyl chloride, only reprotonation of the aminocarbene was observed. However, with benzoyl chloride, which lacks acidic hydrogens, a modest yield of the amidocarbene complex **5** was obtained as a 1:1 mixture of isomers. This quite unstable complex (resembling acetoxycarbene complexes in stability) had spectroscopic properties expected for an amidocarbene complex (see below). A second amidocarbene complex, **6**, was prepared by solvolysis of complex **2a** (eq 7), but it, too, was relatively unstable. A somewhat more stable (*N*-carbobenzoxyamino)carbene complex was prepared as in eq 8. Finally,

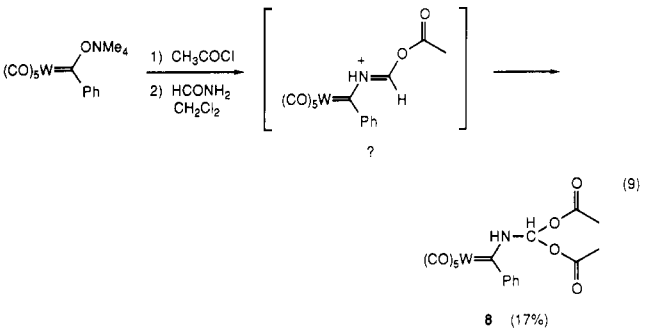



(7)




(8)

yet another new class of carbene complexes resulted from the reaction of tungsten "ate" complexes with acetyl chloride and formamide (eq 9). In this instance, acetate appears to have added to the imidate carbon to produce complex **8**. Because of the low yield, the chemistry of this unusual species was not explored.




(9)

In contrast to the (*O*-acyl imidato)carbene complexes, the amidocarbene complexes **5** and **6** and the carbamato complex **7** displayed the spectral changes anticipated for N-acylation of aminocarbene complexes. In the $^1H$ NMR spectrum of **6**, the acetamido methyl group appeared at $\delta$ 2.65 and the NH at $\delta$ 12.50. In the $^{13}C$ NMR spectrum, the carbene carbon appeared at $\delta$ 316.9, as anticipated, and the amide carbonyl carbon at $\delta$ 183.2. The acetamido carbonyl group absorbed at 1688 $cm^{-1}$ in the infrared spectrum. This complex absorbed at $\lambda_{max}$ = 481 nm ($\epsilon$ = 6.2 × $10^4$) in the visible spectrum and had a weak parent ion ($m/e$ 339) in the methane chemical ionization mass spectrum. It was too unstable to afford an acceptable elemental analysis, and its structure was inferred from its synthesis and spectroscopic characteristics.

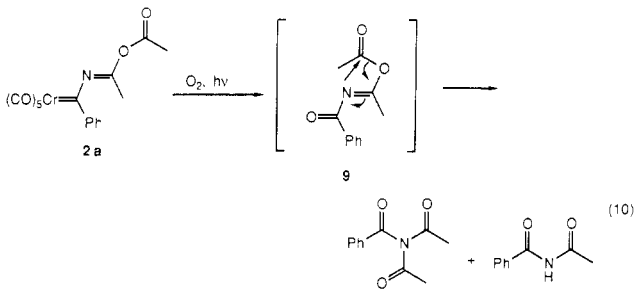
Complex **5** had similar spectroscopic properties. The $^1H$ NMR signals for the two isomeric *N*-methyl groups appeared at $\delta$ 3.20 and 4.18, compared with $\delta$ 3.30 and 3.87 for the $(CO)_5Cr{=}C(Me)NMe_2$ complex. The signal for its carbene carbon appeared at $\delta$ 285.8 and 280.7 in the $^{13}C$ spectrum, while the signal for the acyl carbon of the amide group appeared at $\delta$ 174.7 and 172.9, in contrast to those of the (*O*-acyl imidato)carbene complexes above. The carbonyl group of the amide absorbed at 1730 $cm^{-1}$ in the infrared spectrum. Complex **5** had a visible absorption at $\lambda_{max}$ = 367 nm ($\epsilon$ = 4.6 × $10^4$) and a mass spectrum consistent with the assigned structure.

Complex **7** was by far the most stable of the *N*-acyl carbenes made. The signal for its carbene carbon was at $\delta$ 327.6 and the signal for the carbamoyl carbonyl carbon, at $\delta$ 144.9. The carbonyl group of the carbamate was observed at 1779 $cm^{-1}$ in the infrared spectrum.

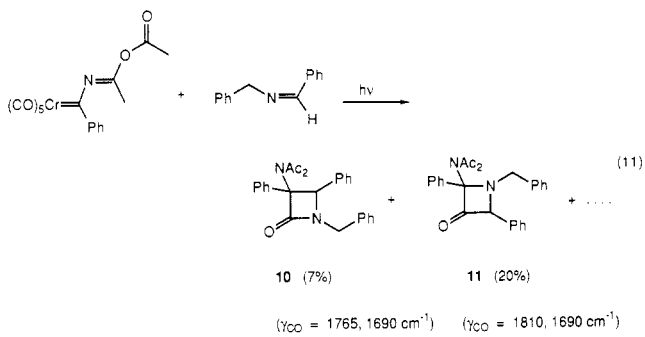
**Reactions.** Amidocarbene complexes **5** and **6** were thermally unstable and in many ways resembled acetoxycarbene complexes **3**. Thus they were difficult to purify and, even when pure, decomposed at temperatures above about 0 °C. Hence, attempts to carry out reactions with these complexes under a variety of conditions resulted in thermal decomposition rather than productive reactions.

