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Photochemistry of Imine−Group VI Carbene Complexes with Alkenes: Synthetic Scope and Photochemical Aspects

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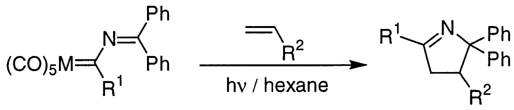
The irradiation of imine−group VI carbene complexes with alkenes leads to the formation of 1-pyrrolines through a mechanism involving an initial cyclopropanation followed by a light-induced [1,3]-sigmatropic rearrangement. The reaction has no limitations on the structural nature of the imine−carbene complexes and is general for terminal and acyclic or cyclic 1,2-disubstituted electron-poor olefins. From the studies on photochemical aspects such as excited-state quenching, quantum yield, excited-state sensitizers and Stern−Volmer plots, it is concluded that both excited states, singlet and triplet, undergo the photoreaction. As far as we know, this is the first photochemical study on these kinds of compounds.

Introduction

The formal [1 + 2 + 1] photochemical cycloaddition reactions of group VI metal heteroatom-stabilized pentacarbonyl carbene complexes with imines or olefins and carbonyl ligands represent a valuable route toward functionalized β-lactams or cyclobutanones, respectively.[1] However, despite the fact that many efforts have been made to explore the photochemical scope and limitations of alkoxy or amino complexes, only one photoreaction of imino complexes with imines has been described, which occurs with formation of a mixture of different products.[2] In preceding papers, we reported the first examples of photochemical cyclopentannulation of 3-aza-1-metalla-1,3-butadiene with electron-poor olefins[3] and heteroatom-containing double bonds.[4] The reaction with olefins occurred with good yields, giving 1-pyrroline derivatives with regiospecificity. The 1-pyrroline ring system is found in natural products, especially hydroporphyrins,[5] and constitutes an adequate substrate for the synthesis of pyrroles.[6] In addition, much attention is still being paid to the synthesis of 1-pyrroline derivatives.[7] Herein, we report a thorough study of the photocycloaddition of group VI metal pentacarbonyl imino carbene complexes with olefins: the scope and limitations of this reaction and a photochemical study.

Scheme 1



Results and Discussion

Synthetic Scope: Alkene and Carbene Complex Survey. After preparing the imine−group VI carbene complexes by direct reaction of methoxycarbenes with benzophenone imine,[3,8] we carried out its irradiation in the presence of alkenes to provide 1-pyrrolines (Scheme 1). The preliminary studies are shown in Table 1 (entries 1−7).[3] The best results were obtained by irradiation in hexane through Pyrex glass[9] and 10 equiv of alkene, and the reaction was extended to complexes substituted by an alkyl or phenyl group on the carbenic carbon, but always with two phenyl groups on the imine moiety. The reaction gave a single regioisomer, and complexes of chromium, molybdenum, and tungsten could be used in a similar way. The configuration assignment was made on the basis of difference NOESY experiments (**5** or **6**, positive NOE of H_{Ph} with H_{OEt} or H_{COMe}, respectively) or by comparison with the ^1H and ^{13}C NMR chemical shifts of **5** and **6** (**7** and **8**). To expand the applicability of this process, we decided to evaluate the effect of different substituents on the alkene and the imine group.

Different acrylates bearing a large aliphatic chain (*n*-butyl and isodecyl; Table 1, entries 8 and 9) or a bulky group (*tert*-butyl acrylate; Table 1, entry 10) reacted with **1** under irradiation to give the corresponding 1-pyrrolines **9**−**11** with moderate yields. 1,2-Disubsti-

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[1] Reviews: (a) Hegedus, L. S. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: New York, 1995; Vol. 12, p 549. (b) Hegedus, L. S. *Tetrahedron* **1997**, *53*, 4105.

[2] Hegedus, L. S.; Schultze, L. M.; Montgomery, J. *Organometallics* **1989**, *8*, 2189.

[3] Campos, P. J.; Sampedro, D.; Rodríguez, M. A. *Organometallics* **2000**, *19*, 3082.

[4] Campos, P. J.; Sampedro, D.; Rodríguez, M. A. *Tetrahedron Lett.* **2002**, *43*, 73.

[5] Montforts, F.-P.; Gerlach, B.; Höper, F. *Chem. Rev.* **1994**, *94*, 327 and references therein.

[6] Tehrani, K. A.; Borremans, D.; De Kimpe, N. *Tetrahedron* **1999**, *55*, 4133 and references therein.

[7] (a) Gagosz, F.; Zard, S. Z. *Synlett* **1999**, 1978. (b) Duncan, D.; Livinghouse, T. *Organometallics* **1999**, *18*, 4421. (c) Bolvin, J.; Schiano, A.-M.; Zard, S. Z.; Zhang, H. *Tetrahedron Lett.* **1999**, *40*, 4531.

[8] Kanauss, L.; Fischer, E. O. *Chem. Ber.* **1970**, *103*, 3744.

[9] The UV−visible spectra for imine−carbene complexes consist of several discernible absorptions: a very weak band at ca. 400 nm ($\epsilon \approx 100\ M^{-1}\ s^{-1}$) assigned as a spin-forbidden MLCT, a moderately intense band between 295 and 310 nm ($\epsilon \approx 15\,000\ M^{-1}\ s^{-1}$) assigned as a spin-allowed MLCT, and a strong absorption at ca. 245 nm ($\epsilon \approx 35\,000\ M^{-1}\ s^{-1}$) due to the CO ligands.

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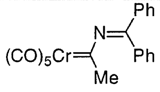
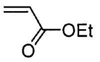
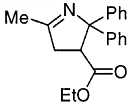
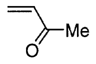
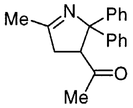
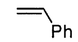
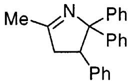
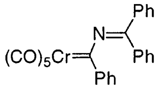
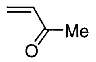
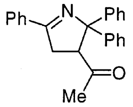
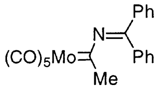
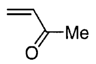
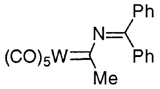
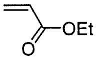
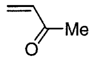
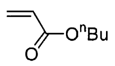
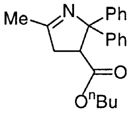
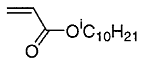
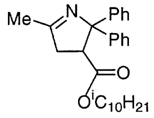
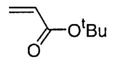
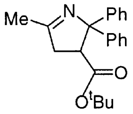
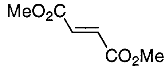
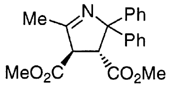
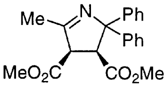
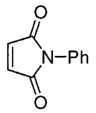
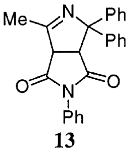
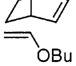
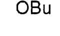
Table 1. Photocycloaddition Reaction of Imine–Carbene Complexes 1–4 with Alkenes[a]

entry	carbene complex	alkene	product	yield[b] (%)
1	 **1**		 **5**	54
2	**1**		 **6**	76
3	**1**		 **7**	24
4	 **2**		 **8**	61
5	 **3**		**6**	54
6	 **4**		**5**	43
7	**4**		**6**	50
8	**1**		 **9**	47
9	**1**		 **10**	37
10	**1**		 **11**	35
11	**1**		  **12a** 20:1 **12b**	58[c]
12	**1**		 **13**	38
13	**1**		-------	traces[d, e]
14	**1**		-------	traces[d, e]
15	**1**		-------	-------[e]

