Photoinduced Reactions of Metal Carbenes in Organic Synthesis

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Abstract The photoinduced reactions of metal carbene complexes, particularly Group 6 Fischer carbenes, are comprehensively presented in this chapter with a complete listing of published examples. A majority of these processes involve CO insertion to produce species that have ketene-like reactivity. Cycloaddition reactions presented include reaction with imines to form β-lactams, with alkenes to form cyclobutanones, with aldehydes to form β-lactones, and with azoarenes to form diazetidinones. Photoinduced benzannulation processes are included. Reactions involving nucleophilic attack to form esters, amino acids, peptides, allenes, acylated arenes, and aza-Cope rearrangement products are detailed. A number of photoinduced reactions of carbenes do not involve CO insertion. These include reactions with sulfur ylides and sulfilimines, cyclopropanation, 1,3-dipolar cycloadditions, and acyl migrations.

Keywords Metal carbenes · Photochemical reactions · Metal-ketene complexes

Abbreviations

Bn   Benzyl
Cbz   Benzyloxycarbonyl
DMAP   Dimethylaminopyridine
HOMO   Highest occupied molecular orbital
LF   Ligand field
LUMO   Lowest unoccupied molecular orbital
MLCT   Metal-to-ligand charge transfer
PMB   Para-methoxybenzyl
PMP   Para-methoxyphenyl
PPTS   Pyridinium para-toluenesulfonate
tBOC   *t*-Butyloxycarbonyl

1
Introduction

Although many transition metals form carbene complexes, only Group 6 (Cr, Mo, W) heteroatom-stabilized Fischer carbenes of the type

$$(CO)_5M = \left\langle \begin{array}{c} Z \\ R \end{array} \right. \quad (Z = OR', NR_2', \text{etc.}) \tag{Intro}$$

have been extensively studied as reagents for organic synthesis (with the obvious exception of olefin metathesis chemistry [1]). Synthetically useful photochemical reactions have largely been restricted to Cr and Mo carbene complexes, thus this chapter will deal primarily with the chemistry of these. Since photochemical reactions involve excited-state chemistry at some stage, the electronic (UV-VIS) spectra of Fischer carbenes are central to a consideration of this chemistry.

The visible spectra of Fischer carbene complexes consist of a very weak band above 500 nm, assigned to a spin-forbidden metal-to-ligand charge transfer band (MLCT), a moderately intense band between 350 and 450 nm assigned as a spin-allowed MLCT, and a weaker band at 300–350 nm assigned as a ligand field (LF) transition [2]. A lower energy LF band is usually masked by the more intense MLCT, although it has been observed in some nonheteroatom-stabilized carbene complexes [3]. The HOMO is metal $d\pi$–$p\pi$ centered while the LUMO is carbene-carbon $p\pi$ centered [4]. As a result, irradiation into the MLCT band should lead to charge transfer from the metal to the ligand, a formal oxidation of the metal.

In attempts to understand the photochemical reactions of Fischer carbene complexes, several matrix isolation and flash photolysis studies have been conducted using both Cr and W (but not Mo) complexes [5–11]. Although the complexes studied and conditions used varied, several general conclusions were drawn:

1. For chromium alkoxycarbene complexes the MLCT and the lowest energy LF bands overlap. Irradiation at $\lambda > 385$ nm led to *anti–syn* isomerization

of the OMe group and 30% loss of CO. Loss of CO was even observed at $\lambda > 400$ nm [9].

2. Tungsten alkoxycarbene complexes underwent similar *anti–syn* rearrangements but were much less prone to undergo CO loss [5–10].

3. No CO-insertion products (metal-ketene complexes) were observed, even when specifically sought [9, 10].

These results suggest that there should be little useful organic chemistry resulting from photoinduced reactions of Fischer carbene complexes. However, this was shown not to be the case.

In studies designed to develop new approaches to β-lactams, Michael McGuire, then a graduate student in the author's research group, discovered that photolysis of a range of Cr Fischer carbene complexes with visible light through Pyrex produced a short-lived species that had ketene-like reactivity [12]. Subsequent studies [13] suggested that irradiation promoted reversible insertion of one of the four *cis*-COs into the metal-carbene-carbon double bond, producing a short-lived metallacyclopropanone-metal-ketene complex (Eq. 1). In the absence of reactive substrates, rapid deinsertion occurred, regenerating the carbene complex.

$$(1)$$
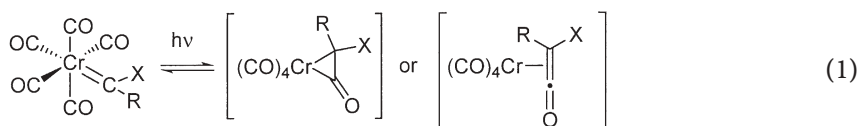
Several stable Group 6 metal-ketene complexes are known [14], and photo-driven insertion of CO into a tungsten-carbyne-carbon triple bond has been demonstrated [15]. In addition, *thermal* decomposition of the nonheteroatom-stabilized carbene complexes $(CO)_5M=CPh_2$ (M=Cr, W) produces diphenylketene [16]. Thus, the intermediacy of transient metal-ketene complexes in the photodriven reactions of Group 6 Fischer carbenes seems at least possible.

2
Photoinduced Reactions of Fischer Carbene Complexes

2.1
Involving CO Insertion

2.1.1
Cycloaddition Reactions

2.1.1.1
With Imines to Form β-Lactams

The reaction of ketenes (usually formed from treatment of acid chlorides with tertiary amines) with imines is a classic way to form β-lactams [17, 18]. Although widely used, it suffers limitations in scope and efficiency, since free ketenes are

highly reactive, and prone to dimerization and multiple incorporations into products. Whatever the nature of the photogenerated species from Fischer carbene complexes, *free* ketenes are not produced, and these by-products are not expected.

Photolysis of chromium alkoxycarbene complexes with a wide range of acyclic imines of aromatic aldehydes produced *β*-lactams in good to excellent yield (Table 1). The reaction was highly diastereoselective in virtually all cases, giving the relative stereochemistry shown. Cyclic and heterocyclic imines were similarly reactive, again producing single diastereoisomers (Table 2). Of particular note is the clean conversion of protected imidazolines to azapenams. The transformation using ketenes generated from acid chlorides does not take place [27]. Bis-carbene complexes underwent photoreaction with imidazolines to give bis-azapenams as 1:1 mixtures of diastereoisomers. (The *relative* configuration of each azapenam had the two heteroatoms *trans*, as expected, but a 1:1 mixture of [(R,R)(S,S)] and (R,S) diastereomers resulted)
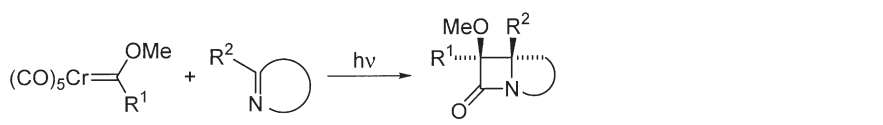
Table 1 Reaction of chromium alkoxycarbenes with acyclic aryl aldimines

R^1	R^2	Ar	Yield, %	Ref
Me	Me	Ph	76	[19]
Me	Ph	Ph	52	[19]
Ph	Me	Ph	72	[19]
Ph	Ph	Ph	20	[19]
Me	pMeOPh	Ph	60	[19]
Me	Bn	PhCHCH	45	[19]
Me	CH$_2$P(O)(OEt)$_2$	Ph	90	[20]
Me	CHP(O)(OEt)$_2$	Ph	80	[20]
Me	CO$_2$Me CHCH$_2$	Ph	41	[20]
Me	Bn	Ph	53	[20]
(decahydrophenanthrene structure with CH$_2$OMe)	Me	Ph	71	[21]
Me	pMeOPh	Fc[a]	79[b]	[22]
Me	Fc	pMeOPh	85[c]	[22]
Me	Fc	Fc	88[c]	[22]

[a]Fc = ferrocenyl; [b]As a 57:43 cis/trans mixture; [c]The ethoxycarbene was used.

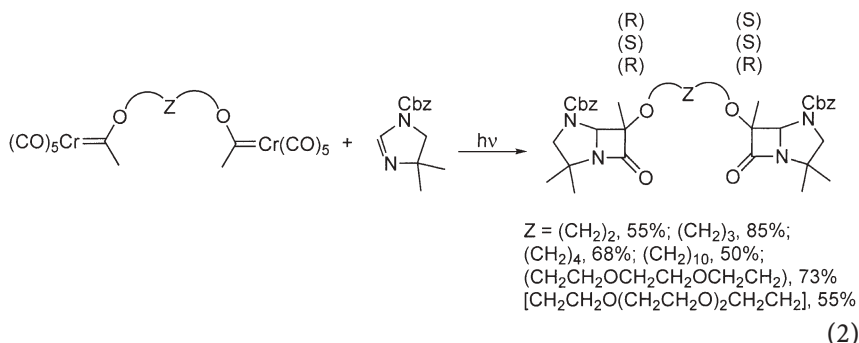**Table 2**   Reaction of chromium alkoxycarbenes with cyclic imines

R^1	Imine		Yield, %	Ref.
Me	Ph-pyrroline (imine)		70	[23]
Me	Ph-tetrahydropyridine (imine)		63	[23]
Me	Ph-thiazoline		52	[19]
Me	H-thiazoline		81	[19]
Me	dimethoxy benzothiazine (OMe, OMe)	R = Ph	51	[19]
Me	dimethoxy benzothiazine (OMe, OMe)	R = Me	38	[19]
Me		R = H	37	[19]
Ph		R = Ph	27	[19]
Me	benzothiazine (S, OMe, OMe)	R = Ph	61	[19]
Ph		R = Ph	25	[19]
Me	dimethoxy dihydroisoquinoline (OMe, OMe)		43	[19]
Me	quinoline		38	[19]
Me	thiazine, CO_2Me		52	[20]
Me	Cbz-imidazoline		69	[24]
n-C_6H_{13}	Cbz-imidazoline		71	[25]
(methylenecyclopropane)	"		52	[25]

Table 2 (continued)

R[1]	Imine	Yield, %	Ref.
i-Pr[a]	"	77	[25]
pMeOPh	"	39	[25]
c-hex	"	37	[25]
t-Bu[a]	"	20	[25]
Me[b]	"	74	[26]
Me[c]	"	77	[26]

[a]The ethoxy carbene complex was used. [b]The PMB alkoxycarbene was used. [c]The OCH$_2$CH$_2$NHCO quinoxaline carbene was used.

(Eq. 2) [28, 29]. Bis-carbenes linked through the alkyl (rather than alkoxy) groups reacted similarly but in lower yields [30].

Z = (CH$_2$)$_2$, 55%; (CH$_2$)$_3$, 85%;
(CH$_2$)$_4$, 68%; (CH$_2$)$_{10}$, 50%;
(CH$_2$CH$_2$OCH$_2$CH$_2$OCH$_2$CH$_2$), 73%
[CH$_2$CH$_2$O(CH$_2$CH$_2$O)$_2$CH$_2$CH$_2$], 55%

(2)

A few heterocyclic imines reacted poorly if at all with chromium alkoxycarbene complexes. Oxazines required the use of the more reactive (and less stable) molybdenum alkoxycarbenes, producing oxacephams in ≈40% yield. Oxazolines gave low yields (≈12%) of the oxapenam system, along with similar amounts of oxazinone, resulting from incorporation of *two* equivalents of ketene (Eq. 3) [20].