*O*-Acyl imidato complexes **2a–f** were somewhat more stable, although these, too, underwent substantial decomposition upon standing, heating, or irradiating. Given their unusual structural and spectroscopic characteristics, unusual reactivity was anticipated and observed. Oxidation of chromium carbene complexes normally results in the conversion of the carbene ligand into the corresponding carboxylic acid derivative. However, air oxidation of **2a** in the presence of light produced not the expected *O*-acyl imidate **9** but rather deacylation and rearrangement products (eq 10). Photolysis of "normal" methoxy- or aminocarbene complexes results in a photodriven CO in-

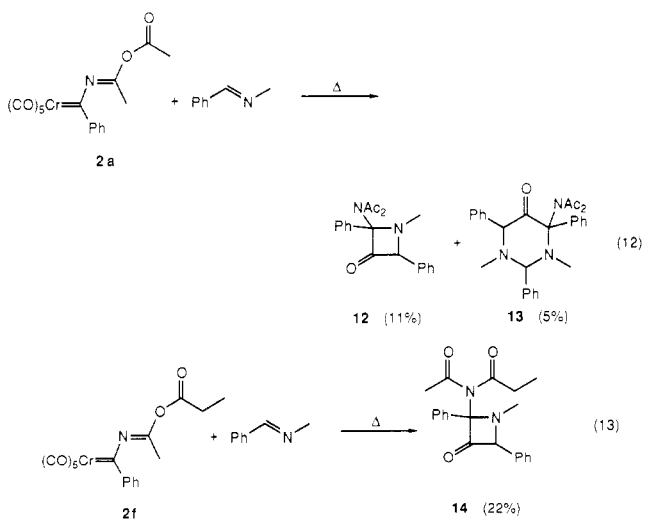
(17) Kupfer, R.; Wurthwein, E. U.; Nagel, M.; Aumann, R. *Chem. Ber.* **1985**, *118*, 643.



sertion to produce a metal–ketene complex,[18] readily intercepted by imines to produce β-lactams.[1,2,4,6] In contrast, photolysis of **2a** in the presence of the *N*-benzylimine of benzaldehyde produced only *very* small amounts of β-lactam **10** and larger quantities of 3-azetidinone **11** as well as a variety of unidentified compounds from decomposition of the carbene (eq 11). Under thermal conditions, in the



absence of light 3-azetidinone was the sole identifiable product. (The 3-azetidinone ring system is characterized by a strong $\gamma_{CO}$ at 1810 $cm^{-1}$.[19]) In both **10** and **11**, the *O*-acyl imidate had undergone rearrangement to the bis(acylamino) group during or after reaction. Similarly, complexes **2a** and **2f** underwent thermal reactions with imines to produce 3-azetidinones (eq 12 and 13).



The products of these reactions are all consistent with a highly electrophilic carbene carbon and are thought to arise as in Figure 1. Note that, in all cases, transfer of the *O*-acyl imidate ligand from chromium to an organic substrate results in rearrangement to the more stable bis(acylamino) group. While complexed, the nitrogen of the *O*-acyl imidate is not nucleophilic, since its lone pair

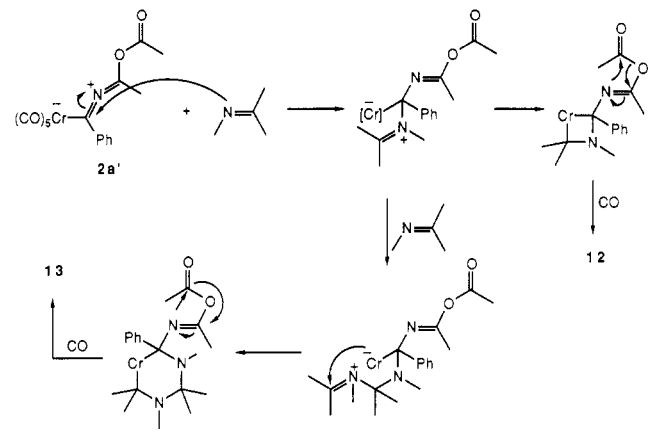
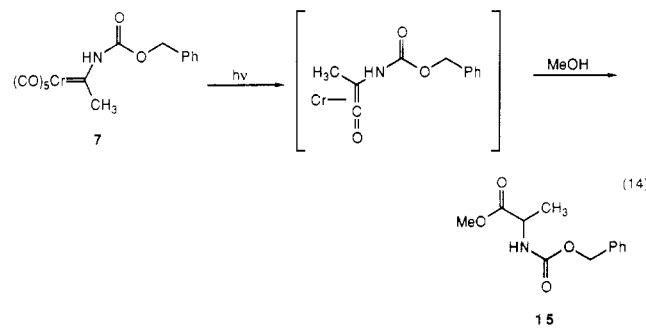


**Figure 1.**

is strongly interacting with the carbene carbon as in **2a'**. Once transferred from the metal, the lone pair is no longer delocalized and *O*- to *N*-acyl transfer readily occurs.

Although the above reactions are interesting, because of their low yields they are of little synthetic value. More useful in this regard is the relatively stable (*N*-carbobenzoxyamino)carbene complex **7**. In contrast to the (*O*-acyl imidato)carbene complexes, **7** can be made in good yield, is easily purified and handled, and, in preliminary experiments, undergoes reactions similar to those of aminocarbene complexes. Thus, photolysis of **7** in methanol produced the expected[18] methyl ester **23** in 67% yield (eq 14), indicating that photoinsertion of CO is efficient with



this complex. Results of studies dealing with photochemical reactions of this complex with imines, alcohols, amino acids, and olefins will be forthcoming.