[a] Conditions: 2 h (**1**, **2**) or 5 h (**3**, **4**) of irradiation in hexane through Pyrex for 0.25 mmol of carbene and 2.5 mmol of alkene. [b] Isolated yield based on the corresponding carbene complex **1**–**4**. [c] Isomer ratio determined by 300 MHz ^{1}H NMR analysis of the crude products. [d] Determined by GC/MS analysis. [e] Metathesis compound **14** was isolated in 7–15% yield.

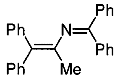


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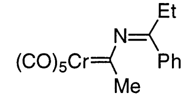
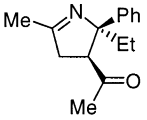
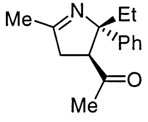
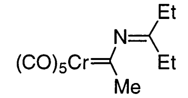
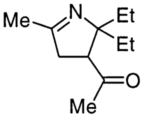
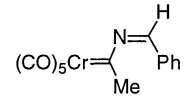
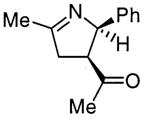
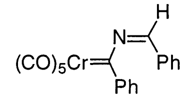
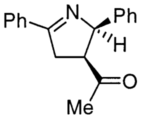
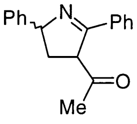
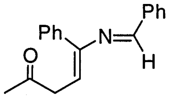
Table 2. Photocycloaddition Reaction of Methyl Vinyl Ketone with Chromium Carbene Complexes 15–18[a]

entry	carbene complex	product	yield[b] (%)
1	 **15**	  **19a** 1.6:1 **19b**	81[c]
2	 **16**	 **20**	54
3	 **17**	 **21**	43[d]
4	 **18**	  **22a** 1:1 **22b**	43[c,e]

[a] Conditions: 2 h of irradiation in hexane through Pyrex for 2.5 mmol of methyl vinyl ketone and 0.25 mmol of carbene. [b] Isolated yield based on the corresponding carbene complex **15–18**. [c] Isomer ratio determined by 300 MHz ^{1}H NMR analysis of the crude products. [d] Only one diastereomer pair observed in ^{1}H and ^{13}C NMR spectroscopy. [e] **22a** and **22b** were isolated by column chromatography. Compound **23** was also isolated in 15% yield.



23

tuted olefins with either an acyclic (dimethyl fumarate) or a cyclic nature (*N*-phenylmaleimide) provided the corresponding 1-pyrroline **12** or **13** on reaction with **1** (Table 1, entries 11 and 12). **12** was obtained as a 20:1 mixture of diastereoisomer pairs (**12a** and **12b**), presumably due to the photoisomerization of dimethyl fumarate to dimethyl maleate prior to the reaction with **1**. From this mixture of **12**, only the major isomer **12a** was obtained in pure form from the chromatographic purification on a silica gel column and was tentatively assigned as the trans diastereoisomer pair. On the other hand, we could only detect traces of 1-pyrroline (GC/MS spectroscopy) for the irradiation of chromium carbene complex **1** in the presence of electronically neutral alkenes (hexene and norbornene; Table 1, entries 13 and 14). For the activated alkene butyl vinyl ether (Table 1, entry 15), 1-pyrroline was not detected. In these cases, the reaction occurred with formation of a 7–15% yield of the 2-aza-1,3-butadiene derivative **14**, resulting from a metathesis reaction between the carbene Cr=C bond and the imine N=C bond of another carbene molecule.[3]

With regard to the carbene complex survey, a mixture of the corresponding imine–chromium carbene and 10 equiv of methyl vinyl ketone was irradiated in hexane at room temperature under an Ar atmosphere, through Pyrex glass with a 125 W medium-pressure mercury lamp. Table 2 summarizes our findings. The chromium imine–carbene complexes substituted at the imine position by one or two ethyl groups (**15** or **16**, respectively)[3,8] or by a hydrogen (**17** and **18**)[10,11] also underwent the expected photocycloaddition, giving the corresponding 1-pyrrolines **19–22** with good to moderate yields. Thus, no limitations on the structural nature of the imine carbene complexes to the photocycloadditions with methyl vinyl ketone were identified. In the reactions with carbenes **15–17**, the corresponding 1-pyrrolines were isolated as a single regioisomer, but complex **18** gave an equimolecular mixture of the regioisomers **22a** and **22b** (together with a small amount of azadiene **23**; Table 2). The formation of this mixture of regioisomers could indicate that the reaction was totally nonregioselective in this case, but this fact could also be explained by considering an isomerization to **22b** after initial formation of **22a**. This was demonstrated by irradiation through Pyrex glass of the isolated compound **22a**, which causes the isomerization, yielding compound **22b**.

With regard to the stereochemistry of the light-induced cycloaddition, two diastereomer pairs were obtained from **15**. The stereochemical assignment and the isomer ratio (**19a**:**19b** = 1.6:1) were determined on the basis of the ^{1}H NMR chemical shifts of the signal corresponding to H_{COMe}, since these methyl hydrogens are shielded by the diamagnetic anisotropy of the phenyl ring in the cis form (**19a**, δ 1.52 ppm) but not in the trans form (**19b**, δ 2.14 ppm).[12] Interestingly, the major diastereoisomer pair corresponds to a relative cis relationship between the more bulky groups, Ph and COMe, instead of the expected cis relationship between Et and COMe.[13] This tendency was enhanced when the difference in steric demand increased. Thus, the irradiation of **17** or **18** in the presence of methyl vinyl ketone

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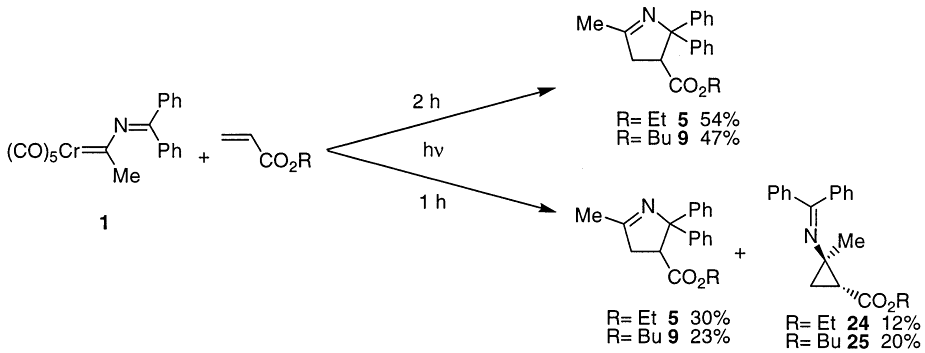
[10] Aumann, R.; Althaus, S.; Krüger, C.; Betz, P. *Chem. Ber.* **1989**, *122*, 357.