(R = H, Bn)
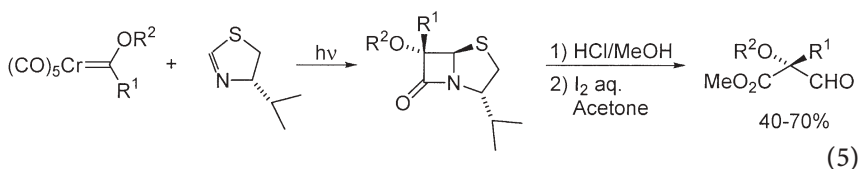
13%   13%

(3)
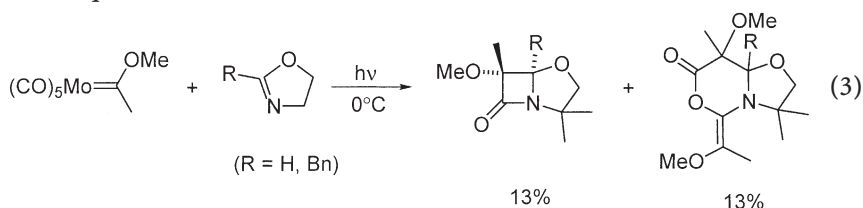
CBz-protected benzimidazole gave primarily oxazinone [31], while 3*H*-indoles incorporated two equivalents of imine (Eq. 4) [32]. In these cases it appears that the initially formed zwitterionic ketene–imine adduct could not close, and reacted with additional photoactivated carbene or substrate.

$$(CO)_5Cr = \overset{OMe}{\underset{}{|}} \quad + \quad \text{[MeO-indole]} \quad \xrightarrow{h\nu} \quad \text{[product]} \qquad (4)$$

10%
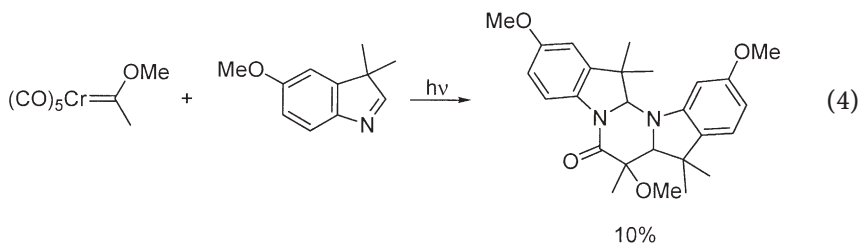
Other miscellaneous imines that underwent photoreaction with chromium alkoxycarbenes include iminodithiocarbonates [33], the mono-*N*-phenyl imine of benzil and the bis-*N*-phenyl imine of acetoin [20]. By preparing the chromium carbene complex from ^{13}CO-labeled chromium hexacarbonyl, β-lactams with two adjacent ^{13}C labels were synthesized [34].

Induction of asymmetry into the β-lactam-forming process was inefficient with acyclic imines having chiral groups on the nitrogen [19] but efficient with rigid, cyclic chiral imines (Table 3). One of these was used as a chiral template to produce highly functionalized quaternary systems (Eq. 5) [34].

$$(CO)_5Cr = \overset{OR^2}{\underset{R^1}{|}} \quad + \quad \text{[thiazoline]} \quad \xrightarrow{h\nu} \quad \text{[bicyclic]} \quad \xrightarrow[\text{2) I}_2\text{ aq.}]{\text{1) HCl/MeOH}} \quad \text{[product]} \qquad (5)$$

Acetone

40-70%

The mechanism of the classic ketene–imine reaction to form β-lactams [17, 18] is thought to involve perpendicular attack of the imine nitrogen on the ketene carbonyl carbon from the side of the sterically smaller of the two groups, followed by conrotatory closure of the zwitterionic intermediate (Eq. 6). This
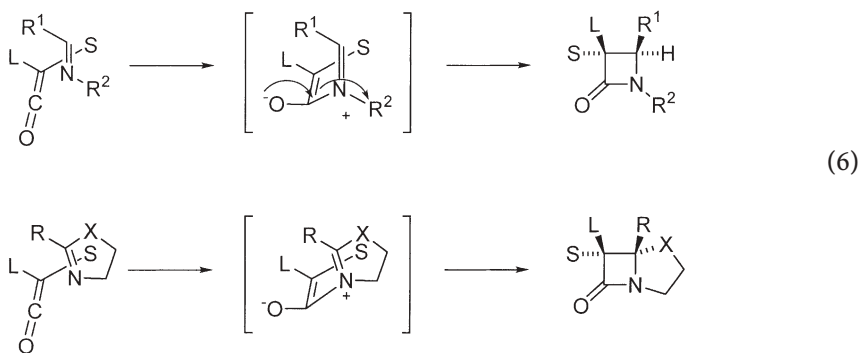
$$\qquad (6)$$

Table 3 Reaction of chromium alkoxycarbenes with chiral heterocyclic imines

| R¹	R²	R³	X	Yield, %	eeᵃ	Ref.
Me	Bn	i-Pr	S	76	>97%	[35]
n-Bu	Bn	i-Pr	S	78	>97%	[35]
	Bn	i-Pr	S	39	>97%	[35]
Ph	Bn	i-Pr	S	42	>97%	[35]
p-MeOPh	Bn	i-Pr	S	42	>97%	[35]
			S	29	>97%	[35]
Me	Me	b		42	>97% (X-ray)	[19]
Me	Me	i-Pr	NCbz	41	>97% (X-ray)	[24]
Me	Bn	i-Pr	NCbz	54	>97%	[24]
—(CH₂)₃—		i-Pr	NCbz	69	>97%	[24]
Me	Me	Me	NCbz	23	>97%	[36]
Me	Me	Ph	NCbz	35	>97%	[36]
Me	Me	c	NCbz	75	>97%	[36]

ᵃAbsolute configuration determined by conversions to compounds of known absolute configuration, and by correlation to closely related compounds for which X-ray structures are available. ᵇThe substrate was
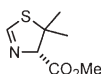
ᶜThe substrate was

places the large substituent of the ketene *cis* to the *anti*-substituent of the imine. In *all* the cases cited above, the observed stereochemistry was exactly opposite that expected on these steric grounds. Initially, this difference was thought to be due to the presence of the metal during the cycloadditions, biasing the process to produce the contrasteric product. However, subsequent considerations [37], supported by theoretical calculations relating the closure step of β-lactam formation to the electronic bias observed ("torquoselectivity") in the ring opening of cyclobutenes bearing heteroatom substituents [38], suggested that the observed stereoselectivity was due to the presence of the donor methoxy group on the ketene. This greatly lowers the energy for closure of the zwitterion resulting from attack over the large R group, from the face opposite the donor groups, leading to the contrasteric product (Eq. 7).

(7)
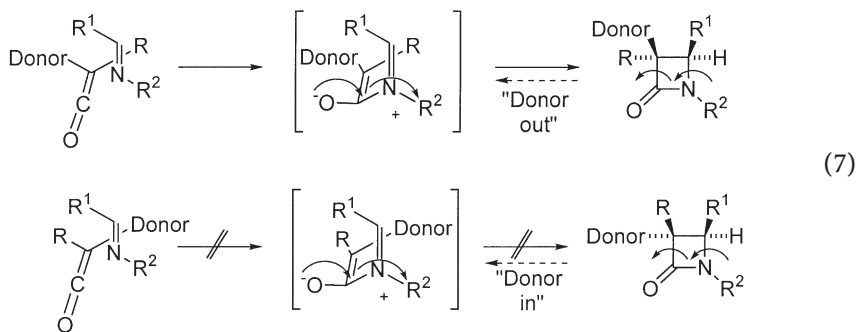
Chromium aminocarbenes [39] are readily available from the reaction of $K_2Cr(CO)_5$ with iminium chlorides [40] or amides and trimethylsilyl chloride [41]. Those from *formamides* (H on carbene carbon) readily underwent photoreaction with a variety of imines to produce β-lactams, while those having R-groups (e.g., Me) on the carbene carbon produced little or no β-lactam products [13]. The dibenzylaminocarbene complex underwent reaction with high diastereoselectivity (Table 4). As previously observed, cyclic, optically active imines produced β-lactams with high enantioselectivity, while acyclic, optically active imines induced little asymmetry. An intramolecular version produced an unusual anti-Bredt lactam rather than the expected β-lactam (Eq. 8) [44].

(8)

n = 2 85%
n = 3 72%
n = 4 40%
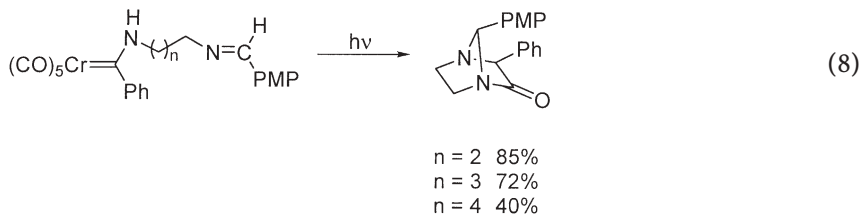
With optically active formamide-derived aminocarbene complexes high enantioselectivity was observed in most cases (Table 5). This chemistry was used in the synthesis of 1-carbacephalathin and 3-ANA precursors (Eq. 9) [48], as well as the synthesis of α,α'-disubstituted amino acids (Scheme 1) [49].

32%   (9)
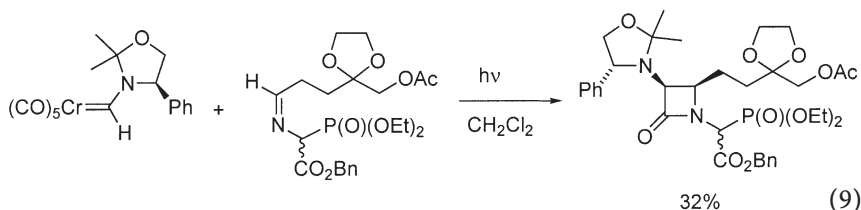
Although the photodriven reactions of chromium carbene complexes with imines superficially resemble those of free ketenes, there are major differences. The optically active oxazolidine carbene (Table 5) gave excellent yields and high ee values when allowed to react with imidates, oxazines, thiazines, and

Table 4 Reaction of chromium aminocarbenes with imines

$(CO)_5Cr=\overset{NBn_2}{\underset{H}{\big|}}$ + $R-\overset{\frown}{N}$ $\xrightarrow{h\nu}$ $Bn_2N\;R$ product (azetidinone)

Imine	Product	Yield, %	Ref.
		51[a]	[40]
		74 (7:4)	[40]
		32	[40]
		81	[40]
$R^1 = Me, R^2 = Bn$		79	[40]
$R^1 = Et,\; R^2 = Ph$		76	[40]
$R^1 = R^2 = R^3 = H$		73	[40]
$R^1 = CO_2Et, R^2 = OH, R^3 = Me$		76	[40]
$R^1 = Bu^t, R^2, R^3 = H$		72	[42]
$R^1 = Bn, R^2, R^3 = Me$		56	[42]
$R^1 = Bn, R^2, R^3 = H$		72	[42]
$R^1 = p\text{-}MeOC_6H_4, R^2, R^3 = H$		44	[42]
$n = 1$		54	[42]
$n = 2$		85	[42]
$R = Menthyl$		80	
$R = Bn$		50	[43]
		93[b]	[40]
		46 (1:1)	[42]

[a]Single isomer. [b]Single enantiomer.

Table 5   Reaction of optically active aminocarbenes with imines

Z	R¹	R²	R³	Yield (%)	de (%)	ref
(S) iPr	Bn	Me	Me	59	70 (S,S)	[45]
(S) iPr	Bn	Me	H (trans)	40	≥97 (S,S)	[45]
(S) iPr	Bn	H	Me (cis)	14	≥97 (S,S)	[45]
(S) iPr	−(CH$_2$)$_4$−		H	55	≥97 (S,S)	[45]
(S) iPr	Bn	OMe	H	76	≥97 (S,S)	[45]
(S) iPr	−(CH$_2$)$_3$O−		H	70	≥97 (S,S)	[45]
(R)Ph	Bn	H	H	74	70 (R,R)	[45]
(R)Ph	Bn	Me	Me	79	70 (R,R)	[45]
(R)Ph	Bn	Me	H (trans)	41	≥97 (R,R)	[45]
(R)Ph	Bn	H	Me (cis)	20	≥97 (R,R)	[45]
(R)Ph	−(CH$_2$)$_3$−		H	75	≥97 (R,R)	[45]
(R)Ph	−(CH$_2$)$_4$−		H	91	≥97 (R,R)	[45]
(R)Ph	Bn	OMe	H	91	≥97 (R,R)	[45]
(R)Ph	−(CH$_2$)$_3$O−		H	95	≥97 (R,R)	[45]
(S)Ph	Bn	SMe	SMe	61	60 (S,S)	[46]
(S)Ph	PMP	SMe	SMe	60	60 (S,S)	[46]
			p = tBoc	78	>97 (S,S)	[47]
(S)Ph			p = pTs	93	96 (S,S)	[47]
			p = BnSO$_2$	86	80 (S,S)	[47]
			p = Cbz	80	80 (S,S)	[47]

aliphatic imines, but modest yields of mixtures of *cis* and *trans* isomers with aryl or α,β-unsaturated imines [50]. In contrast, the corresponding *oxazolidinone* ketene (from the acid chloride [51]) gave excellent yields and ee values with aryl and α,β-unsaturated imines but very low yields of β-lactams with other imines. Clearly chromium is influencing the outcome of the process.