## Experimental Section

**General Data.** All melting points were obtained with a Mel-temp melting point apparatus and are uncorrected. Infrared spectra were recorded on a Beckman 4240 spectrophotometer. All 60-MHz $^1H$ NMR spectra were recorded on a Varian Model T-60 spectrometer using $Me_4Si$ as an internal standard and are reported in δ. High-field $^1H$ NMR and $^{13}C$ NMR spectra were recorded on either an IBM WP270sy, Bruker AM500, or Nicolet NT360 spectrometer. Mass spectra were recorded on a V.G. Micromass 16F spectrometer. All chromatographic isolations were accomplished by radial-layer chromatography, using a Chromatotron Model 7294 and Kiesel gel PF silica gel. Analyses were performed by M-H-W Laboratories, Phoenix, AZ.

**Materials.** All solvents were freshly distilled and stored under argon. Immediately before use, they were degassed and saturated with argon. Diethyl ether (Fisher, Reagent grade) was predried over sodium sulfate, heated at reflux over sodium with benzophenone, and distilled at atmospheric pressure under nitrogen. Petroleum ether (Skelly solve F, petroleum naphtha) was heated at reflux over calcium hydride and distilled at atmospheric pressure under nitrogen. Methylene chloride and acetonitrile (Fisher, Reagent grade) were distilled over calcium hydride at atmospheric pressure under an argon atmosphere. Methyllithium was purchased from Aldrich as a 1.4 M solution in ether. Phe-

(18) Hegedus, L. S.; deWeck, G.; D'Andrea, S. *J. Am. Chem. Soc.* **1988**, *110*, 2122.
(19) Chatterjee, S. S.; Shoeb, A. *Synthesis* **1973**, 153.

nyllithium was purchased from Alfa as a 1.9 M solution in 75:25 benzene/diethyl ether. (Methylmethoxycarbene)- and (phenylmethoxycarbene)pentacarbonylchromium(0), (methylmethoxycarbene)- and (phenylmethoxycarbene)pentacarbonylmolybdenum(0), and (methylmethoxycarbene)- and (phenylmethoxycarbene)pentacarbonyltungsten(0) complexes were synthesized by literature procedures.[20,21] The aminocarbenes were obtained in >95% yield by bubbling the amine into diethyl ether solutions of the corresponding methoxycarbenes at 0 °C.[22] The tetramethylammonium pentacarbonylacylmetalates of chromium(0) and tungsten(0) were prepared by the literature method.[23] Acyclic aldimines were prepared by the procedure given in ref 1. The thiazoline was also prepared by a literature procedure.[24]

**General Procedure for the Acylation of Aminocarbenes. Synthesis of [(O-Acetyl ethanimidato)phenylcarbene]pentacarbonylchromium(0) (2a).** A 10-mL Airlessware flask was equipped with a rubber serum cap, magnetic stirbar, and argon-filled balloon. The flask was charged with (aminophenylcarbene)pentacarbonylchromium(0) (443 mg, 1.5 mmol), and the reaction vessel was evacuated and filled with argon (four cycles). Freshly distilled diethyl ether (5 mL) was added, and the bright yellow solution was cooled to −5 to 0 °C. Methyllithium (1.1 mL, 1.5 mmol) was slowly added by syringe. The resulting light brown solution was allowed to stir for approximately 15 min. The anion was quenched with acetic anhydride (306 mg, 3.0 mmol), and the mixture was allowed to stir for 20 min, gradually warming to room temperature. The solution was filtered through Celite, and the solvent was removed in vacuo to give a red oil. Purification by radial chromatography (2-mm silica gel, 5:1 petroleum ether/diethyl ether) gave a dark red oil (257 mg, 45%), $R_f$ = 0.38 (1:1 petroleum ether/diethyl ether).

$^1$H NMR (60 MHz, $CDCl_3$): δ 2.21 (s, 3 H, $COCH_3$), 2.35 (s, 3 H, $CH_3C{=}N$), 7.40 (m, 5 H, Ph). $^{13}$C NMR (67 MHz, $CDCl_3$): δ 252.6 ($C_{carb}$), 224.4 (trans CO), 217.0 (cis CO), 166.2 (C=O), 142.7 (Ph), 131.6 (Ph), 130.0 (C=N), 128.5 (Ph), 127.1 (Ph), 20.6 ($CH_3$), 19.1 ($CH_3$). IR ($CDCl_3$): 2050 (s), 1982 (sh), 1938 (vs), 1842 (w), 1775 (w) cm$^{-1}$. Mass spectrum: *m/e* (% relative intensity) $NH_3$ CI 381 (0.5, P). UV (hexane): $\lambda_{max}$ (nm) = 445 ($\epsilon = 3.6 \times 10^4$). Anal. Calcd for $C_{16}H_{11}NO_7Cr$: C, 50.41; H, 2.91; N, 3.67. Found: C, 50.01; H, 2.95; N, 3.96.

**Synthesis of [(O-Acetyl ethanimidato)methylcarbene]pentacarbonylchromium(0) (2b).** Using the procedure described above, (aminomethylcarbene)pentacarbonylchromium(0) (470 mg, 2.0 mmol) in 5 mL of diethyl ether at 0 °C was treated with methyllithium (1.72 mL, 2.0 mmol). After 10 min, acetyl chloride (313 mg, 4.0 mmol) was added, and the mixture was allowed to stir for 20 min, gradually warming to room temperature. The solution was filtered through a short Florisil column, and the solvent was removed in vacuo. Purification by radial chromatography (2-mm silica gel; 10:1 petroleum ether/diethyl ether followed by 5:1) gave 174 mg (27%) of a dark yellow oil, $R_f$ = 0.42 (5:1 petroleum ether/diethyl ether).