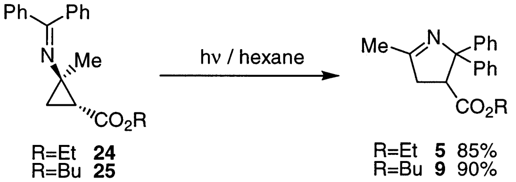
[11] Murray, C. K.; Warner, B. P.; Dragisich, V.; Wulff, W. D. *Organometallics* **1990**, *9*, 3142.

[12] See, for example: Jackman, L. M.; Sternhell, S. *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*; Pergamon Press: Oxford, U.K., 1972; p 94.

Scheme 2



Scheme 3



yielded **21** or **22a**, respectively, with a trans relationship between H and COMe, as the single diastereoisomer pair.

Search for Intermediates. To gain in mechanistic insight, we searched for intermediates in the course of the photoreaction. We always carried out the irradiation of imine–carbene complexes in the presence of alkenes until the complete consumption of the complex monitored by TLC. When this reaction was irradiated for a shorter period of time, the formation of a new product was observed in some cases. Interestingly, while the irradiation of **1** and ethyl acrylate for 2 h gave the 1-pyrroline **5**, the irradiation for 1 h yielded **5** together with the *N*-cyclopropyl ketimine **24** (Scheme 2). In a similar way, 1-pyrroline **9** and ketimime **25** were also obtained after 1 h of irradiation of **1** and butyl acrylate. The configuration for **24** and **25** was tentatively assigned as trans between carboxylate and imine groups.[14]

These cyclopropyl imines could be intermediates in the formation of 1-pyrrolines. In this way, the irradiation for 0.5 h of **24** or **25** under the same experimental conditions used for the reaction between imine–carbene complexes and alkenes (hexane, Pyrex glass, 125 W medium-pressure mercury lamp) led to the formation of 1-pyrrolines **5** and **9**, respectively (Scheme 3). This reaction may be considered an azavinylcyclopropane–cyclopentene rearrangement but, despite the high interest of such processes,[15] as far as we know, there is no thermal or photochemical precedent with the nitrogen atom placed on such position. The study of this interesting reaction is in progress.[16]

Photochemical Aspects. Since understanding a photoreaction requires knowing what happens at the molecular level from the absorptive act to the formation of products, we report in this section the standard studies such as excited-state quenching, quantum yields, excited-state sensitizers, and Stern–Volmer plots.

First, taking into account that the overall reaction consists of two photochemical steps, *N*-cyclopropyl ketimine formation and its rearrangement, we tried to study each step separately. Since *N*-cyclopropyl ketimine **25** does not absorb above 370 nm, irradation of carbene complex **1** in the presence of butyl acrylate was carried out through a solution filter which removes λ radiation under 410 nm.[17] However, the reaction afforded a mixture of **25** and 1-pyrroline **9** in a 3:1 ratio, probably due to energy transfer from the excited carbene complex to ketimine **25**. A similar result was obtained by using ethyl acrylate as starting alkene. Thus, we decided to study the overall process.

Next, we essayed the effect of molecular oxygen on the excited state of carbene complex **1**. O_2 is a ground-state triplet possesing two low-lying single states with energies of ~23 and 38 kcal/mol, and thus, it can be considered an effective quencher for a large number of photoreactions. We carried out the irradiation through Pyrex of two 5×10^{-3} M solutions of **1** in hexane, one saturated in argon and the other in oxygen,[18] at the same time using an annular photoreactor provided with a carousel assembly and a 400 W medium-pressure mercury lamp. After 1 h, the metathesis reaction product **14** ratio for the Ar/O_2 solutions was 2:1 (determined by GC/MS), which indicates that the excited state of **1** could be quenched by dissolved oxygen. This effect has also been observed for a variety of $M(CO)_6$ and $M(CO)_5L$ (M = Cr, Mo, W) type complexes[19] but has not been described for imino–group VI carbene complexes yet. Since the triplet state is often involved in the photochemical behavior of the former complexes[19] and the O_2 quenches this reaction, we found it of interest to study the effect of triplet state quenchers and sensitizers on the reaction of imino–carbene complexes with alkenes.[20]

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(13) Steric demand may be classified by the conformational free-energy values for substituted cyclohexanes ($-\Delta G°$ (kcal/mol): Ph, 3.1; Et, 1.75). See, for example: Isaacs, N. S. *Physical Organic Chemistry*; Longman: Harlow, U.K., 1987; p 312.

(14) Cycloaddition reactions of Fischer carbene complexes and alkenes usually proceed stereospecifically to give the isomer with a relative trans relationship between the more bulky groups. See for example: Barluenga, J.; Tomás, M.; López-Pelegrín, J.; Rubio, E. *J. Chem. Soc., Chem. Commun.* **1995**, 655.

(15) Review: Hudlicky, T.; Reed, J. W. In *Comprehensive Organic Chemistry*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, U.K., 1991; Vol. 5, p 899.

(16) For a preliminary communication see: Campos, P. J.; Soldevilla, A.; Sampedro, D.; Rodríguez, M. A. *Org. Lett.* **2001**, *3*, 4087.

(17) Concentrations: $NaNO_3$, 75 g/L; $CuSO_4 \cdot 5H_2O$, 4.4 g/L; NH_3, 2.7 M. See for example: *CRC Handbook of Organic Photochemistry*; Scaiano, J. C., Ed.; CRC Press: Boca Raton, FL, 1989; Vol. I, p 48.

(18) [O_2] in hexane (20 °C) 0.015 M: Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd ed.; Marcel Dekker: New York, 1993; p 289.

(19) Lees, A. J. *Chem. Rev.* **1987**, *87*, 711.

(20) The use of O_2 as quencher is complicated by the fact that carbene complexes undergo a facile photooxidation.

Table 3. Irradiation of 1 and Methyl Vinyl Ketone in the Presence of Different Triplet Quenchers and Sensitizers

entry	ketone	$E_T{}^a$ (kcal/mol)	ratio
1	acetone	79	2.26
2	acetophenone	74	1.22
3	benzophenone	69	1.06
4	none		1
5	2-acetylnaphthalene	59	0.68

[a] See ref 21.