Pyrrolocarbenes produced low yields of β-lactams in photodriven reactions with imines [52], while *o*-acylimidatocarbene complexes gave a mixture of compounds with β-lactams being minor components [53].
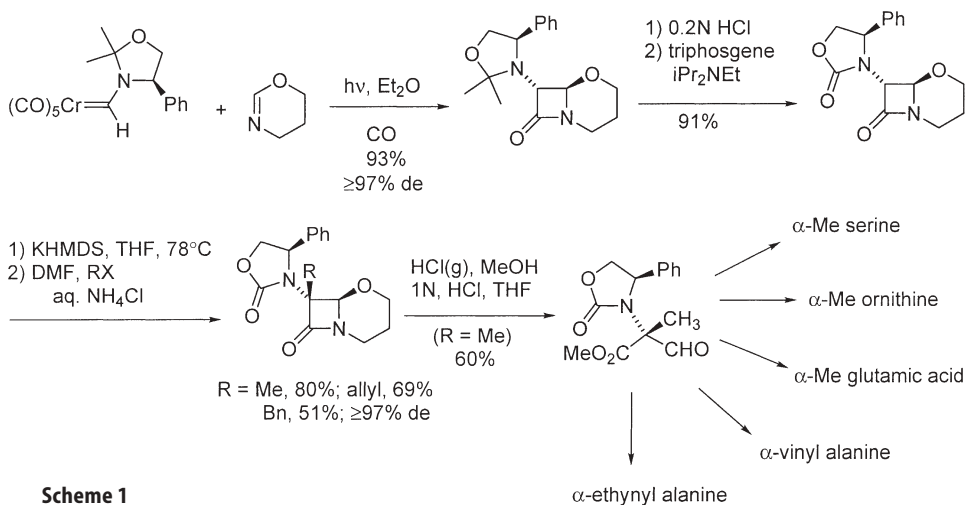
Scheme 1

2.1.1.2
With Olefins to Give Cyclobutanones

The first report of the reaction of a chromium alkoxycarbene with an alkene to give a cyclobutanone came in 1974 [54], when it was reported that treatment of the (phenyl)(methoxy) chromium carbene complex with N-vinyl pyrrolidinone under 150 atm of CO pressure produced the corresponding cyclobutanone, presumably via the ketene or ketene complex produced by pressure-driven insertion of CO into the metal-carbene-carbon bond. It wasn't until 1989 that the photodriven version of this process was reported [55]. Monosubstituted, electron-rich alkenes underwent photochemical reaction with chromium alkoxycarbenes to produce cyclobutanones in fair to good yield and with high stereoselectivity for the *more hindered* cyclobutanone (Table 6) [56], the same selectivity as that observed with free ketenes [57]. Di- and trisubstituted alkenes were somewhat less efficient (Table 7) [56], while dienes underwent cycloaddition to one of the two alkenes (Table 8) [56]. Intramolecular versions were also efficient to form five- and six-membered rings, but larger rings failed to form and tethered alkynes gave complex mixtures of unidentified products (Table 9) [56].
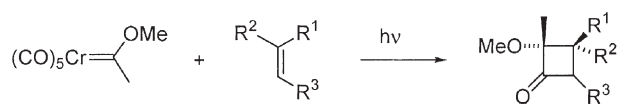
Alkoxycarbene complexes with unsaturation in the alkyl side chain rather than the alkoxy chain underwent similar intramolecular photoreactions (Eqs. 10 and 11) [60]. Cyclopropyl carbene complexes underwent a facile vinyl-cyclopropane rearrangement, presumably from the metal-bound ketene intermediate (Eqs. 12 and 13) [61]. A cycloheptatriene carbene complex underwent a related [6+2] cycloaddition (Eq. 14) [62].

(10)

78%

(cis ⟶ complex mixture)
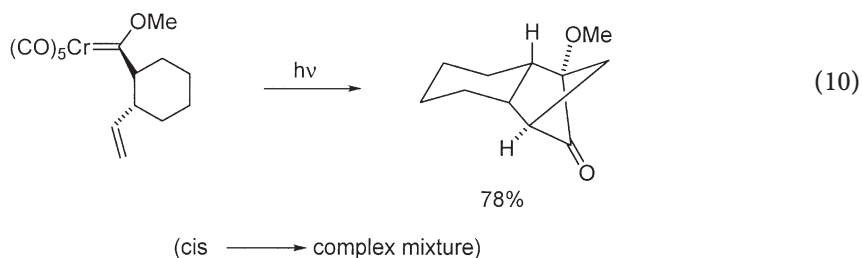
Table 6 Reaction of alkoxycarbenes with monosubstituted alkenes

Z	Yield (%)	ratio	ref
Ph	44	10:1	[56]
CH_2OAc	31	10:1	[56]
OEt	87	6:1	[56]
OAc	19	20:1	[56]
NHAc	96	8:1	[56]
	78	7:1	[56]
nBu	55	>20:1	[58]
$TMSCH_2$	78	>20:1	[58]
$-(CH_2)_3-$[a]	84	>20:1	[58]
$-CH=CH-CH_2$[b]	80	>20:1	[58]
p-HOPh	51	>20:1	[58]
pMeOPh	59	>20:1	[58]
PhS	58	>20:1	[58]
$-(CH_2)_3O-$	80[c]	>20:1	[58]
tBuO	51	>20:1	[58]
BnO	82	>20:1	[58]
(±)	68	1:1	[58]
$2,4,6\text{-iPrPhCH}_2O$	72	1:1	[58]
(±) $2,4,6\text{-iPrPhCHO}$	67	1:1	[58]

[a]cyclopentene; [b]cyclopentadiene; [c]dihydropyran.

Table 7 Reaction of alkoxycarbenes with polysubstituted alkenes
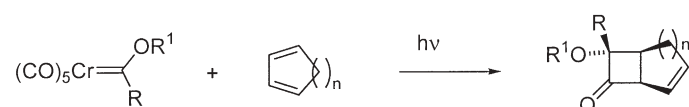
R¹	R²	R³	ratio	yield	ref
Me	H	Me	5:1	51	[56]
H	Me	Me	5:1	13	[56]
–(CH$_2$)$_5$–		H	---	45	[56]
Me	Me	Me	>95:5	77	[56]
OAc	Me	H	1:1	16	[56]
R¹R³ = O(CH$_2$)$_4$		R² = H	11:1	80	[56]
			---	47	[59]

Table 8 Reaction of alkoxycarbenes with cyclic dienes
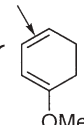
R	R¹	n	ratio	yield	ref
Me	Me	1	10:1	67	[56]
Me	Me	2	14:1	52	[56]
(cyclopropyl)	Me	2	13:1	46	[56]
Me	Et	2	10:1	85	[56]
Ph	Me	2	20:1	75	[56]
nBu	Et	2	14:1	96	[56]
Me	Bn	2	9:1	70	[56]
Me	TMS	2	5:1	37	[56]
PhCHCH	Me	2	---	0	[56]
R=R'=OMe			---	15:1	73	[59]
			---	3:1	67	[59]

Table 9 Intramolecular cyclobutanone-forming reactions

R^1	R^2	R^3	R^4	R^5	n	yield (%)	ref
Me	H	H	H	H	0	88	[56]
Me	H	Me	H	H	0	62	[56]
Me	H	H	Et	H	0	47	[56]
Me	H	H	H	Et	0	29[a]	[56]
Me	Me	H	H	H	0	62[b]	[56]
Me	H	H	Me	Me	0	80[c]	[56]
Me	H	H	H	H	1	73	[56]
◁	H	Me	H	H	0	65	[56]
Bn	H	Me	H	H	0	95	[56]
Ph	H	H	Et	H	0	42	[59][d]
Ph	H	H	H	Et	0	72	[59][e]

97[f]   [56]

[a] accompanied by 22%.   [b] a 1:1 mixture of isomers at R^2.

[c] sole product.

[d] 2:1 mixture of bridged bicyclic to fused bicyclic ketone.
[e] 1:1 mixture of bridged bicyclic to fused bicyclic ketone.
[f] 2:1 mixture of trans isomers at 6,6 ring junction.

$$(CO)_5Cr \text{=} \overset{OBn}{\underset{}{\diagup}} \quad \xrightarrow{h\nu} \quad \text{(structure)} \quad (11)$$

57%

$$(CO)_5Cr \text{=} \overset{OR}{\underset{}{\diagup}} \quad \xrightarrow{h\nu} \quad \left[\text{(structure)} \right] \quad \longrightarrow \quad \text{(structure)} \quad (12)$$

83%

$$(CO)_5Cr \text{=} \overset{OBn}{\underset{}{\diagup}} \quad \xrightarrow{h\nu} \quad \text{(structure)} \quad (13)$$

68%

$$(CO)_5Cr \text{=} \overset{OEt}{\underset{}{\diagup}} \quad \xrightarrow{h\nu} \quad \left[\text{(structure)} \right] \quad \longrightarrow \quad \text{(structure)} \quad (14)$$

95%
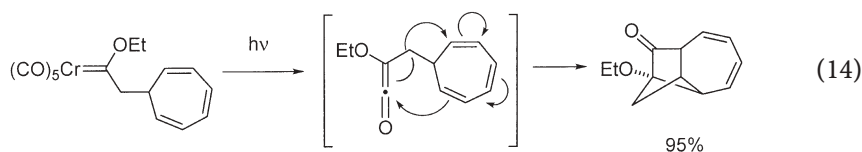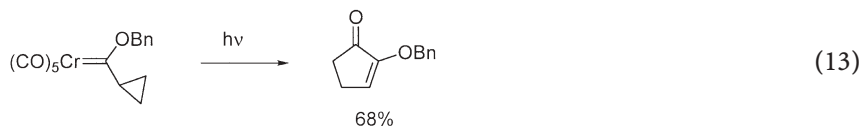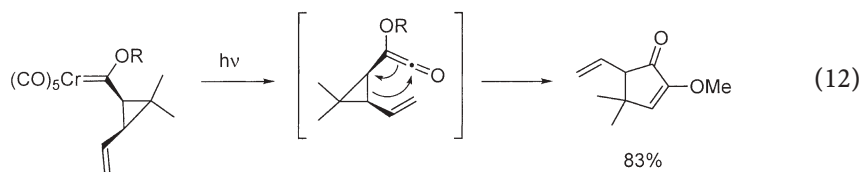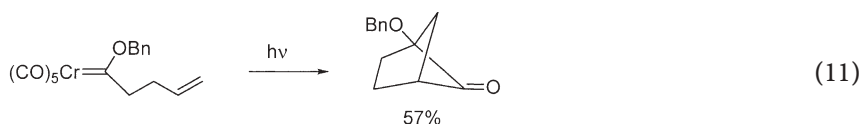
In contrast to alkoxycarbene complexes, most aminocarbene complexes appear too electron-rich to undergo photodriven reaction with olefins. By replacing aliphatic amino groups with the substantially less basic aryl amino groups, modest yields of cyclobutanones were achieved (Table 10) [63], (Table 11) [64]. Both reacted with dihydropyran to give modest yields of cyclobutanone. Thiocarbene complexes appeared to enjoy reactivity similar to that of alkoxycarbenes (Eq. 15) [59].

$$(CO)_5Cr \text{=} \overset{SPh}{\underset{}{\diagup}} \quad (15)$$

hν
64%

hν
83%
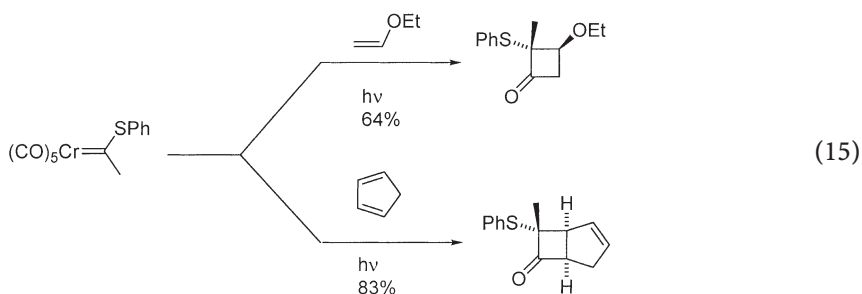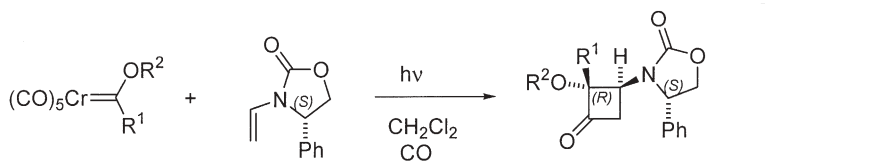
Of perhaps greater use for organic synthesis was the observation that photodriven reactions of alkoxycarbenes with unsubstituted optically active ene carbamates [65] produced aminocyclobutanones in fair yield with high diastereoselectivity (Table 12) [66]. In contrast, with a gem-disubstituted ene carbamate, the *syn–anti* selectivity was low but high asymmetric induction α to nitrogen was observed (Eq. 16). *Trans*-monosubstituted ene carbamates failed to react, as did α,β-unsaturated chromium carbene complexes.