$^1$H NMR (60 MHz, $CDCl_3$): δ 2.21 (s, 3 H, $COCH_3$), 2.29 (s, 3 H, $CH_3C{=}N$), 2.76 (s, 3 H, $CCH_3$). $^{13}$C NMR ($CDCl_3$, −20 °C): δ 249.6 ($C_{carb}$), 223.8 (trans CO), 216.8 (cis CO), 166.1 (C=O), 129.1 (C=N), 38.2 ($C_{carb}CH_3$), 21.1 ($CH_3$), 19.0 ($CH_3$). IR ($CDCl_3$): 2055 (s), 1981 (sh), 1930 (vs), 1850 (w), 1771 (w) cm$^{-1}$. UV (hexane): $\lambda_{max}$ (nm) = 389 ($\epsilon = 6.2 \times 10^3$). Mass spectrum: *m/e* (% relative intensity) $NH_3$ CI 319 (0.6, P). High-resolution exact mass measurement (FAB): calcd $C_{11}H_9NO_7{}^{52}Cr$, 318.9784; found, 318.9783.

**Synthesis of [(O-Acetyl ethanimidato)phenylcarbene]pentacarbonylmolybdenum(0) (2c).** Using the procedure described for **2a**, (aminophenylcarbene)pentacarbonylmolybdenum(0) (1.36 g, 4.0 mmol) in 10 mL of diethyl ether at −40 °C was treated with methyllithium (2.12 mL, 4.0 mmol). The anion was allowed to warm to 0 °C, and acetic anhydride (1.51 mL, 8.0 mmol) was added by syringe. After 10 min, the solution was warmed to room temperature, was filtered through Celite, and was concentrated in vacuo. Purification by radial chromatography (2 mm silica gel, 5:1 petroleum ether/diethyl ether) gave 445 mg (26%) of a red oil.

$^1$H NMR (270 MHz, $CDCl_3$): δ 2.19 (s, 3 H, $COCH_3$), 2.34 (s, 3 H, $CH_3C{=}N$), 7.18–7.65 (m, 5 H, Ph). $^{13}$C NMR ($CDCl_3$): δ 236.2 ($C_{carb}$), 213.8 (trans CO), 206.1 (cis CO), 166.0 (C=O), 140.6 (C=N), 129.8–125.7 (Ph), 20.5 ($CH_3$), 18.9 ($CH_3$). Mass spectrum: *m/e* $NH_3$ CI 424.

**Synthesis of [(O-Acetyl ethanimidato)phenylcarbene]pentacarbonyltungsten(0) (2d).** Using the procedure described for **2a**, (aminophenylcarbene)pentacarbonyltungsten(0) (858 mg, 2.0 mmol) in 10 mL of diethyl ether was treated with methyllithium (1.17 mL, 2.0 mmol) at −40 °C. After the solution was warmed to 0 °C, the anion was quenched with acetic anhydride (0.38 mL, 4.0 mmol), and the mixture was allowed to warm to room temperature over a 20-min period. The solution was filtered through Celite, and the solvent was removed in vacuo. Purification by radial chromatography (2-mm silica gel; 5:1 petroleum ether/diethyl ether) gave 300 mg (30%) of a red oil, $R_f$ = 0.33 (1:1 petroleum ether/diethyl ether).

$^1$H NMR (270 MHz, $CDCl_3$): δ 2.25 (s, 3 H, $COCH_3$), 2.40 (s, 3 H, $CH_3C{=}N$), 7.48 (m, 3 H, Ph), 7.75 (d, 2 H, Ph). $^{13}$C NMR ($CDCl_3$): δ 230.9 ($C_{carb}$), 203.9 (trans CO), 198.2 (cis CO), 166.1 (C=O), 142.7, 129.7, 129.3, 128.7 (Ph), 132.4 (C=N), 20.7 ($CH_3$), 19.2 ($CH_3$). IR ($CHCl_3$): 2058 (s), 1980 (sh), 1912 (vs), 1856 (sh), 1780 (w) cm$^{-1}$. Mass spectrum: *m/e* (% relative intensity): $NH_3$ CI 513 (0.4, P). Anal. Calcd: $C_{16}H_{11}NO_7W$: C, 37.43; H, 2.14; N, 2.73. Found: C, 37.37; H, 2.21; N, 2.86.

**General Procedure for Reaction of Acetoxycarbene Complexes with Amides. Preparation of [(O-Acetyl ethanimidato)phenylcarbene]pentacarbonylchromium(0) (2e).** A 100-mL Airlessware flask was fitted with a rubber serum cap, magnetic stirbar, and an argon-filled balloon. The apparatus was charged with tetramethylammonium pentacarbonylphenylchromiumate (743 mg, 2.0 mmol) and dry $CH_2Cl_2$ (50–60 mL). The solution was cooled to −23 °C, stirring was commenced, and acetyl chloride (313 mg, 4.0 mmol) was slowly injected. The resulting deep red solution was allowed to stir for approximately 20 min before being allowed to warm to −5 to 0 °C. The propionamide (154 mg, 2.1 mmol) was added to the acetoxycarbene solution, and the mixture was allowed to stir for 30 min. After being slowly warmed to 25 °C, the solution was filtered through Celite and the solvent was removed in vacuo, leaving a dark red oil. The oil was extracted with several 10-mL portions of diethyl ether. The ether extracts were combined, filtered through Florisil, and concentrated. Purification by radial chromatography (2-mm silica gel; 5:1 petroleum ether/diethyl ether) gave a dark red oil (267 mg, 34%), $R_f$ = 0.33 (1:1 petroleum ether/diethyl ether).