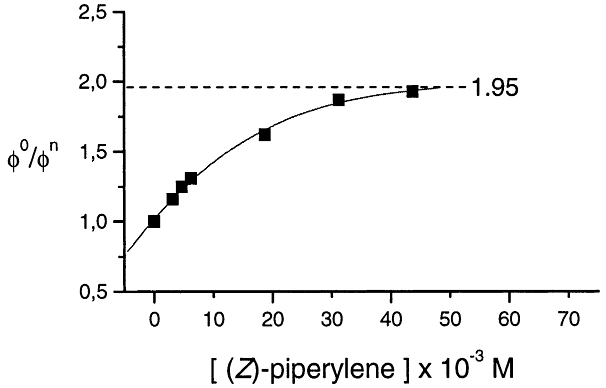


Figure 1. Experimental plot of quantum yield rate versus concentration of (*Z*)-piperylene for the reaction of carbene complex **1** with methyl vinyl ketone.

Table 3 summarizes the data for the reaction of carbene **1** (5×10^{-3} M) with methyl vinyl ketone (10 equiv), to give the 1-pyrroline **6**, in the presence of 10 equiv of different ketones in deoxigenated hexane. Ketones can act as triplet state sensitizers or quenchers depending on their relative energies compared with that of **1**. We used ketones with triplet state energy in the range 79–59 kcal/mol.[21] The reaction was faster when acetone, acetophenone, or benzophenone (2.26, 1.22, or 1.06 times faster, respectively) was added but slower with 2-acetylnaphthalene (0.68 times). These results indicate that the excited state possesses a considerable triplet character and places the energy for the triplet state of **1** between 69 and 59 kcal/mol.

Next, we checked the quenching of the photoreactivity of **1** with methyl vinyl ketone. We chose the common triplet-state quencher (*Z*)-piperylene, since it possesses an adequate triplet energy (57 kcal/mol)[21] and does not show any absorption at the irradiation wavelengths (Pyrex filter, >290 nm).[22] The plot of quantum yield rate (ϕ^0/ϕ, where the superscript zero denotes the absence of quencher) vs concentration of (*Z*)-piperylene (see Figure 1) is typical for a situation in which two excited states (singlet and triplet) undergo the same reaction, and only one of them is selectively quenched.[23] Extrapolation of the plateau to the ϕ^0/ϕ coordinate yields 1.95. Assuming that this unquenchable reaction is due to the reaction of **1** with methyl vinyl ketone from the singlet state, the contribution of the triplet state reaction to the slope may be determined by subtracting 1.95 from the experimental values of ϕ^0/ϕ. Thus, a normal Stern–Volmer plot results with an intercept of 0.98 ± 0.03 and a slope of $k_q\tau = 153.6 \pm 7.4$ M^{-1}, where k_q is the quenching rate constant, for the triplet reaction alone (Figure 2).

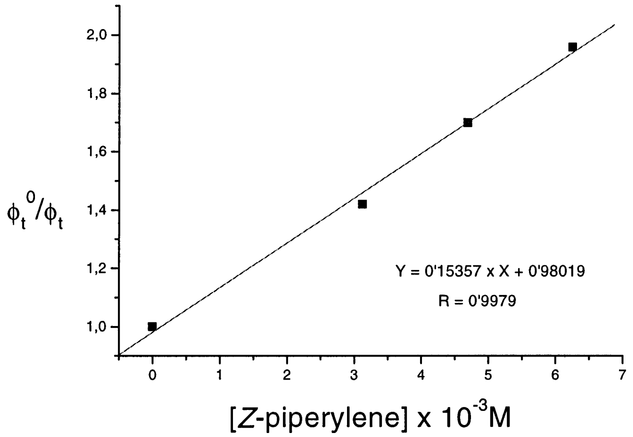
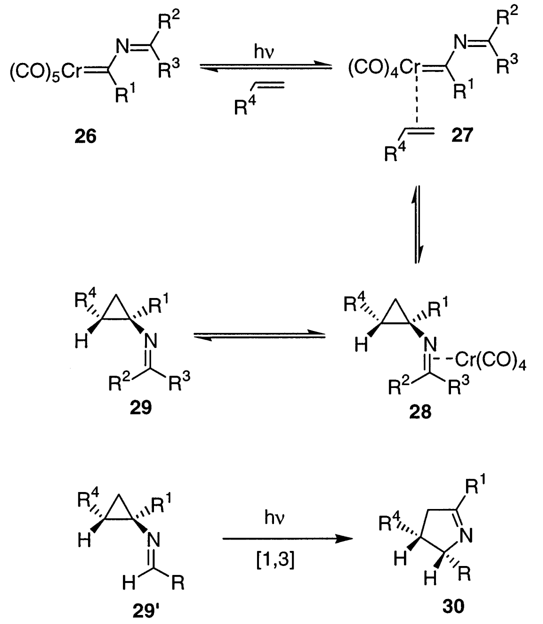


Figure 2. Stern–Volmer plot for the reaction of carbene complex **1** with methyl vinyl ketone after subtracting singlet contribution (see Figure 3).

Scheme 4



Finally, we determined the quantum yield of the efficiency of appearance of **6** from the photoreaction of **1** with methyl vinyl ketone. 2-Hexanone was used as actinometer, whose quantum yield of disappearance in hexane at 313 nm is 0.327.[24] To irradiate at this wavelength, we used an aqueous solution filter containing 200 g/l of $NiSO_4{\cdot}6H_2O$, 0.2 g/l of K_2CrO_4, and 5 g/L of potassium hydrogen phthalate ($\lambda_{max} = 313$ nm, range 305–335 nm).[25] For a solution of 1.2×10^{-4} M of **1** and 10 equiv of methyl vinyl ketone in deoxygenated hexane, the quantum yield of formation of **6** was 4.6×10^{-4}.

Proposed Reaction Mechanism. Our results demonstrate that cyclopropyl ketimines **24** and **25** are intermediates in the synthesis of 1-pyrrolines **5** and **9**. Accordingly, a plausible mechanism to explain these results is presented in Scheme 4. The initial dissociation of a CO ligand from the imine–carbene complex **26** after

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(21) See ref 18, p 54.
(22) See ref 18, p 183.
(23) Turro, N. J. *Modern Molecular Photochemistry*; University Science Books: Sausalito, CA, 1991; p 253.
(24) See ref 18, p 309.
(25) See ref 18, p 314.