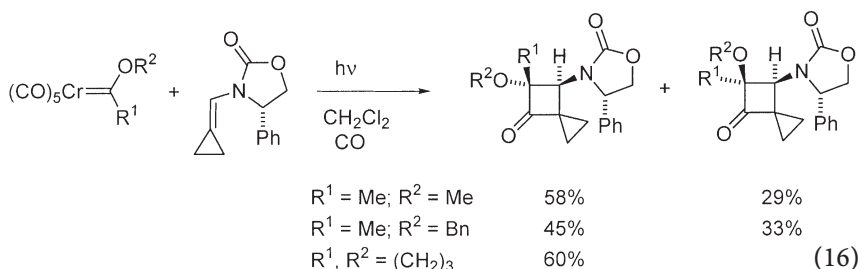**Table 10** Reaction of arylaminocarbenes with alkenes

Z	n	yield (%)	ref
PhNMe	1	44	[63]
	2	37	[63]
pMeOPhNMe	1	37	[63]
Ph$_2$N	1	45	[63]
2,6-Me$_2$PhNMe	1	38	[63]
tetrahydroquinolyl	1	44	[63]
3-Me indolyl	1	38	[63]

Table 11 Reaction of chromium pyrrolocarbene complexes with alkenes

Alkene	Product	yield (%)	ref
OEt		35	[64]
		49	[64]
		58	[64]
			[64]
		n = 1 24, 18	[64]
		n = 2 12, 12	[64]

Table 12 Reaction of alkoxycarbenes with optically active ene carbamates

R¹	R²	yield (%)	de (%)	ref
Me	Me	61	94	[66]
Me	Bn	56	86	[66]
Ph	Me	67	≥97	[66]
▷ (cyclopropyl)	Me	59	≥97	[66]
MeCH=CH	Me	---		
–(CH₂)₄–		50	≥97	[66]

R¹ = Me; R² = Me   58%   29%

R¹ = Me; R² = Bn   45%   33%

R¹, R² = (CH₂)₃   60%   (16)

Although optically active functionalized cyclobutanones themselves are of little intrinsic interest, they are highly reactive and have been converted to a number of synthetically useful intermediates. Further functionalization was achieved at both the α-position using enolate chemistry, and by nucleophilic attack at the ketone carbonyl [67]. They underwent facile Baeyer–Villiger ring expansion and elimination of the oxazolidinone group to produce optically active butenolides, which were subjected to a number of 1,4-addition reactions and 1,3-dipolar cycloaddition reactions [68]. This facile approach to optically active butenolides was used to prepare several biologically active systems, including two butenolides isolated from *Plakortis lita* [a, b, Eq. 17], tetrahydro-cerulenin [69], and cerulenin (Scheme 2) [70]. By using cyclic alkoxycarbene complexes, optically active spiroketals were synthesized (Eq. 18) [71]. Optically active cyclobutanones produced as in Table 12 have also been used as precursors for palladium-catalyzed ring expansion to cyclopentenones [72], and for the study of the effect of adjacent chiral tertiary and quaternary centers on metal-catalyzed allylic substitutions [73].

(17)

Scheme 2   (+)-cerulenin

(18)
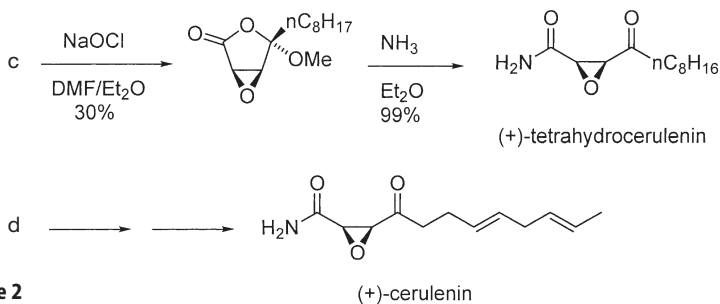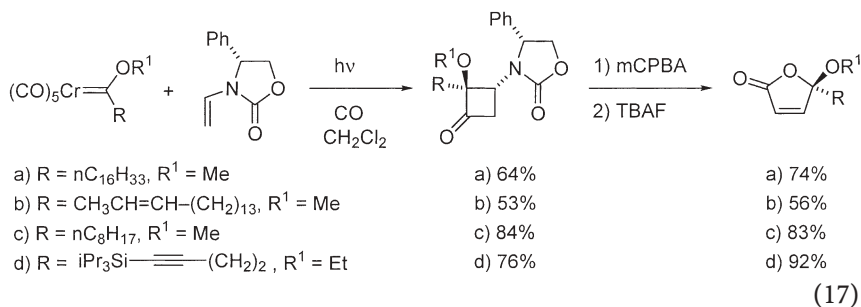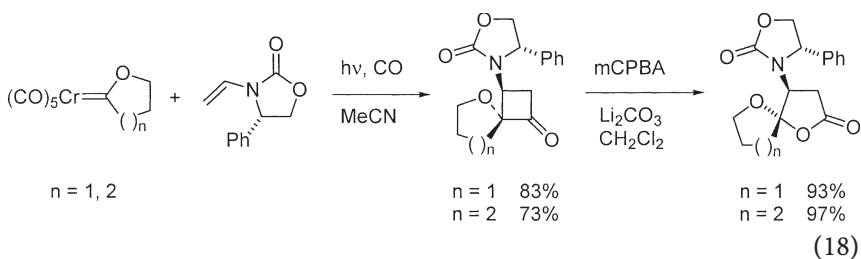
The optically active cyclobutanone from the (benzyloxymethyl)(ethoxy) carbene complex has been developed as a template for the synthesis of 4′-substituted nucleoside analogs (Schemes 3 and 4) [74]. Photochemical ring expansion in acetic acid directly produced the acylated ketal. Treatment with a Lewis acid and a silylated nucleophile produced 4′-disubstituted deoxyribo analogs [75]. Baeyer–Villiger oxidation followed by oxazolidinone elimination gave the (benzyloxymethyl)(ethoxy)butenolide. Carbonyl reduction and acylation gave a 1:1 mixture of epimeric allyl acetates, which were subjected to Vörbruggen coupling to give an epimeric mixture of 4,4′-disubstituted didehydrodideoxy ribonucleoside derivatives [76]. Palladium-catalyzed allylic amination with common nucleoside bases in the presence of chiral phosphines resulted in kinetic resolution to give a single β-epimer (Scheme 3) [77]. This same optically active cyclobutanone intermediate was the starting point for the synthesis of (−)-cyclobut-A, (±)-3′-epi-cyclobut-A [78], carbovir and aristeromycin [79], and (+)-neplanocin A [80], as well as aminocyclopentitols [81] and, from the (methoxy)(methyl) analog, 6-deoxy-4-aminohexoses (Scheme 4) [82].

Scheme 3
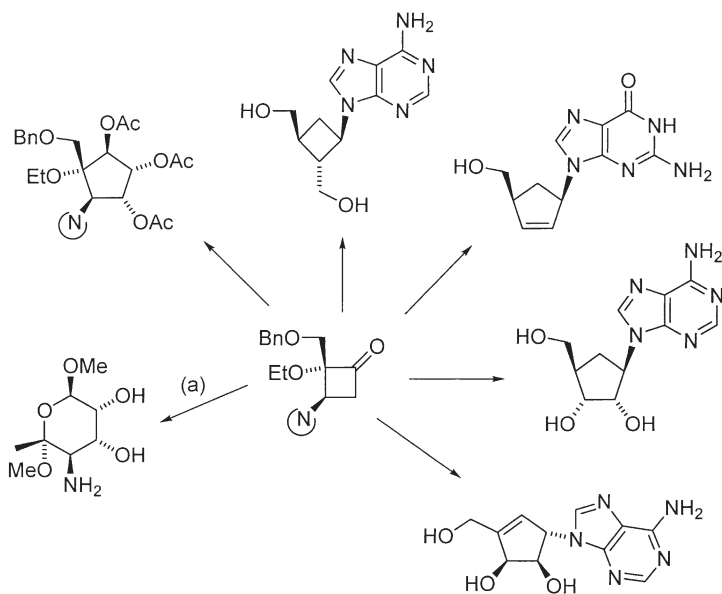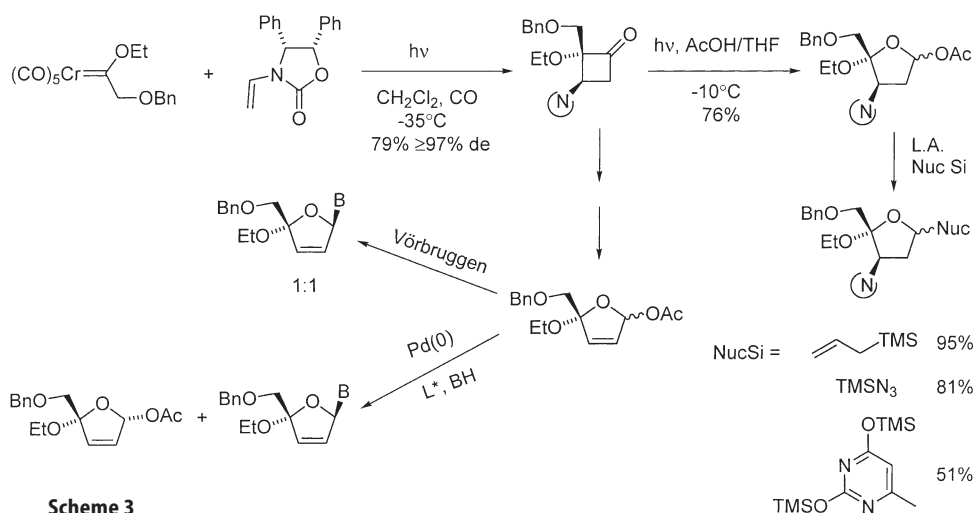
Scheme 4   [a]From the (methoxy)(methyl) analog of the cyclobutanone

2.1.1.3
With Aldehydes to Give β-Lactones

Photolysis of chromium alkoxycarbene complexes with aldehydes in the presence of Lewis acids produced β-lactones [83]. Intermolecular reactions were slow, low-yielding, and nonstereoselective, while intramolecular reactions were more efficient (Eqs. 19 and 20). Subsequent studies showed that amines, particularly DMAP, could also catalyze this process (Table 13) [84], resulting in reasonable yields and diastereoselectivity in intermolecular cases.