$^1$H NMR (270 MHz, $CDCl_3$): δ 1.20 (t, 3 H, $J$ = 7.4 Hz, $CH_2CH_3$), 2.26 (s, 3 H, $COCH_3$), 2.73 (dq, 1 H, $J$ = 18.9 Hz, $J$ = 7.4 Hz, $CH_2CH_3$), 2.64 (dq, 1 H, $J$ = 18.9 Hz, $J$ = 7.4 Hz, $CH_2CH_3$), 7.45 (m, 3 H, Ph), 7.56 (m, 2 H, Ph). $^{13}$C NMR ($CDCl_3$): δ 249.7 ($C_{carb}$), 224.2 (trans CO), 217.2 (cis CO), 166.0 (C=O), 143.4, 134.5, 128.6, 128.3 (Ph), 131.3 (C=N), 25.9 ($CH_2$), 20.7 ($CH_3$), 8.9 ($CH_2CH_3$). IR ($CDCl_3$): 2050 (s), 1981 (w, sh), 1933 (vs), 1843 (w), 1772 (w) cm$^{-1}$. Mass spectrum: *m/e* (% relative intensity) $NH_3$ CI 395 (1.4, P). High-resolution exact mass spectrum (FAB): calcd $^{52}CrC_{17}H_{13}NO_7$, 395.0097; found, 395.0097.

**Preparation of [(O-Propionyl ethanimidato)phenylcarbene]pentacarbonylchromium(0) (2f).** Using the procedure described for the synthesis of **2e**, the tetramethylammonium pentacarbonylphenylchromiumate (743 mg, 2.0 mmol) and propionyl chloride (370 mg, 4.0 mmol) were combined at −23 °C in 60 mL of $CH_2Cl_2$. After 20 min, acetamide (124 mg, 2.1 mmol) was added at −5 °C and the mixture was allowed to stir for 30 min. After being slowly warmed to room temperature, the solution was filtered through Celite and was concentrated, leaving a dark red oil. The oil was extracted with several 10-mL portions of diethyl ether. The ether extracts were combined and filtered through Florisil. Further purification by radial chromatography (2-mm silica gel; 5:1 petroleum ether/diethyl ether) gave a dark red oil (287 mg, 36%), $R_f$ = 0.39 (1:1 petroleum ether/diethyl ether).

$^1$H NMR (270 MHz, $CDCl_3$): δ 1.18 (t, 3 H, $J$ = 7.4 Hz, $CH_2CH_3$), 2.36 (s, 3 H, $CH_3C{=}N$), 2.51 (q, 2 H, $J$ = 7.4 Hz, $OCH_2CH_3$), 7.44 (m, 3 H, Ph), 7.62 (m, 2 H, Ph). $^{13}$C NMR

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($CDCl_3$): δ 253.0 ($C_{carb}$), 224.2 (trans CO), 217.0 (cis CO), 169.6 (C=O), 142.9, 130.2, 128.4, 126.9 (Ph), 131.4 (C=N), 27.6 (CO-$CH_2$), 19.1 ($CH_3$C=N), 8.3 ($CH_2CH_3$). IR ($CDCl_3$): 2050 (s), 1982 (w, sh), 1940 (vs), 1846 (w), 1768 (w) $cm^{-1}$. Mass spectrum: *m/e* $NH_3$ CI 395. This material decomposed before acceptable elemental analysis could be obtained.

**Synthesis of [(*N*-Benzoyl-*N*-methylamino)phenylcarbene]pentacarbonylchromium(0) (5).** Using the procedure described for **2a**, [(*N*-methylamino)phenylcarbene]pentacarbonylchromium(0) (156 mg, 0.5 mmol) in 15 mL of diethyl ether at 0 °C was treated with methyllithium (0.35 mL, 0.5 mmol). After 15 min, benzoyl chloride (84 mg, 0.6 mmol) was added by syringe, and the mixture was allowed to gradually warm to room temperature over a 20-min period. Filtration through Celite and removal of the solvent in vacuo gave a brown residue. Purification by radial chromatography (2-mm silica gel, 100% hexane to 15% ethyl acetate/hexane) provided 103 mg (49%) of a brown oil, $R_f$ = 0.21 (10% ethyl acetate/hexane).

$^1H$ NMR (270 MHz, $CDCl_3$): δ 3.20 (b s, 3 H, NMe), 4.18 (b s, 3 H, NMe), 6.62–8.09 (m, 10 H, Ph). $^{13}C$ NMR ($CDCl_3$, −20 °C): δ two isomers 285.8, 280.7 ($C_{carb}$), 224.0, 223.5 (trans CO), 216.6, 216.1 (cis CO), 174.7, 172.9 (C=O), 151.9–118.2 (Ph, 16 carbons), 46.2, 42.8 (N-Me). IR ($CDCl_3$): 2050 (s), 1986 (w, sh), 1942 (vs), 1920 (sh), 1730 (m) (C=O) $cm^{-1}$. UV (diethyl ether): $\lambda_{max}$ (nm) = 367 ($\epsilon = 4.6 \times 10^4$). Mass spectrum: *m/e* (% relative intensity) EI 415 (0.4, P). The instability of this complex precluded acquisition of acceptable elemental analysis.

**Synthesis of [(*N*-Acetylamino)phenylcarbene]pentacarbonylchromium(0) (6).** A solution of the [(*O*-acetyl ethanimidato)phenylcarbene]pentacarbonylchromium(0) complex (235 mg, 0.6 mmol) in ether (20 mL) was treated with a solution of sodium methoxide (32 mg, 0.6 mmol) in methanol (1 mL). After 0.5 h, the solution was concentrated to dryness in vacuo. Examination of the crude product by TLC showed two products were formed. The higher $R_f$ fraction was the (aminophenylcarbene)-pentacarbonylchromium(0) complex (61 mg, 33%). The lower $R_f$ fraction, obtained by radial chromatography (2-mm silica gel; 30% ethyl acetate/hexane), was the monoacylcarbene complex (136 mg, 65%) as an extremely dark red solid: $R_f$ = 0.22 (40% ethyl acetate/hexane).