irradiation[26] (from the triplet state and single excited state) followed by coordination of the alkene should give the carbene–alkene π complex **27**.[27] This complex could evolve by cyclopropanation to give **28**,[28] from which decomplexation of the metal fragment leads to cyclopropane derivative **29**. Since electron-rich olefins do not easily undergo cyclopropanation processes, the reaction does not work with butyl vinyl ether.[29] Taking into account that imines do undergo efficient syn–anti photo and thermal interconversions, the location of R^2 and R^3 in **29** depends on their relative steric demand. Thus, in **29′** the anti isomer should be more favorable. Furthermore, the formation of 1-pyrrolines with a relative cis relationship between the more bulky group seems more feasible for a concerted reaction than for a stepwise one. Therefore, we suggest that **29′** suffers a light-induced *symmetry-allowed* [1,3]-sigmatropic suprafacial rearrangement to give the 1-pyrroline **30**.[16]

Conclusion

The results reported herein represent a detailed study on the photochemical behavior of imine–group VI carbene complexes with alkenes. The reaction has no limitations on the structural nature of the imine–carbene complexes and is general for terminal or either acyclic or cyclic 1,2-disubstituted electron-poor olefins. It leads to the formation of 1-pyrrolines through a mechanism involving an initial cyclopropanation followed by a light-induced [1,3]-sigmatropic rearrangement. We have also carried out studies on photochemical aspects such as excited-state quenching, quantum yield, excited-state sensitizers, and Stern–Volmer plots, which indicate that both excited states, singlet and triplet, undergo the photoreaction. As far as we know, this is the first photochemical study on these kinds of compounds.

Experimental Section

General Comments. All solvents were purified and dried by standard procedures and freshly distilled under dry Ar prior to use. ^{1}H and ^{13}C spectra were recorded on a Bruker ARX-300 spectrometer in $CDCl_3$ with TMS as internal standard. Electrospray mass spectra were obtained on an HP 5989 B apparatus with an HP 59987 A interface, in negative-ion mode (for complexes **15** and **16**) or positive-ion mode. GC/MS spectra were recorded on an HP G1800A apparatus. IR spectra were obtained on a Perkin-Elmer 1000 spectrophotometer in CH_2Cl_2. UV spectra were recorded on an HP 8451A spectrophotometer. Elemental analyses were performed using a Model 1110 CE instrument. Melting points were obtained on a Büchi SMP-20 apparatus and are uncorrected. Reagents were of commercial grades (Aldrich).

General Procedure for the Preparation of Iminocarbene Complexes. The alkoxycarbene complex (5 mmol) and the corresponding imine[30] (5.5 mmol) were combined in deoxygenated Et_2O (20 mL). The mixture was stirred for 4 h at room temperature. The solvent was removed under vacuum to give a red oil. Purification by column chromatography (silica gel, hexane/CH_2Cl_2 5:1) gave carbene complexes as a solid. The formation of compounds **1**–**8**[3] and compounds **17** and **18**[10] has been previously reported.

Pentacarbonyl[((ethylphenylmethylene)amino)methylmethylene]chromium (15). Orange oil. Yield: 1.28 g, 73%. ^{1}H NMR: δ 1.30 (t, 3H, CH_2CH_3), 2.65 (s, 3H, $Cr{=}CCH_3$), 2.86 (q, 2H, CH_2CH_3), 7.52 (bs, 5H, arom). ^{13}C NMR: δ 9.4 (CH_2CH_3), 23.1 (CH_2CH_3), 34.7 ($Cr{=}CCH_3$), 123.6 (N=C), 127.2, 129.3, 130.2, 131.3, 206.0 (Cr=C), 217.6 (CO-cis), 223.3 (CO-trans). ES (−): m/z 350 (M − 1), 322 (M − CO), 294 (M − 2CO − 1). Anal. Calcd for $C_{16}H_{13}CrNO_5$: C, 54.71; H, 3.73; N, 3.99. Found: C, 54.82; H, 3.76; N, 3.79.

Pentacarbonyl[(diethylmethyleneamino)methylmethylene]chromium (16). Yellow oil. Yield: 1.10 mg, 73%. ^{1}H NMR: δ 1.12 (t, 6H, CH_3), 2.34 (q, 4H, CH_2), 2.50 (s, 3H, $Cr{=}C{-}CH_3$). ^{13}C NMR: δ 9.4 (CH_3), 26.6 (CH_2), 35.4 ($Cr{=}CCH_3$), 129.5 (N=C), 203.5 (Cr=C), 217.9 (CO-cis), 223.5 (CO-trans). ES (−): 302 (M − 1), 274 (M − CO − 1), 246 (M − 2CO − 1). Anal. Calcd for $C_{12}H_{13}CrNO_5$: C, 47.53; H, 4.32; N, 4.62. Found: C, 47.42; H, 4.38; N, 4.67.

General Procedure for Irradiation. The carbene complex (0.25 mmol) was dissolved in 50 mL of deoxygenated hexane. Ten equivalents of the unsaturated compound was added, and the mixture was irradiated at room temperature under an Ar atmosphere, through Pyrex glass with a 125 W medium-pressure mercury lamp, until the carbene was consumed (TLC, hexane/CH_2Cl_2 1:1). The solvent was removed with a rotary evaporator, and the crude product was filtered through Celite to remove chromium residues. The products were separated by column chromatography (silica gel, hexane/Et_2O).

4-(Butoxycarbonyl)-2-methyl-5,5-diphenyl-1-pyrroline (9). Colorless oil. Yield: 39 mg, 47%. ^{1}H NMR: δ 0.81 (t, 3H, $CH_2CH_2CH_2CH_3$), 1.2 (m, 4H, $CH_2CH_2CH_2CH_3$), 2.17 (s, 3H, $N{=}CCH_3$), 2.74 (dd, J = 9, 17 Hz, 1H, H_{3a}), 3.2 (dd, J = 6, 17 Hz, 1H, H_{3b}), 3.4 (m, 1H, $CO_2C(H)HCH_2$), 3.6 (m, 1H, $CO_2C(H)HCH_2$), 3.96 (dd, J = 6, 9 Hz, 1H, H_4), 7.0–7.7 (m, 10 H, arom). ^{13}C NMR: δ 13.6, 19.1, 19.6 ($N{=}CCH_3$), 30.1, 42.9 ($N{=}CCH_2$), 53.0 (CO_2CH_2), 64.6 ($CHCO_2$), 87.7 (CPh_2), 126.8, 127.0, 127.4, 127.6, 128.0, 128.4, 142.9, 145.9, 172.4 (N=C), 172.6 (CO_2). GC-MS: m/z 335 (M, 11), 234 (14), 207 (91), 165 (100), 139 (8), 115 (21); ES: m/z 336 (M + 1). IR ν 1733 (s), 1661 (m) cm^{-1}. Anal. Calcd for $C_{22}H_{25}NO_2$: C, 78.77; H, 7.51; N, 4.18. Found: C, 78.86; H, 7.64; N, 4.17.