$$ (19) $$

n = 2 50%
n = 3 59%
n = 4   8%

$$ (20) $$

72%
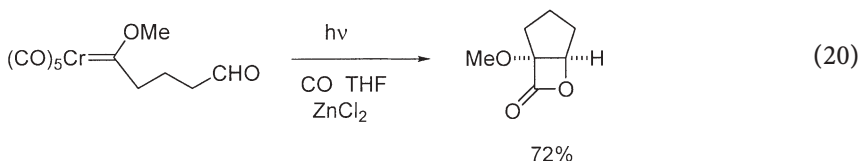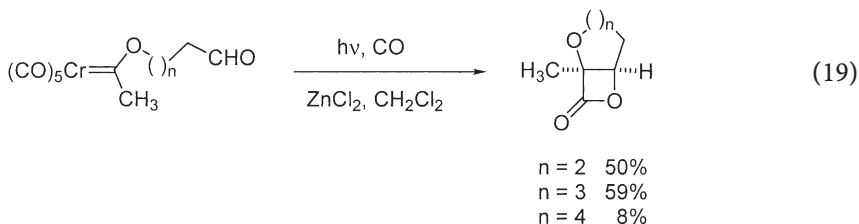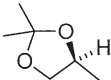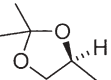
Table 13   Reaction of alkoxycarbenes with aldehydes

R	R	yield (%), (*syn/anti*)
C_2H_5	C_2H_5	53 (15/1)
CH_3	CH_3	55 (8/1)
i-Pr	i-Pr	35 (4/1)
n-Pr	n-Pr	43 (23/1)
Ph	Ph	33 (15/1)
		(1.3/1 *syn* diast.) 65 ≥99/1

2.1.1.4
With Azoarenes to Give Diazetidinones

Photolysis of chromium alkoxycarbenes with azoarenes produced 1,2- and 1,3-diazetidinones, along with imidates from formal azo metathesis (Eq. 21) [85, 86]. Elegant mechanistic studies [87–89] indicated the primary photoprocess was *trans*-to-*cis* isomerization of the azoarene followed by subsequent thermal reaction with the carbene complex. Because of the low yields and mixtures obtained the process is of little synthetic use.

$$(21)$$
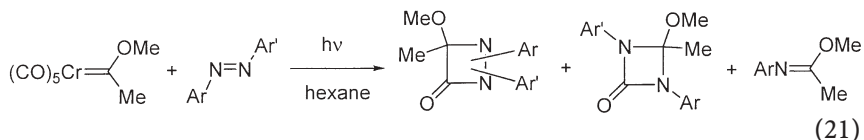
2.1.1.5
Photochemical Benzannulation Reactions

The *thermal* benzannulation of Group 6 carbene complexes with alkynes (the Dötz reaction) is highly developed and has been used extensively in synthesis [90, 91]. It is thought to proceed through a chromium vinylketene intermediate generated by sequential insertion of the alkyne followed by carbon monoxide into the chromium-carbene-carbon double bond [92]. The realization that photodriven CO insertion into Z-dienylcarbene complexes should generate the same vinylketene intermediate led to the development of a photochemical variant of the Dötz reaction (Table 14).

Table 14 Photo-driven Benzannulation Reactions

Carbene	Product		yield (%)	ref
		X = H	90	[93]
		X = OH	78	[93]
		R = Ph	87	[93]
		R = Me	90	[93]

Table 14 (continued)
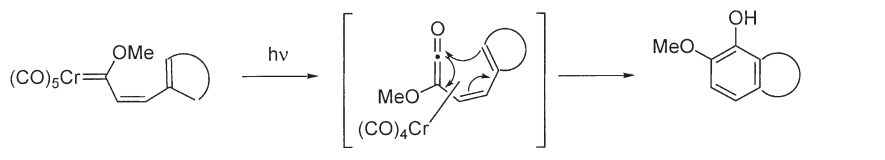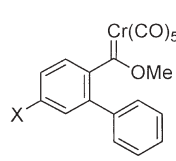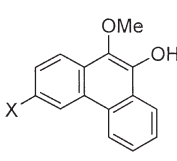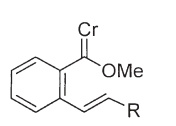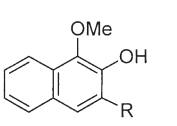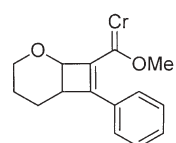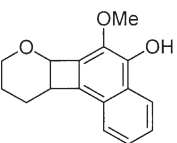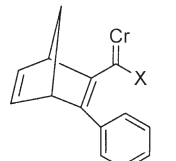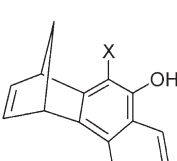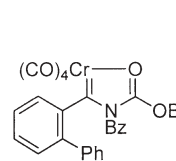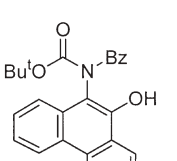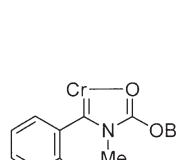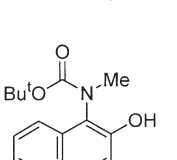
Carbene	Product		yield (%)	ref
		X = H X = OH	90 78	[93] [93]
		R = Ph R = Me	87 90	[93] [93]
			50	[93]
		X = OMe X = NMe$_2$	93 75	[93] [94]
			62	[94]
			81	[94]

Table 14 (continued)

Carbene	Product	yield (%)	ref
		83	[94]
		28	[94]
		33	[94]
		65	[95]
		83 (11:1)	[95]
			[95]

Table 14 (continued)
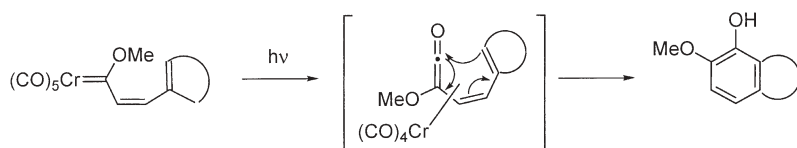
Carbene	Product	yield (%)	ref
X = OH[a]		65 (1.2:1)	
X = Me		71 (1.2:1)	
X = CHO		71 (1:1.3)	[95]
X = CH(OMe)$_2$		74 (1:1.5)	
X = F		66 (1:5)	
X = OMe		70 (1:7)	
X = Cl		89 (1:14)	
X = CF$_3$		69 (<1:>25)	
X = OH[b]		75 (5.4:1)	
X = Me		96 (1:12)	
X = CHO		88 (1:3)	
C = CH(OMe)$_2$		92 (<1:>25)	
X = F		58 (<1:>25)	
X = Cl		89 (<1:>25)	

[a]THF solvent. [b]toluene solvent.

This photodriven benzannulation was used in the synthesis of indolocar-bazoles (Eq. 22) [96] and calphostins (Eq. 23) [97]. The thermal insertion of isonitriles into these same classes of carbenes provided a complementary ap-proach to similar benzannulations [98–100]. Manganese alkoxycarbene com-plexes underwent both inter- [101] and intramolecular [102] photodriven benz-annulation reactions with alkynes (Eqs. 24 and 25).

(22)

R = R^1 = Me   51%

R = (allyl), R^1 = MOM   63%

(23)

36%

(24)

R = Me   28%
R = H   30%

(25)

R^1 = H, Me, OMe   n = 0, 1
R^2 = H, Et
R^3 = H, Me, Et, Ph, TMS
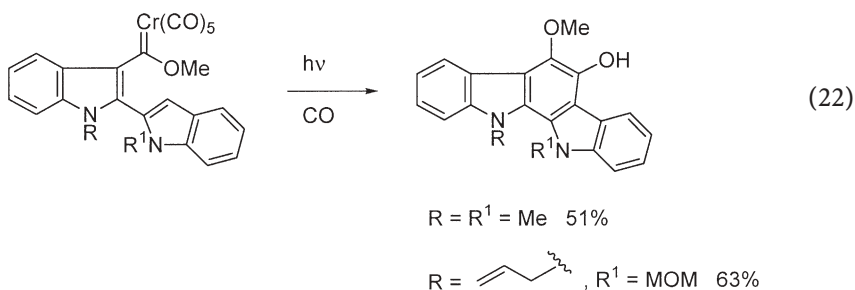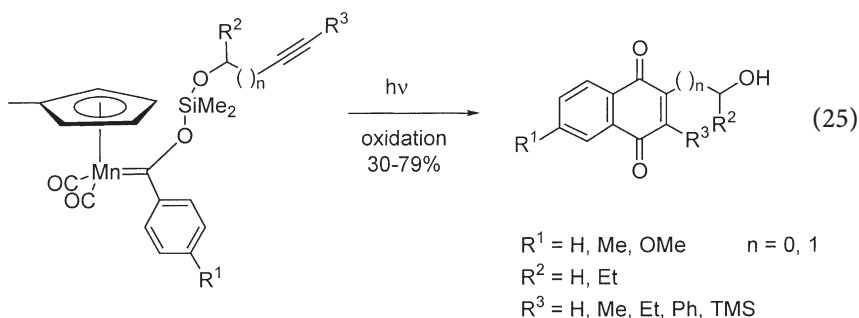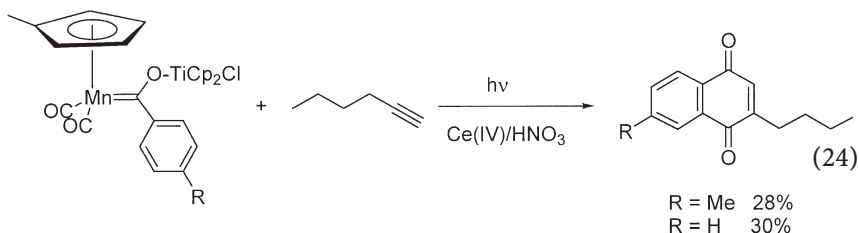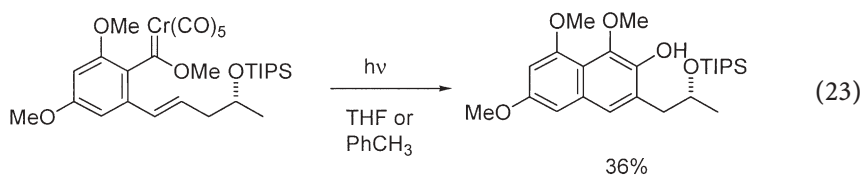
2.1.2
Nucleophilic Attack

2.1.2.1
By Alcohols to Give Esters

Photodriven reactions of Fischer carbenes with alcohols produces esters, the expected product from nucleophilic addition to ketenes. Hydroxycarbene complexes, generated in situ by protonation of the corresponding "ate" complex, produced α-hydroxyesters in modest yield (Table 15) [103]. Ketals, presumably formed by thermal decomposition of the carbenes, were major by-products. The discovery that amides were readily converted to aminocarbene complexes [104] resulted in an efficient approach to α-amino acids by photodriven reaction of these aminocarbenes with alcohols (Table 16) [105, 106]. α-Alkylation of the (methyl)(dibenzylamino)carbene complex followed by photolysis produced a range of *racemic* alanine derivatives (Eq. 26). With chiral oxazolidine carbene complexes optically active amino acid derivatives were available (Eq. 27). Since both enantiomers of the optically active chromium aminocarbene are equally available, both the natural *S* and unnatural *R* amino acid derivatives are equally

Table 15 Photo-driven reactions of hydroxycarbene complexes with alcohols
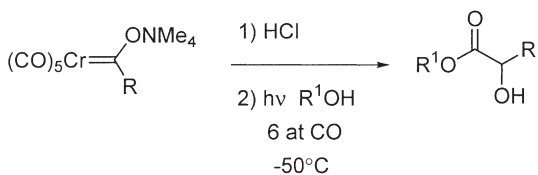
R	R^1	yield, %
Ph	Me	60
Ph	Et	19
Me	Me	10
Me	Bn	---^{a}
nBu	Bn	21
nBu	Me	62
sec Bu	Me	28
PhCH$_2$CH$_2$	Me	22
(cyclopropyl)	Bn	4
(cyclopropyl)	Me	19

^{a}the dibenzyl ketal of acetaldehyde was the sole product isolated (30%).