$^1H$ NMR (270 MHz, $CD_3COCD_3$): δ 2.65 (s, 3 H, $COCH_3$), 7.57 (s, 3 H, Ph), 7.82 (s, 2 H, Ph), 12.47 (b s, 1 H, NH), major isomer >90%. $^{13}C$ NMR ($CD_3COCD_3$): δ 316.9 ($C_{carb}$), 212.1 (trans CO), 205.6 (cis CO), 183.2 (C=O), 147.5, 131.8, 128.8, 126.4 (Ph), 20.9 ($COCH_3$). IR ($CH_2Cl_2$): 3335 (NH, s), 2003 (s), 1955 (w, sh), 1930 (vs), 1858 (m), 1688 (C=O) $cm^{-1}$. UV (diethyl ether): $\lambda_{max}$ (nm) = 481 ($\epsilon = 6.2 \times 10^4$). Mass spectrum: *m/e* (% relative intensity) $CH_4$ CI 339 (0.4, P). Anal. Calcd for $C_{14}H_9NO_6Cr$: C, 49.56; H, 2.65; N, 4.13. Found: C, 49.32; H, 2.60; N, 4.41.

**Synthesis of [(*N*-Carbobenzoxyamino)methylcarbene]-pentacarbonylchromium(0) (7).** A 100-mL Airlessware flask was fitted with a rubber septum, magnetic stirbar, and an argon-filled balloon. The apparatus was charged with tetramethylammonium pentacarbonylmethylchromium"ate" (1.00 g, 3.24 mmol) and freshly distilled and degassed $CH_2Cl_2$ (50 mL). The solution was stirred until homogeneous and was then cooled to −40 °C. (Some of the chromate was insoluble at −40 °C.) Acetyl bromide (0.40 g, 3.24 mmol) was slowly injected, and the resulting deep red solution was stirred for 1 h at −40 °C. A 50-mL Airlessware flask was fitted with a rubber septum and a magnetic stirbar. The apparatus was charged with *O*-benzyl carbamate (0.73 g, 4.86 mmol) and freshly distilled and degassed $CH_2Cl_2$ (20 mL). The solution was stirred until homogeneous and was then cooled to 0 °C. The carbamate solution was transferred via a cannula into the acetoxycarbene complex solution, and the temperature was maintained at −40 °C with stirring for 6 h. The solution was warmed to −15 °C and was left without stirring for 22 h. The mixture was then warmed quickly to room temperature and was filtered through Celite. The crude product was adsorbed onto silica gel, the solvent was evaporated, and the residue was dried under vacuum for a short time to remove all of the solvent. The orange powder was then transferred onto the top of a silica gel column. Elution with hexane gave a yellow band ($R_f$ = 0.43, 3:1 hexane/ethyl acetate). Further elution with 7:1 hexane/ethyl acetate gave the pure complex **7** as a red band. The solvent was evaporated to yield 0.79 g (66%) of carbene **7** as an orange oil ($R_f$ = 0.36, 3:1 hexane/ethyl acetate).

$^1H$ NMR (270 MHz, $CDCl_3$): δ major rotamer 3.42 (s, 3 H, $CH_3$), 5.25 (s, 2 H, $OCH_2$), 7.43 (s, 5 H, $C_6H_5$), 10.26 (b s, 1 H, NH). $^{13}C$ NMR ($CDCl_3$): δ 43.2 ($CH_3$), 69.5 ($CH_2O$), 128.9, 129.1, 129.4, 133.7 (Ph), 144.9 ($PhCH_2OCO$), 216.1 (cis CO), 223.2 (trans CO), 328.0 ($C_{carb}$). IR (neat): 3368, 3313 (w, NH), 2058 (s), 1982 (w, sh), 1925 (vs, Cr–CO), 1779 (m, C(O)OBn), 1715 $cm^{-1}$. Mass spectrum: *m/e* (% relative intensity) EI 369 (0.5%, $M^+$). Anal. Calcd for $C_{15}H_{11}NO_7Cr$: C, 48.78; H, 2.98; N, 3.79. Found: C, 48.58; H, 3.02; N, 4.03.

**Synthesis of [((Diacetoxymethyl)amino)phenylcarbene]pentacarbonyltungsten(0) (8).** Tetramethylammonium pentacarbonylphenyltungsten"ate" complex (1.01 g, 2.00 mmol) in 70 mL of $CH_2Cl_2$ was cooled to −30 °C under an argon atmosphere, and acetyl chloride (0.31 g, 4.00 mmol) was slowly added by syringe, producing a deep red-brown solution. After 20 min at −30 °C, formamide (0.09 g, 2.10 mmol) was added and the mixture was allowed to warm to room temperature. The crude reaction mixture was filtered through a bed of Celite, and solvent was removed under vacuum. Separation by radial layer chromatography (2-mm silica gel plate, 5:1 hexane/diethyl ether) gave 0.17 g (17%) of 8 as a fluffy yellow solid, mp 116–117 °C dec.

$^1H$ NMR (270 MHz, $CDCl_3$): δ 2.18 (s, 6 H, $CH_3CO$), 7.35 (m, 2 H, ArH), 7.43 (m, 3 H, ArH), 8.07 (d, 1 H, $J$ = 7.8 Hz, CH), 9.09 (br s, 1 H, NH). $^{13}C$ NMR ($CDCl_3$): δ 269.7 ($C_{carbene}$), 203.5 (trans CO), 197.1 (cis CO), 197.1 (OC–), 129.2, 128.5, 121.7 (PhC), 97.9 (CH), 20.5 ($CH_3$). Infrared spectrum ($CDCl_3$): ν 3322, 3290, 2058 (CO), 1940, 1905 (CO), 1774 ($CO_2R$), 1636, 1505 $cm^{-1}$. Mass spectrum ($NH_3$ CI): *m/e* 558 (P). Anal. Calcd for $C_{17}H_{13}NO_9W$: C, 36.52; H, 2.34; N, 2.50. Found: C, 36.54; H, 2.41; N, 2.53.