4-((Isodecyloxy)carbonyl)-2-methyl-5,5-diphenyl-1-pyrroline (10). Yellow oil. Yield: 39 mg, 37%. ^{1}H NMR: δ 0.8–1.3 (m, 19H), 2.16 (s, 3H, $CH_3C{=}N$), 2.74 (dd, J = 9, 15 Hz, 1H, H_{3a}), 3.16 (dd, J = 6, 15 Hz, 1H, H_{3b}), 3.35 (m, 1H, CO_2CH_2), 3.56 (m, 1H, CO_2CH_2), 3.96 (dd, J = 6, 9 Hz, 1H, H_4), 6.9–7.7 (m, 10H, arom). ^{13}C NMR: δ 14.0, 19.4 ($N{=}CCH_3$), 20.0, 22.6, 26.3, 26.5, 29.3, 29.7, 30.0, 32.1, 43.0 ($N{=}CCH_2$), 54.0 ($CHCO_2$), 81.3 (CO_2CH_2), 87.6 (CPh_2), 126.1, 126.6, 127.2, 127.7, 128.0, 128.3, 143.1, 146.6, 171.1 (C=N), 173.2 (C=O). GC-MS: m/z 419 (M, 4), 348 (8), 234 (12), 207 (97), 165 (100), 115 (22), 91 (13), 55 (54). ES (+): m/z 420 (M + 1). Anal. Calcd for $C_{28}H_{37}NO_2$: C, 80.15; H, 8.89; N, 3.34. Found: C, 80.37; H, 8.65; N, 3.28.

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[26] We have checked that irradiation of carbene complex **1** in the presence of 1 equiv of PPh_3 leads to the substitution of one CO by the phosphine ligand. However, this substitution does not take place by heating **1** with PPh_3 at 110 °C for 12 h. On the other hand, the irradiation of **1** and methyl vinyl ketone under a CO atmosphere for 1 h only inhibits the formation of **6** in a 5% amount.

[27] After irradiation of Fischer carbene complexes, similar coordinated structures has been isolated for intramolecular processes: (a) Barluenga, J.; Aznar, F.; Gutiérrez, I.; Martín, A.; García-Granda, S.; Llorca-Baragaño, M. A. *J. Am. Chem. Soc.* **2000**, *122*, 1314. (b) Toledano, C. A.; Rudler, H.; Daran, J.-C.; Jeannin, Y. *J. Chem. Soc., Chem. Commun.* **1984**, 574.

[28] (a) Barluenga, J.; López, S.; Trabanco, A. A.; Fernández-Acebes, A.; Flórez, J. *J. Am. Chem. Soc.* **2000**, *122*, 8145. (b) Buchert, M.; Reissig, H.-U. *Chem. Ber.* **1992**, *128*, 2723. (c) Harvey, D. F.; Lund, K. P. *J. Am. Chem. Soc.* **1991**, *113*, 8916.

[29] To carry out cyclopropanation processes with electron-rich olefins, it is necessary to use high CO pressures to avoid metathesis. See for example: (a) Fischer, E. O.; Dötz, K. H. *Chem. Ber.* **1972**, *105*, 3966. (b) Dorrer, B.; Fischer, E. O.; Kalbfus, W. *J. Organomet. Chem.* **1974**, *81*, C20. (c) Wulff, W. D.; Yang, D. C.; Murray, C. K. *Pure Appl. Chem.* **1988**, *60*, 137.

[30] Propiophenone and 2-pentanone imines were prepared according to: Barluenga, J.; Joglar, J.; Fustero, S.; Gotor, V.; Krüger, C.; Romao, M. J. *Chem. Ber.* **1985**, *118*, 3652.

4-(*tert*-Butoxycarbonyl)-2-methyl-5,5-diphenyl-1-pyrroline (11). Colorless oil. Yield: 29 mg, 35%. ^{1}H NMR: δ 1.05 (s, 9H, ^{t}Bu), 2.22 (s, 3H, CH_3), 2.80 (dd, J = 9, 18 Hz, 1H, H_{3a}), 3.26 (dd, J = 6, 18 Hz, H_{3b}), 3.92 (dd, J = 6, 9 Hz, 1H, H_4), 7.0−7.8 (m, 10H, arom). ^{13}C NMR δ 19.6 (N=CCH_3), 27.4 (C(CH_3)$_3$), 43.3 (CH_2), 54.0 (CH), 80.9 (*C*(CH_3)$_3$), 87.6 (*C*Ph_2), 126.8, 126.9, 127.2, 127.6, 127.8, 128.1, 143.5, 146.4, 171.2 (C=N), 172.5 (C=O). GC-MS: *m*/*z* 335 (M, 8), 278 (8), 262 (9), 234 (10), 207 (89), 165 (100), 115 (23), 57 (21). ES (+): *m*/*z* 336 (M + 1). Anal. Calcd for $C_{22}H_{25}NO_2$: C, 78.77; H, 7.51; N, 4.18. Found: C, 78.85; H, 7.59; N, 4.06.

(3*R,4*R**)-3,4-Bis(methoxycarbonyl)-2-methyl-5,5-diphenyl-1-pyrroline (12a).** Yellow oil. Yield: 49 mg, 56%. ^{1}H NMR: δ 1.61 (s, 3H, CH_3C=N), 2.36 (d, J = 6 Hz, 1H, H_4), 2.46 (d, J = 6 Hz, 1H, H_3), 3.45 (s, 3H, CO_2CH_3), 3.74 (s, 3H, CO_2CH_3), 7.2−7.6 (m, 10H, arom). ^{13}C NMR: δ 20.5 (*C*H_3C=N), 34.2 (CO_2*C*H_3), 34.5 (CO_2*C*H_3), 51.3 (CH), 51.8 (CH), 53.3, 127.9, 128.2, 128.4, 128.6, 129.9, 130.2, 137.3, 140.0, 168.7 (*C*O_2CH_3), 169.7 (*C*O_2CH_3), 172.1 (C=N). GC-MS: *m*/*z* 351 (M, 9), 292 (10), 260 (6), 207 (100), 166 (78), 115 (9). ES (+): *m*/*z* 352 (M + 1).

4,4,7-Triphenyl-6,8-dioxo-3,7-diazabicyclo[3.3.0]oct-2-ene (13). Yellow solid. Yield: 36 mg, 38%. Mp: 123−125 °C. ^{1}H NMR: δ 2.33 (s, 3H, CH_3), 4.21 (d, J = 15 Hz, 1H, H_3), 4.35 (d, J = 15 Hz, 1H, H_4), 6.6−7.8 (m, 15H, arom). ^{13}C NMR: δ 22.9 (CH_3), 55.3 (N=C*C*H), 68.2 (*C*HCPh_2), 87.6 (*C*Ph_2), 125.9, 127.2, 127.7, 128.2, 128.5, 128.9, 129.1, 130.1, 130.9, 131.2, 141.1, 144.7, 166.8 (C=N), 172.1 (C=O), 173.6 (C=O). GC-MS: *m*/*z* 380 (M, 4), 261 (3), 232 (6), 207 (58), 165 (100), 139 (12), 115 (16), 91 (22), 77 (24), 51 (19). ES (+): *m*/*z* 381 (M + 1). Anal. Calcd for $C_{25}H_{20}N_2O_2$: C, 78.93; H, 5.30; N, 7.36. Found: C, 79.05; H, 5.38; N, 7.29.