available. Even α-deuteroglycine (Eq. 28) [107] and ¹³C-labeled, α-deuterated amino acids [34] were available by this methodology (Eq. 29). 2,6-Imino-D-allonates were prepared using this chemistry (Eq. 30) [108].
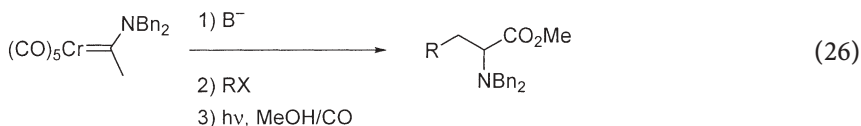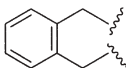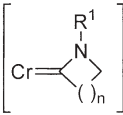
R = nBu, 48%; Bn, 72%; allyl, 72%
R = pMeOPhCH$_2$, 73%; EtO$_2$CCH$_2$, 66%

$$(26)$$
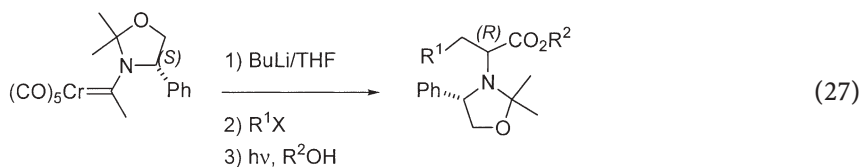
R^1 = Bn, R^2 = t-Bu, 42% yield, ≥93% de
R^1 = t-BuO$_2$CCH$_2$, R^2 = Me, 52% yield, ≥93% de

$$(27)$$

Table 16 Photo-driven reactions of aminocarbenes to produce α amino acids

$$K_2Cr(CO)_5 \ + \ \underset{\substack{\| \\ O}}{RC}\!-\!NR_2^{1} \ \xrightarrow{\text{TMSCl}} \ (CO)_5Cr\!\!=\!\!\underset{R}{\overset{NR_2^{1}}{<}} \ \xrightarrow[\text{MeOH}]{h\nu} \ MeO\!\!-\!\!\underset{\substack{\| \\ O}}{C}\!\!-\!\!\underset{NR_2^{1}}{\overset{R}{<}}$$

R	R¹	Complex yield %	Amino acid yield %
Me	Bn	44	87
Me	(isoquinoline group)	57	84
Me	(morpholine group)	78	98
(cyclopropyl)	Me	43	85
BnOCH₂	Me	50	82
Ph	Et	91	98
pCF₃Ph	Me	63	88
3-furyl	Me	96	76
Ph	H	96	84
(Cr carbene, n = 1)	Bn	35	45
n = 2	Bn	49	---[a]
n = 2	Me	98	---[a]
n = 3	Me	97	90
n = 3	Bn	32	90
n = 4	Bn	29	58
n = 10	Bn	36	96

[a]only slow photochemical decomposition was observed. The same was true for styryl-, phenylacetylidiyl, and o-chlorophenyl carbenes

$$(28)$$

(R)
(S)

(R,R) 93% yield
(S,S) ≥97% D 86% de

(R) 82%
(S) 82%

(29)

(S)

R = Me, 78%
R = t-BuO$_2$CCH$_2$, 97%
R = allyl, 57%
R = Bn, 70%
>95% de (R)

(30)
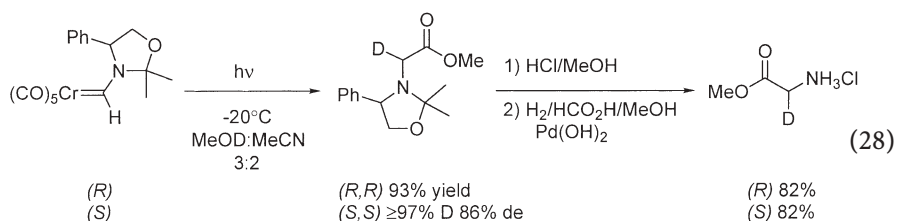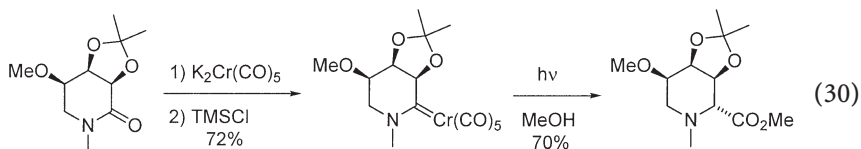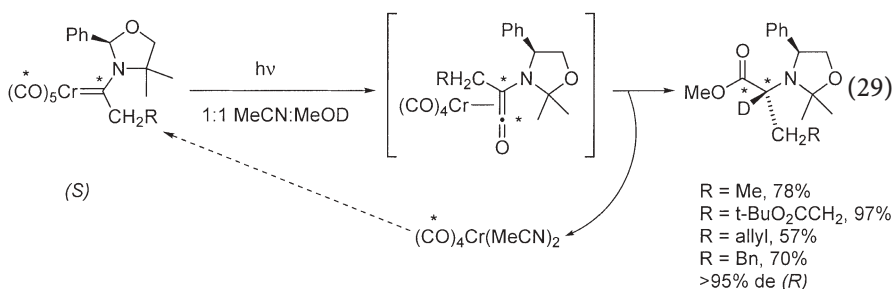
Activated esters for use in peptide-coupling reactions were produced by pho-tolysis of optically active chromium aminocarbenes with alcohols which are good leaving groups, such as phenol, pentafluorophenol, 2,4,5-trichlorophenol, and N-hydroxysuccinimide (Table 17) [109]. Since arylcarbenes bearing the op-

Table 17   Synthesis of optically active activated amino esters

R	R^1	Product yield, % (config.)	de
Me	Ph	55 (S,R)	86
Me	2,4,5-Cl$_3$Ph	52 (S,R)	90
Me	2,4,5-Cl$_3$Ph	57 (R,S)	91
Me	C$_6$F$_5$	38 (S,R)	80
(allyl)	2,4,5-Cl$_3$Ph	60 (R,S)	95
Bn	2,4,5-Cl$_3$Ph	51 (S,R)	92
tBuO$_2$CCH$_2$	2,4,5-Cl$_3$Ph	48 (S,R)	85
nC$_8$H$_{17}$	2,4,5-Cl$_3$Ph	40 (R,S)	a
MeO$_2$CCH$_2$	2,4,5-Cl$_3$Ph	29 (R,S)	86
(cyclohexanone)	2,4,5-Cl$_3$Ph	36 (R,S)	a

[a]de could not be determined

tically active oxazolidine auxilliary are difficult to synthesize and often unstable, the above chemistry does not afford an effective approach to aryl glycines. In contrast, a wide range of arylcarbenes having an optically active diphenyl-amino alcohol as a chiral auxilliary were readily synthesized [110]. Photolysis of these resulted in intramolecular trapping of the ketene-like intermediate, producing aryl-substituted oxazinones in good yield. Although diastereoselectivity for the process was only fair, diastereoisomers were readily separated to provide reasonable yields of optically pure aryl glycines (Table 18). Intramolecular trapping by a pendant OH group from aldol reactions at the α-carbon produced 2-aminobutyrolactones (Table 19) [111]. These were converted to homoserines and were used in the total synthesis of (+)-bulgecinine.

Table 18 Synthesis of aryl glycines
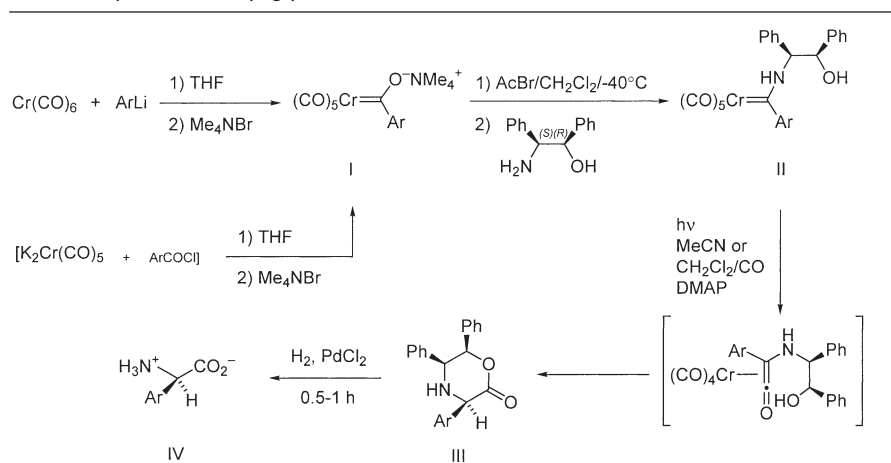
I (% yield)[a]	II (% yield)[a]	III (% yield)[a]	de[b] (ratio)	III (% yield)[c]	IV (% yield)[a,d]	ee (Mosher amide)[e]
Ph, 62	79	81	64 (82:18)	67	69 (23)[d]	94
p-meOPh, 78	81	82	76 (88:12)	72	91 (41)	96
p-ClPh, 64	73	73	60 (80:20)	59	81 (22)	84
p-FPh, 62	77	77	72 (86:14)	69	80 (26)	98
p-CF$_3$Ph, 80	84	84	60 (80:20)	73	86 (42)	98
o-MeOPh, 81	86	78	76 (88:12)	61	24[f] (11)	64[g]
2,6-F$_2$Ph, 63	78	62	64 (82:18)	63	95 (29)	56
1-Naphth, 75	51	76	62 (81:19)	66	40[h] (10)	91
3-Thienyl, 80	55	75	66 (83:17)	62	[h,i]	

[a]Reported yields are for isolated, purified materials. [b]Determined by integration of appropriate signals in the ^{1}H NMR spectrum in the crude reaction mixture. [c]Yield of isolated, pure, single (major) diastereoisomer based on ArLi. [d]Overall yield of amino acid, from ArLi + Cr(CO)$_6$. [e]Determined by integration of appropriate peaks in ^{1}H NMR spectra of the Mosher's amide. [f]As the hydrochloride salt. The free amine unstable. [g]The amino acid decomposed during conversion to Mosher's amide, complicating the ee determination. [g]Oxidative removal of the chiral auxiliary was used. [i]Deprotection was unsuccessful.

Table 19 Photo-driven synthesis of α-aminobutyrolactones
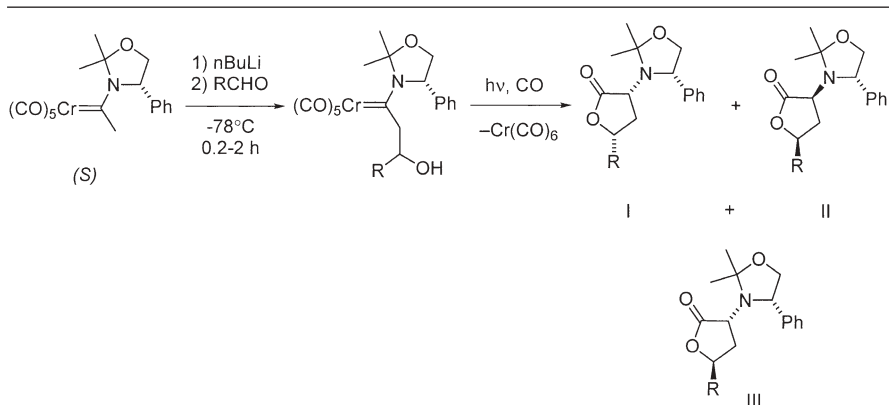
R	yield (%)[a]	I	II	III
C$_6$H$_5$	78	92	8	---
pMeOPh	39[b]	100	---	---
2-furyl	44	100	---	---
tBu	32 (50)[c]	100	---	---
Me	61	22	67	11
iPr	59	22	68	10[d]
CH=CH$_2$	37[e]	41	41	18

[a]Combined yield of separated, isolatled, pure diastereoisomers. [b]Aldol product was purified before photolysis; yield for the aldol reaction 53%, yield for the photolysis 74%. [c]The aldol reaction was stirred at 0°C for 4 h under artificial light. After recooling to -78°C and quenching, only the lactone and starting carbene were isolated. [d]Ratio determined by GC. [e]Aldol reaction was carried out at -100°C.