**General Procedure for Treating (*O*-Acetyl imidato)-carbene Synthesis of 10 and 11.** A 100-mL round-bottomed flask, equipped with a magnetic stirbar, rubber serum cap, and argon-filled balloon, was charged with complex **2a** (0.38 g, 1.0 mmol). The flask was evacuated and flushed with argon (four cycles). The carbene complex was dissolved in $CH_2Cl_2$ (30 mL), and *N*-benzylbenzylideneimine (0.20 g, 1.0 mmol) was injected into the solution. The flask was irradiated with sunlight or six 20-W Vitalite fluorescent tubes. After 5 days, the solution was allowed to air oxidize in 40% ethyl acetate/hexane until the solution was colorless. Filtration and concentration in vacuo gave 0.19 g of a yellow oil. Purification was accomplished by radial chromatography (2-mm silica gel; 20% ethyl acetate/hexane to 40%), $R_f$ = 0.16 (20% ethyl acetate/hexane).

**Compound 10**: colorless oil (0.30 g, 7.0%). $^1H$ NMR (270 MHz, $CDCl_3$): δ 2.33 (s, 6 H, $COCH_3$), 3.90 (d, 1 H, $J$ = 14.8 Hz, $CH_2Ph$), 4.96 (d, 1 H, $J$ = 14.8 Hz, $CH_2Ph$), 5.12 (s, 1 H, CH), 7.25–7.45 (m, 15 H, Ph). IR ($CDCl_3$): 1765 (s, C=O), 1690 (m, $(MeCO)_2N$) $cm^{-1}$. Mass spectrum: *m/e* (% relative intensity) $NH_3$ CI 413 (12.0, P + 1). Anal. Calcd for $C_{26}H_{24}N_2O_3$: C, 75.70; H, 5.86; N, 6.79. Found: C, 75.54; H, 5.96; N, 6.67.

**Compound 11**: white solid (0.83 g, 20%); mp 164–165 °C; $R_f$ = 0.12 (20% EtOAc/hexane). $^1H$ NMR (270 MHz, ($CDCl_3$): δ 1.51 (s, 3 H, $COCH_3$), 2.15 (s, 3 H, $COCH_3$), 4.47 (d, 1 H, $J$ = 18.4 Hz, $CH_2Ph$), 5.60 (d, 1 H, $J$ = 18.6 Hz, $CH_2Ph$), 6.66 (bs, 2 H, Ph), 6.86 (s, 1 H, CH), 7.05–7.42 (m, 11 H, Ph), 7.79 (d, 2 H, $J$ = 7.1 Hz, Ph). IR ($CDCl_3$): 1810 (C=O), 1690 $(MeCO)_2N$), 1650 $cm^{-1}$. Mass spectrum: *m/e* (% relative intensity) $NH_3$ CI, 413 (11.7, P + 1), 412 (42.3, P). Anal. Calcd for $C_{26}H_{24}N_2O_3$: C, 75.70; H, 5.86; N, 6.79. Found: C, 75.68; H, 5.84; N, 6.69.

**Synthesis of 12 and 13.** Complex **2a** (0.39 g, 1.00 mmol) and *N*-methylbenzylideneimine (0.12 g, 1.00 mmol) were combined in the usual manner in $CH_3CN$ (40 mL). The mixture was allowed to stir in the dark for 18 h. The acetonitrile was removed in vacuo, leaving a dark brown residue. The residue was taken up in 30% ethyl acetate/hexane and was air oxidized under sunlight. Filtration and concentration gave 0.27 g of a yellow oil.

Thin-layer chromatography revealed that two major components were present along with starting imine and benzaldehyde. Other minor products were not isolated. Purification was achieved by radial chromatography (2-mm silica gel; 20% ethyl acetate/hexane followed by 30% and 50%).

**Compound 12**: white solid (0.37 g, 11%); mp 199–201 °C; $R_f$ = 0.13 (30% EtOAc/hexane). $^1H$ NMR (270 MHz, $CDCl_3$): δ 1.76 (s, 3 H, $COCH_3$), 2.12 (s, 3 H, $COCH_3$), 3.14 (s, 3 H, $NCH_3$),

6.74 (s, 1 H, CH), 7.30–7.43 (m, 8 H, Ph), 7.69 (m, 2 H, Ph). $^{13}C$ NMR ($CDCl_3$): δ 202.4 (C=O), 171.4 (NC=O), 162.3 (NC=O), 135.5, 129.2, 128.9, 128.7, 128.6, 128.4, 126.0, 125.8 (ArC), 69.5 (NCN), 61.8 (N—C), 33.6 ($NCH_3$), 21.6 ($CH_3$), 14.9 ($CH_3$). IR ($CDCl_3$): 1810 (C=O), 1689 ($CH_3CON$–), 1645 $cm^{-1}$. Mass spectrum, *m/e* (% relative intensity) $NH_3$ CI 337 (4.0, P). Anal. Calcd for $C_{20}H_{20}N_2O_3$: C, 71.41; H, 5.99; N, 8.32. Found: C, 71.21; H, 5.96; N, 8.28.