3-Methyl-1,1,4,4-tetraphenyl-2-aza-1,3-butadiene (14). Yellow solid. Yield: 23 mg, 25%. Mp: 89−91 °C. ^{1}H NMR: δ 1.87 (s, 3H, CH_3), 6.70−7.60 (m, 20H, arom). ^{13}C NMR: δ 21.3 (CH_3), 121.7 (C_4), 125.1, 126.2, 127.4, 127.5, 127.7, 127.9, 128.1, 128.5, 128.9, 129.0, 130.2, 130.6, 137.0, 139.0, 141.4, 142.4, 144.1 (C_3), 166.0 (C_1). GC-MS: 373 (M, 5), 358 (3), 296 (6), 165 (100), 139 (15), 115 (26) 91 (18), 77 (22), 51 (20). ES (+): *m*/*z* 374 (M + 1). IR ν 3682 (w), 3600 (w), 3026 (m), 2924 (m), 1713 (m), 1620 (s), 1596 (s), 1492 (s), 1444 (s), 1316 (m) cm^{-1}. Anal. Calcd for $C_{28}H_{23}N$: C, 90.04; H, 6.21; N, 3.75. Found: C, 90.14; H, 6.23; N, 3.63.

(4*S,5*R**)-4-Acetyl-5-ethyl-2-methyl-5-phenyl-1-pyrroline (19a) and (4*S**,5*S**)-2-Methyl-4-acetyl-5-ethyl-5-phenyl-1-pyrroline (19b).** These two compounds were obtained as a mixture. **19a**: yield 50%; ^{1}H NMR δ 0.9 (t, 3H, CH_2*C*H_3), 1.52 (s, 3H, CO−CH_3), 2.1 (q, 2H, *C*H_2CH_3) 2.29 (s, 3H, N=C−CH_3), 2.74 (dd, J = 9, 15 Hz, 1H, H_{3a}), 2.95 (dd, J = 6, 15 Hz, 1H, H_{3b}), 3.4 (m, 1H, H_4), 7.2−7.5 (m, 5H, arom); ^{13}C NMR δ 8.6 (CH_2*C*H_3), 19.5 (N=C*C*H_3), 28.6 (CO*C*H_3), 35.1 (*C*H_2CH_3), 42.6 (N=C*C*H_2), 60.9 (CO-*C*H), 84.3 (Ph*C*), 125.8, 126.6, 128.3, 141.3, 173.2 (N=C), 208.3 (CO). **19b**: yield 31%; ^{1}H NMR δ 0.9 (t, 3H, CH_2*C*H_3), 2.14 (s, 3H, $COCH_3$), 2.3 (q, 2H, *C*H_2-CH_3), 2.21 (s, 3H, N=CCH_3), 2.54 (dd, J = 9, 15 Hz, 1H, H_{3a}), 3.11 (dd, J = 6, 15 Hz, 1H, H_{3b}), 3.4 (m, 1H, H_4), 7.2−7.5 (m, 5H, arom); ^{13}C NMR δ 8.9 (CH_2*C*H_3), 19.7 (N=C*C*H_3), 29.6 (CO*C*H_3), 35.1 (*C*H_2CH_3), 41.6 (N=C*C*H_2), 63.6 (CO*C*H), 82.6 (Ph*C*), 126.2, 128.1, 128.5, 145.9, 173.0 (N=C), 207.6 (CO). **19a** + **19b**: GC-MS *m*/*z* 229 (M, 5), 186 (35), 134 (20), 117 (100), 96 (29), 77 (15); IR ν 1706 (s), 1657 (m) cm^{-1}. Anal. Calcd for $C_{15}H_{19}NO$: C, 78.56; H, 8.35; N, 6.11. Found: C, 78.43; H, 8.30; N, 6.20.

4-Acetyl-5,5-diethyl-2-methyl-1-pyrroline (20). Yellow oil. Yield: 24 mg, 54%. ^{1}H NMR: δ 0.74 (t, 3H, CH_2*C*H_3), 0.85 (t, 3H, CH_2*C*H_3), 1.4−1.6 (m, 4H, 2CH_2), 2.13 (s, 3H, N=CCH_3), 2.18 (s, 3H, O=CCH_3), 2.38 (dd, J = 6, 16 Hz, 1H, H_{3a}), 3.01 (dd, J = 6, 16 Hz, 1H, H_{3b}), 4.19 (dd, J = 6, 6 Hz, 1H, H_4). ^{13}C NMR: δ 19.6 (N=CCH_3), 25.5 (CH_2*C*H_3), 25.6 (CH_2*C*H_3), 29.4 ($COCH_3$), 31.3 (CH_2), 31.4 (CH_2), 41.6 (N=C*C*H_2), 56.0 (COCH), 80.6 (CEt_2), 165.3 (C=N), 207.8 (CO). GC-MS: *m*/*z* 181 (M, 3), 138 (49), 110 (43), 96 (65), 82 (32), 67 (27), 55 (100). ES (+): *m*/*z* 182 (M + 1). Anal. Calcd for $C_{11}H_{19}NO$: C, 72.88; H, 10.56; N, 7.73. Found: C, 72.94; H, 10.55; N, 7.77.

(4*S,5*R**)-4-Acetyl-2-methyl-5-phenyl-1-pyrroline (21).** Yellow oil. Yield: 22 mg, 43%. ^{1}H NMR: δ 1.59 (s, 3H, CH_3C=N), 2.12 (s, 3H, CH_3CO) 3.12 (dd, J = 9, 17.5, 1H, H_{3a}), 3.74 (m, 1H, H_{3b}), 3.79 (m, 1H, H_4), 5.72 (d, J = 9 Hz, 1H, H_5), 7.2−7.9 (m, 5H, arom). ^{13}C NMR: δ 20.3 (*C*H_3C=N), 30.4 (CO*C*H_3), 34.3 (CH_2), 55.1 (*C*HCO), 77.3 (*C*HPh), 128.0, 128.3, 129.2, 140.4, 168.2 (C=N), 203.9 (CO). GC-MS: *m*/*z* 201 (M, 5), 186 (100), 158 (43), 124 (16), 109 (25), 91 (33). ES (+): *m*/*z* 202 (M + 1). IR ν 1712 (s), 1635 (m) cm^{-1}. Anal. Calcd for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.73; H, 7.44; N, 6.85.