2.1.2.2
By Amino Acids to Give Peptides

A major justification for the synthesis of unnatural amino acids is to incorporate them into peptides to alter their biological activity/stability. By using an amino acid ester as the nucleophile both the peptide bond and the new stereogenic center, the absolute configuration of which is controlled by the carbene not the amino acid, were generated in the coupling step (Table 20) [112]. The reaction was efficient for a range of amino acid esters, including those having side chain functionality [113], and a modest range of carbene complexes. This system experienced modest "double diastereoselection" with (R)(S) or (S)(R) being the "matched" pair and (S)(S) or (R)(R) being the mismatched pair. This effect only slightly eroded diastereoselectivity. Even sterically hindered α,α-dialkyl amino acid esters and N-alkyl amino acid esters coupled reasonably well, because the species photogenerated from the carbene complex was highly reactive [113]. This chemistry worked well on Merrifield resin-supported sys-

Table 20 Synthesis of dipeptides from aminocarbenes and α-aminoesters

R^1	R^2	R^3	R^4	dr	yield, %^{a}	***	ref
H	Me	H	t-Bu	98:2	88	(R)(S)(S)	[112]
H	Me	H	t-Bu	90:10	68	(S)(R)(S)	[112]
H	H	H	t-Bu	94:6	68	(R)(S)(−)	[112]
H	Bn	H	t-Bu	97:3	72	(R)(S)(S)	[112]
H	Bn	H	t-Bu	92:8	65	(S)(R)(S)	[112]
H	Ph	H	t-Bu	98:2	86	(R)(S)(S)	[112]
H	Ph	H	t-Bu	90:10	70	(S)(R)(S)	[112]
H	CH$_3$CH(OH)	H	Me	95:5	56	(R)(S)(S)	[112]
H	2-indolyl	H	Me	90:10	60	(R)(S)(S)	[112]
H	(proline)	H	t-Bu	---	61	(R)(S)(S)	[112]
H	(proline)	H	Me	74:26	60	(R)(S)(S)	[113]
H	CH$_2$OH	H	Me	98:2	61	(R)(S)(S)	[113]
H	CH$_2$SH	H	Me	92:8	37	(R)(S)(S)	[113]
H	(CH$_2$)$_2$SH	H	Me	96:4	68	(R)(S)(S)	[113]
H	pHOPhCH$_2$	H	Me	94:6	64	(R)(S)(S)	[113]
H	(CH$_2$)$_2$CO$_2$Me	H	Me	98:2	75	(R)(S)(S)	[113]
H	CH$_2$CO$_2$Me	H	Me	95:5	64	(R)(S)(S)	[113]
CH$_2$OCO$_2$tBu	Me	H	t-Bu	93:7	77	(R)(S)(S)	[112]
Bn	Me	H	t-Bu	87:13	82	(R)(S)(S)	[112]
(allyl)	Me	H	t-Bu	77:23	57	(R)(S)(S)	[112]
H	Me	Me	Me	98:2	78	(R)(S)(−)	[113]
H	Ph	Ph	Me	98:2	82	(R)(S)(−)	[113]
H	Bn	Me	Me	98:2	84	(R)(S)(S)	[113]
H	nPr	Me	Me	97:3	67	(R)(S)(S)	[113]
H	Bn	nPr	Me	92:8	68	(R)(S)(S)	[113]
H	CH$_2$OH	Me	Me	93:7	68	(R)(S)(S)	[113]
iPr	Me	Me	Me	98:2	76	(R)(S)(−)	[113]
H	Bn	Me	Me	90:10	76	(S)(R)(S)	[113]
H	nPr	Me	Me	95:5	71	(S)(R)(S)	[113]
H	Bn	nPr	Me	91:9	53	(S)(R)(S)	[113]

^{a}Yield of pure, isolated single diastereoisomer.

tems and was used to synthesize an octapeptide having three unnatural, chromium carbene-derived residues in the middle [114]. Soluble poly(ethylene glycol) (PEG)-supported systems also coupled effectively [115]. Photolysis of *o*-silylcarbenes in the presence of *p*-anisidine gave *N*-*p*-anisyl-*α*-hydroxy-amides in fair yield [116].

2.1.2.3
By Stabilized Ylides to Produce Captodative Allenes

Photolysis of alkoxycarbene complexes in the presence of stabilized ylides produced allenes having a donating group at one terminus and an accepting group at the other. These were highly reactive and rearranged to 1,3-dienes under mildly acidic conditions and hydrolyzed to *γ*-keto-*α*,*β*-unsaturated esters (Eq. 31) [117].

$$X = CO_2R, SO_2tolyl$$
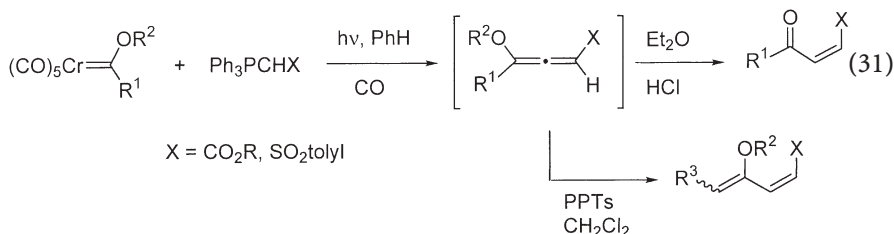
2.1.2.4
By Arenes: Intramolecular Friedel–Crafts Arene Acylation

Chromium carbene complexes having electron-rich arenes tethered to the carbene oxygen or carbon underwent photodriven intramolecular Friedel–Crafts acylation in the presence of zinc chloride (Eqs. 32 and 33) [118]. The process was highly regioselective, undergoing acylation exclusively *para* to the activating group.
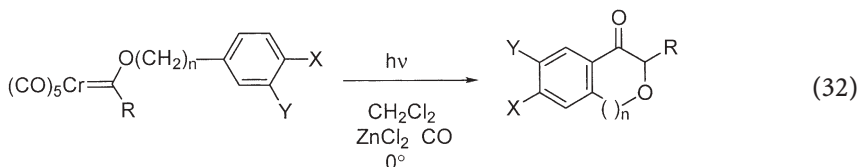
R = Me, n = 1, X = OMe, Y = H   69%
R = Me, n = 1, X = OH, Y = H   59%
R = Me, n = 1, X = Y = OMe   38%
R = Me, n = 2, X = OMe, Y = H   54%

R = ◁, n = 1, X = OMe, Y = H   43%
R = Ph, n = 1, X = OMe, Y = H   15%

$$(33)$$

$$n = 1, Z = H \qquad 60\%$$
$$n = 2, Z = mMeOPhCH_2 \qquad 62\%$$
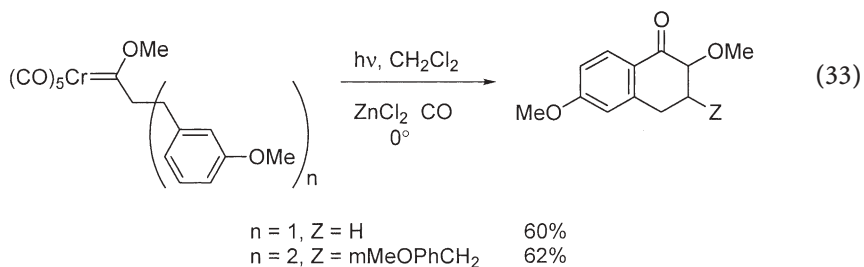
2.1.2.5
By Tertiary Allylic Amines: Zwitterionic Aza-Cope Rearrangement

Ketenes react with tertiary allylic amines in the presence of Lewis acids to give zwitterionic intermediates which undergo [3,3]-sigmatropic rearrangement [119]. Photolysis of chromium carbene complexes in the presence of tertiary amines results in similar chemistry [120]. Cyclic (Table 21) and strained allylic amines (Eq. 34) work best, while acylic amines are less reactive (Eq. 35).

Table 21 Zwitterionic aza-Cope reaction

R^1	X	n	R^2	L.A.	yield, %
Me	OMe	1	H	$ZnCl_2$	71
Me	OBn	1	H	$ZnCl_2$	66
$-(CH_2)_3O-$		1	H	Me_2AlCl	22
H	Me_2N	1	H	Me_2AlCl	9
H	(oxazolidine, Ph)	1	H	$ZnCl_2$	19
Me	OMe	1	Me	$ZnCl_2$	20
Me	OBn	1	Me	$ZnCl_2$	40
Me	OMe	2	H	Me_2AlCl	33

(34)

R = Me. X = OMe   60% (9:1)
R = Me, X = OBn   51%
R,X = (CH$_2$)$_3$O–   10%

R = H, X = N   O   50% (3:1)

Ph

(35)

R = Me, X = OMe   45%
R = Me, X = OBn   68%
R = X = –(CH$_2$)$_3$O–   14%
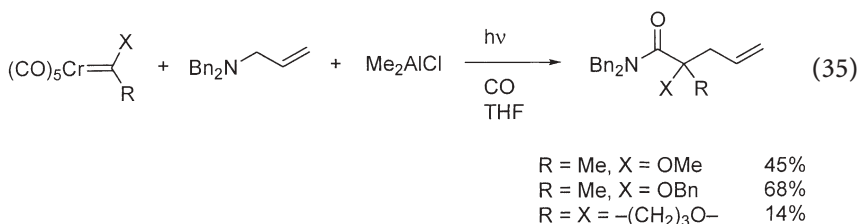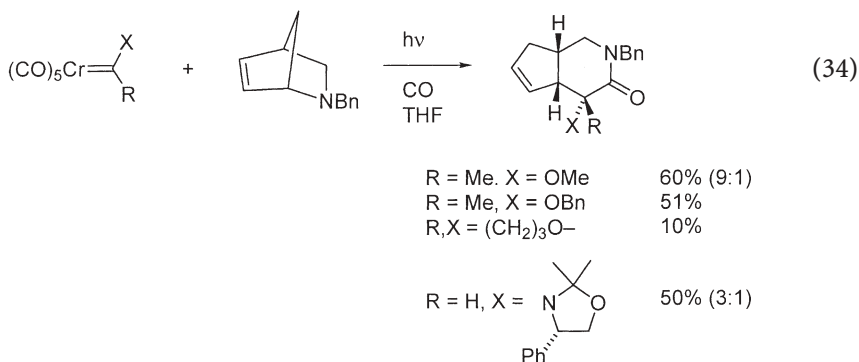
2.2
Photodriven Reactions of Fischer Carbenes Not Involving CO Insertion

2.2.1
Nucleophilic Addition/Elimination at the Carbene Carbon

Sulfur-stabilized ylides underwent photodriven reaction with chromium alkoxy-carbenes to produce 2-acyl vinyl ethers as *E/Z* mixtures with the *E* isomer predominating (Table 22) [121–123]. The reaction is thought to proceed by nucleophilic attack of the ylide carbon at the chromium carbene carbon followed by elimination of (CO)$_5$CrSMe$_2$. The same reaction occurred thermally, but at a reduced rate. Sulfilimines underwent a similar addition/elimination process to produce imidates or their hydrolysis products (Table 23) [124, 125]. Again the reaction also proceeded thermally but much more slowly. Less basic sulfilimines having acyl or sulfonyl groups on nitrogen failed to react.

A narrow range of 2-phenyl-1-azirines underwent photodriven reactions with alkoxycarbenes to give *N*-vinylimidates, in a process probably related to the above reactions (Table 24) [126].