**Compound 13**: white solid (0.22 g, 5%); mp 145–148 °C, $R_f$ = 0.17 (30% ethyl acetate/hexane). $^1H$ NMR (270 MHz, $CDCl_3$): δ 1.57 (s, 3 H, $COCH_3$), 1.62 (s, 3 H, $COCH_3$), 2.18 (s, 3 H, $NCH_3$), 2.90 (s, 3 H, $NCH_3$), 4.44 (s, 1 H, CH), 6.12 (s, 1 H, CH), 7.19 (s, 5 H, Ph), 7.36–7.59 (m, 6 H, Ph), 7.86 (d, 2 H, *J* = 7.4 Hz, Ph), 8.54 (d, 2 H, *J* = 7.6 Hz, Ph). $^{13}C$ NMR ($CDCl_3$): δ 23.0, 23.4, 31.5, 37.4, 68.1, 73.5, 107.0, 128.1, 128.2, 128.4, 128.8, 129.1, 132.0, 132.5, 132.6, 133.2, 133.4, 134.6, 137.4, 157.0, 172.2, 212.0. IR ($CHCl_3$): 1772, 1650 $cm^{-1}$. Mass spectrum: *m/e* (% relative intensity) $NH_3$ CI 412 (0.3, P–$COCH_3$). Anal. Calcd for $C_{28}H_{29}N_3O_3$: C, 73.82; H, 6.42; N, 9.22. Found: C, 73.84; H, 6.50; N, 9.21.

**Synthesis of 14.** Complex **2f** (0.43 g, 1.08 mmol) and *N*-methylbenzylideneimine (0.13 g, 1.08 mmol) were combined in the usual manner in acetonitrile (60 mL) and were stirred for 24 h. After air oxidation in 40% ethyl acetate/hexane, filtration, and solvent removal, a crude yellow oil (0.36 g) was obtained. Purification by radial chromatography (2-mm silica gel/20% ethyl acetate/hexane followed by 30% and 40%) gave 0.77 g (22%) of the β-azetidinone as a mixture of two isomers. Only one isomer was completely characterized: white solid; mp 168–170 °C; $R_f$ = 0.16 (40% EtOAc/hexane). $^1H$ NMR (270 MHz, $CDCl_3$): δ 1.14 (t, 3 H, *J* = 7.5 Hz, $CH_2CH_3$), 1.77 (s, 3 H, $COCH_3$), 2.40 (m, 2 H, $CH_2CH_3$), 3.16 (s, 3 H, $NCH_3$), 6.75 (s, 1 H, CH), 7.27–7.42 (m, 7 H, Ph), 7.68 (m, 3 H, Ph). IR ($CHCl_3$): 1821 (CO), 1688 ($CH_3CON$–), 1655 $cm^{-1}$. Mass spectrum: *m/e* (% relative intensity) $NH_3$ CI 352 (21.5, P + 1), 351 (93.7, P). Anal. Calcd for $C_{21}H_{22}N_2O_3$: C, 71.98; H, 6.33; N, 7.99. Found: C, 71.85; H, 6.52; N, 7.99.

**Synthesis of Carbobenzoxyalanine Methyl Ester (15).** A 15-mL Schlenk tube was equipped with a rubber septum. The tube was evacuated and filled with argon (four cycles) and was charged [(*N*-carbobenzoxyamino)methylcarbene]pentacarbonylchromium (0.17 g, 0.47 mmol) as a solution in methanol (10 mL). Argon was bubbled through the deep red solution for 5 min, and the solution was irradiated with a 450-W mercury lamp for 15.5 h. The solvent was removed by rotary evaporation, and the residue was dissolved in 40 mL of a 1:1 hexane/ethyl acetate mixture. This solution was saturated with air and was oxidized in a light box equipped with six 20-W Vitalite fluorescent lamps for 20 h. This mixture was filtered through Celite, and the solvent was evaporated under rotary evaporation. The resulting clear oil was purified by radial chromatography (1-mm silica gel, 10% hexane/ethyl acetate) to give 0.072 g (67%) of **15**.

$^1H$ NMR (270 MHz, $CDCl_3$): δ 1.34 (d, *J* = 7.1 Hz, 3 H, C–$CH_3$), 3.67 (s, 3 H, $OCH_3$), 4.32 (m, 1 H, C–H), 5.04 (s, 2 H, $CH_2$), 5.27 (b s, 1 H, NH), 7.28 (s, 5 H, $C_6H_5$). IR (neat): 3339 (m, NH), 1721 (s, CO). Mass spectrum: *m/e* (% relative intensity) EI 237 (1.4, $M^+$). Anal. Calcd for $C_{12}H_{15}NO_4$: C, 60.75; H, 6.37; N, 5.90. Found: C, 61.00; H, 6.42; N, 6.02.

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**Registry No.** **1a**, 32370-44-8; **1b**, 22852-50-2; **1c**, 76295-34-6; **1d**, 38669-78-2; **2a**, 121809-06-1; **2b**, 121809-11-8; **2c**, 121809-12-9; **2d**, 121809-13-0; **2e**, 121809-14-1; **2f**, 121809-15-2; **4**, 35797-14-9; **5**, 121809-07-2; **6**, 121809-08-3; **7**, 121809-09-4; **8**, 121809-10-7; **10**, 121790-15-6; **11**, 121790-16-7; **12**, 121790-17-8; **13**, 121790-18-9; **14**, 121790-19-0; **15**, 64562-95-4; $(CO)_5Cr{=}C(Ph)(O^-)NMe_4^+$, 15975-90-3; $(CO)_5Cr{=}C(Me)(O^-)NMe_4^+$, 15975-93-6; $(CO)_5W{=}C(Ph)(O^-)NMe_4^+$, 15975-92-5; $PhCH_2N{=}CHPh$, 780-25-6; PhCH=NMe, 622-29-7.