Table 22 Photo-driven reaction of sulfur-stabilized ylides with alkoxycarbenes

R	R^1	R^2	E/Z	yield, % E	Z
Me	Me	OMe	2.3:1	65	
Me	Me	Ot-Bu	4:1	73	
Me	Me	Ph	100:0	81	
Me	Bn	OMe	5.6:1	60	
Ph	Me	OMe	4:1	70	
Ph	Me	Ph	4.6:1	90	
Me	[allyl chain]	OMe	2.3:1	41	29
Me	[alkynyl chain]	OMe	3.4:1	68	22
Me	[Ph-substituted chain]	OMe	4:1	51	15
Me	[Ph-substituted chain]	Ph	4:1	48	
Me	[menthyl]	OMe	1.6:1	34	23
Bu	Me	OMe	3.5:1	52	20
[cyclopropyl]	Me	OMe	2.4:1	23	30
[naphthyl]	Me	OMe	2.4:1	50	12
[furyl]	Me	OMe	1:1	19	41

2.2.2
Cyclopropanation and Other Cycloadditions

One of the earliest reported *thermal* reactions of Fischer carbene complexes was the reaction with olefins to give cyclopropanes [127]. More recently it has been shown that photolysis accelerates intermolecular cyclopropanation of electron-poor alkenes [128]. Photolysis of Group 6 imine carbenes with alkenes

Table 23 Photo-driven reactions of sulfilimines with alkoxycarbenes

$$(CO)_5Cr{=}\!\!\begin{smallmatrix}OR^2\\R^1\end{smallmatrix} \;+\; R^3{-}\overset{-}{N}{-}\overset{+}{S}R_2{}^4 \quad\xrightarrow[\substack{MeCN\\2)\ O_2\\h\nu}]{1)\ h\nu}\quad \left[(CO)_5\overset{-}{Cr}{-}\!\!\begin{smallmatrix}OR^2\\R^1\\ \\R_2\overset{4}{S}{-}\underset{+}{\overset{N}{}}{-}R^3\end{smallmatrix} \right] \;\longrightarrow\; R^3N{=}\!\!\begin{smallmatrix}OR^2\\R^1\end{smallmatrix}$$

R^1	R^2	R^3	R^4	yield, %
Me	Me	2-Py	Me	80
Me	Et	2-Thiazolyl	Me	65
Me	Me	2-pyrimidinyl	Me	45
Me	Me	pO_2NPh	Me	52
Me	Me	Ph	Me	70
Me	Me	pMeOPh	Me	90
Ph	Me	phth	Me	60
Me	Me	$EtO(CH_2)_2$	Ph	50[a]
Ph	Me	$MeO_2C(CH_2)_2$	Ph	50[a]
Ph	Me	$EtO_2C(CH_2)_2$	Ph	55[a]
Ph	Me	⟨dioxolane⟩–$(CH_2)_2$–	Ph	98[a]
Ph	Me	$PhSO_2(CH_2)_2$	Ph	80
Ph	Me	$NC(CH_2)_2$	Ph	62
Me	Me	pMeOPh	Me	90
Ph	Me	pMeOPh	Me	71
Me	Bn	pMeOPh	Me	85
Me	allyl	pMeOPh	Me	54
Me	$H{-}\!\!\equiv\!\!{-}(CH_2)_2$	pMeOPh	Me	50
⟨cyclopropyl⟩	Me	pMeOPh	Me	63
PhCH=CH	Me	pMeOPh	Me	85
$TMS{-}\!\!\equiv$	Me	pMeOPh	Me	59
Me	⟨2-phenylbutyl⟩	pMeOPh	Me	70
Me	⟨menthyl⟩	pMeOPh	Me	98
Me	⟨norbornenyl-methyl⟩	pMeOPh	Me	40
Me	⟨fenchyl⟩	pMeOPh	Me	66

[a] Directly hydrolyzed to the amide.

Table 24 Photo-driven reaction of 2-phenyl-1-azirines with alkoxycarbenes

R¹	R²	R³	yield, %
Me	Me	Me	77
Ph	Me	Me	74
Me	Me	H	33
Ph	Ph	H	55
Me	Ph	H	61

produced 1-pyrrolines [129, 130]. Although this was initially thought to involve a [3+2] cycloaddition it was subsequently shown to involve *two* photochemical steps, initial cyclopropanation with photolysis simply acting to eject a CO from the carbene to allow cyclopropanation, followed by photodriven rearrangement of the cyclopropyl ketimine to the 1-pyrroline [131]. A wide range of electron-poor alkenes were reactive, as were several imine carbenes (Table 25). A related photodriven reaction of Group 6 imine carbenes with alkynes produced 2*H*-pyrroles. However, this process was thought to proceed via a six-membered aza-metallacycle rather than via cyclopropene intermediates (Table 26) [132].

Finally, chromium imine carbenes underwent photoreaction with imines to give azadienes (metathesis) (Eq. 36), with azobenzene to give both metathesis and cycloaddition products (Eq. 37), and with ketones to give oxazolines (Eq. 38) [133].
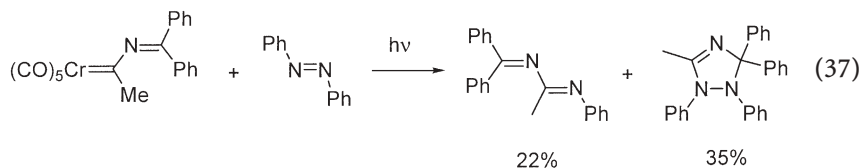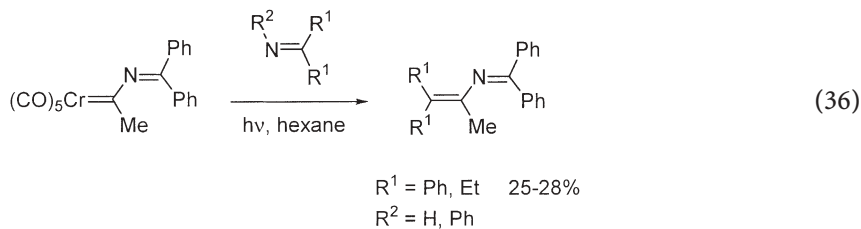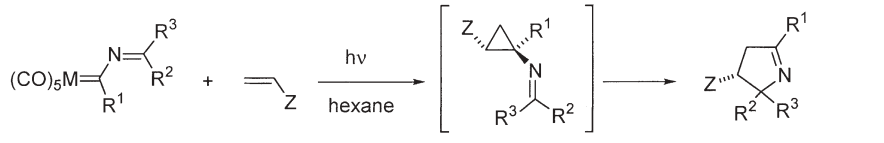

(36)

$R^1 = Ph, Et \quad 25\text{-}28\%$
$R^2 = H, Ph$

(37)

22%   35%
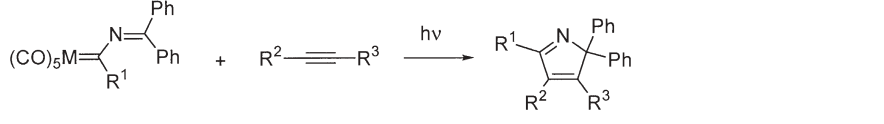
Table 25 Photo-driven reaction of Group 6 imine carbenes with alkenes

M	R^1	R^2	R^3	Z	yield, %
Cr	Me	Ph	Ph	CO_2Et	54
Cr	Me	Ph	Ph	COMe	76
Cr	Me	Ph	Ph	Ph	24
Cr	Ph	Ph	Ph	COMe	61
Mo	Me	Ph	Ph	COMe	54
W	Me	Ph	Ph	CO_2Et	43
W	Me	Ph	Ph	COMe	50
Cr	Me	Ph	Ph	CO_2tBu	35
Cr	Me	Ph	Ph	$CO_2C_{10}H_{21}$	37
Cr	Me	Ph	Ph	CO_2nBu	47
Cr	Me	Ph	Ph		58
Cr	Me	Ph	Et	COMe	81[a]
Cr	Me	Et	Et	COMe	54
Cr	Me	Ph	H	COMe	43
Cr	Ph	Ph	H	COMe	43[b]

[a] 1.6/1 mixture of diastereoisomer. [b] 1:1 mixture of diastereoisomers.

Table 26 Photo-driven reactions of Group 6 imine carbenes with alkynes

M	R^1	R^2	R^3	yield, %
Cr	Me	Ph	Ph	51
Cr	Ph	Ph	Ph	49
Mo	Me	Ph	Ph	21
Cr	Me	Ph	H	43
Cr	Me	CO_2Me	CO_2Me	5
Cr	Me	OEt	H	73
W	Me	OEt	H	63

$$R^1 = Ph, 12\%; Me, 15\%; (CH_2)_4, 14\%$$

(38)
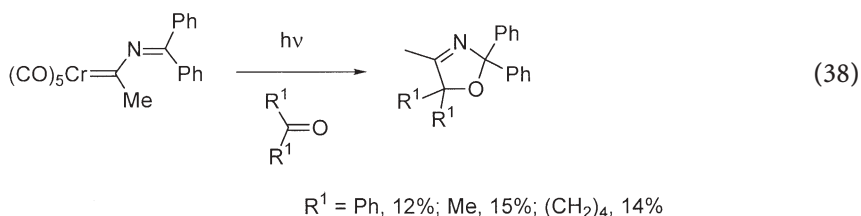
1,3-Dipolar cycloadditions to alkynylcarbenes followed by photolysis led to
β-enamino ketoaldehydes (Eq. 39) [134]. Photolysis of *N*-acylamino carbene
complexes produced munchnones, which were trapped with alkynes to give
pyrroles (Table 27) [135]. This same reaction occurred in the dark under 30 psi
carbon monoxide pressure. Tungsten carbonyl cyclized *N*-(*o*-alkynylphenyl)-
imines into indoles via a photodriven process proceeding through a tungsten-
carbene-containing azomethine ylide (Table 28) [136]. With internal alkynes
1,2-*R* migration occurred (Eq. 40).

Ar = Ph, 32%; pMePh, 31%
pMeO$_2$CPh, 37%;
p-Me$_2$NPh, 43%

(39)
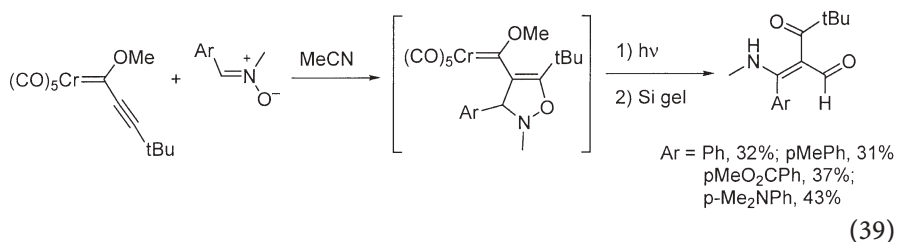
Table 27 Cycloaddition of alkynesto acylaminocarbenes

R^1	R^2	yield, %
MeO$_2$C	CO$_2$Me	90
Bu	CO$_2$Me	36
H	CO$_2$Me	80
Ph	Ph	12
H	Bu	27
Ph	(CO)$_5$Cr=⟨OMe	65

Table 28 Photo-driven tungsten carbonyl- assisted 1,3-dipolar cycloadditions
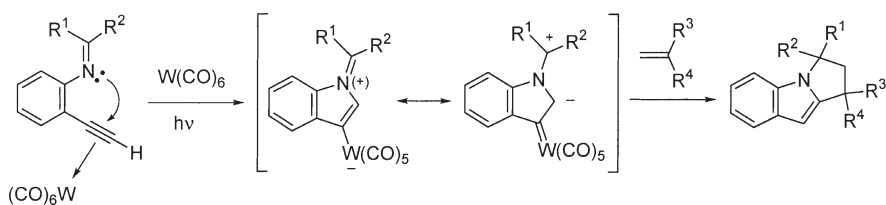
R^1	R^2	R^3	R^4	yield, %
H	Ph	H	OtBu	52
H	Ph	Me	OMe	86
H	Ph			67
H	Ph			74
H	OEt	OTMS	OEt	74
OMe	Me	OTMS	OEt	55

$$R = nPr, 76\%; Me, 55\%; Ph, 61\% \tag{40}$$
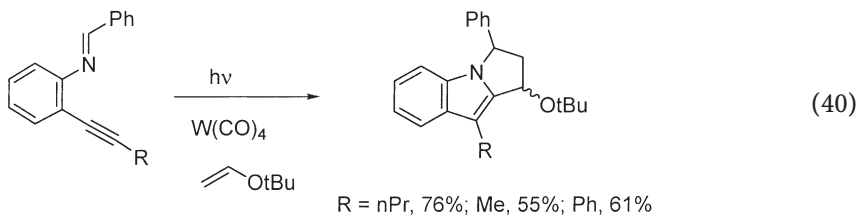
2.2.3
Acyl Migration

Photolysis of (2-acyloxyethenyl)carbene complexes produced 2-butene-1,4-diones (Eq. 41) [137].

$$60\text{-}68\% \tag{41}$$
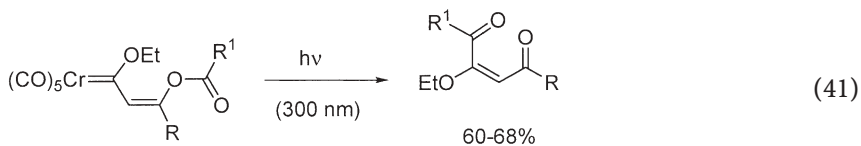
R = Ph, tBu, iPr

R^1 = Ph, iPr, iC$_7$H$_7$CH$_2$, ,tBu, iPr

3
Conclusions

Despite the unpromising UV-visible spectra and flash photolysis studies, the carbene complexes presented in this chapter have a rich photochemistry at wavelengths exceeding 300 nm. A wide range of synthetically useful transformations has been developed, and continued studies are likely to reveal more.

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