(4*S,5*R**)-4-Acetyl-2,5-diphenyl-1-pyrroline (22a).** Yellow solid. Yield: 15 mg, 23%. ^{1}H NMR: δ 1.66 (s, 3H, CH_3), 3.01 (dd, J = 8.5, 17.5 Hz, 1H, H_{3a}), 3.72 (m, 1H, H_{3b}), 3.87 (m, 1H, H_4), 5.77 (d, J = 9 Hz 1H, H_5), 7.2−7.9 (m, 10H, arom). ^{13}C NMR: δ 30.4 (CO*C*H_3), 37.1 (CH_2), 55.7 (*C*HCO), 78.2 (*C*HPh), 127.9, 128.0, 128.5, 128.7, 129.2, 131.0, 133.7, 138.4, 173.1 (C=N), 206.6 (CO. GC-MS: *m*/*z* 263 (M, 3), 220 (100), 193 (34), 158 (11), 115 (14), 89 (12). ES (+): *m*/*z* 264 (M + 1). IR: ν 1708 (s), 1623 (m) cm^{-1}. Anal. Calcd for $C_{18}H_{17}NO$: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.67; H, 7.45; N, 6.99.

3-Acetyl-2,5-diphenyl-1-pyrroline (22b). Yellow oil. Yield: 13 mg, 20%. ^{1}H NMR: δ 2.22 (s, 3H, CH_3), 3.4 (m, 3H, H_5, H_4), 5.4 (m, 1H, H_3), 7.3−7.9 (m, 10H, arom). ^{13}C NMR: δ 30.0 (CH_3), 38.2 (C_4), 59.3 (C_3), 79.0 (C_5), 126.7, 127.6, 128.0, 128.5, 128.8, 131.0, 133.6, 143.1, 171.7 (C=N), 207.4 (CO). GC-MS: *m*/*z* 263 (M, 3), 220 (100), 193 (34), 158 (11), 115 (14), 89 (12). ES (+): *m*/*z* 264 (M + 1). IR: ν 2963 (w), 1710 (s), 1624 (m) cm^{-1}.

Irradiation of Compound 22a. A solution of 10 mg of compound **22a** was irradiated in a Pyrex NMR tube with a 125 W medium-pressure mercury lamp and monitored by ^{1}H NMR. After 30 min of irradiation only compound **22b** could be detected together with some polymeric material.

5,7-Diphenyl-6-aza-4,6-heptadien-2-one (23). Yellow oil. Yield: 7 mg, 15%. ^{1}H NMR: δ 2.22 (s, 3H, CH_3), 3.58 (d, J = 7.5 Hz, 2H, CH_2), 5.71 (t, J = 6 Hz, 1H, CH), 7.4−7.7 (m,10 H, arom), 8.17 (s, 1H, N=C−H). ^{13}C NMR: δ 29.2 (*C*H_3CO), 42.4 (CH_2), 112.8 (CH=C), 127.3, 127.9, 128.4, 128.6, 128.7, 128.8, 137.3, 138.6, 152.3, (*C*N=C), 163.2 (N=C), 208.4 (CO). GC-MS: *m*/*z* 263 (M, 6), 220 (100), 193 (43), 158 (15), 115 (9); ES (+): *m*/*z* 264 (M + 1). IR ν 3015 (w), 2927 (vs), 1723 (vs), 1686 (sh), 1510 (m), 1184 (m) cm^{-1}. Anal. Calcd for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.69; H, 7.39; N, 6.82.

Isolation of Compounds 24 and 25. The reaction was carried out as shown in the General Procedure of Irradiation, except for the reaction time. The mixture was irradiated for 1 h, and then the crude product was worked up as stated above.

Ethyl 2-((Diphenylmethylene)amino)-2-methylcyclopropanecarboxylate (24). Yellow oil. Yield: 9 mg, 12%. ^{1}H NMR: δ 0.84 (dd, J = 5.7, 8.1, 1H), 1.17 (dd, J = 5.7, 5.7, 1H), 1.26 (t, 3H, CH_2*C*H_3), 1.55 (s, 3H), 1.86 (dd, J = 5.7, 8.1, 1H), 4.14 (d, *C*H_2CH_3), 7.2−7.6 (m, 10H, arom). ^{13}C NMR: δ 14.2, 20.0, 25.4, 30.5, 48.9, 62.2, 127.8, 128.0, 128.7, 128.9, 130.0, 132.2, 138.0, 140.2, 170.6 (C=N), 172.5 (C=O). GC-MS: *m*/*z* 307 (M, 9), 234 (15), 207 (81), 165 (100), 115 (33. ES (+): *m*/*z* 308 (M + 1). IR: ν 2964 (m), 1717 (s), 1649 (m) cm^{-1}. Anal. Calcd for $C_{20}H_{21}NO_2$: C, 78.15; H, 6.89; N, 4.56. Found: C, 78.43; H, 6.81; N, 4.43.

Butyl 2-((diphenylmethylene)amino)-2-methylcyclopropanecarboxylate (25). Yellow oil. Yield: 16 mg, 20%. ^{1}H NMR: δ 0.9−1.9 (m, 10H), 1.56 (s, 3H, CH_3), 4.1 (m, 2H, CO_2-CH_2), 7.2−7.5 (m, 10H, arom). ^{13}C NMR: δ 13.7, 19.2, 22.8, 26.5, 29.8, 30.8, 48.8, 64.3, 127.9, 128.0, 128.5, 128.7, 130.0, 132.4, 138.3, 140.7, 170.7 (C═N), 171.4 (C═O). GC-MS: *m*/*z* 335 (M, 8), 234 (9), 207 (82), 165 (100), 115 (21). ES (+): *m*/*z* 336 (M + 1). IR: ν 2964 (m), 1719 (s), 1622 (m) cm^{-1}. Anal. Calcd for $C_{22}H_{25}NO_2$: C, 78.77; H, 7.51; N, 4.18. Found: C, 78.65; H, 7.49; N, 4.25.

Irradiation of Compounds 24 and 25. A solution of 10 mg of compound **24** or **25** was irradiated in a Pyrex NMR tube with a 125 W medium-pressure mercury lamp and monitored by ^{1}H NMR. After 30 min of irradiation only compound **5** or **9** could be detected together with some polymeric material.

Measurement of Quantum Yield. The solution filter was prepared with $NiSO_4\cdot6H_2O$ (200 g/L), K_2CrO_4 (0.2 g/L), and potassium hydrogen phthalate (5 g/L). This solution transmits in the range 305−335 nm, with a λ_{max} value of 313 nm. The absorbances of a solution of carbene **1** in hexane (ca. 10^{-4} M) and methyl vinyl ketone (10 equiv) and a solution of the actinometer (2-hexanone) in hexane were adjusted to be equal at 313 nm. The two solutions were irradiated through the solution filter with a 125 W medium-pressure mercury lamp for 4 min. The chemical changes in both solutions were monitored by GC/MS with an internal standard of biphenyl (ca. 10^{-4} M).

Stern−Volmer Analysis. A solution of carbene complex **1** (5×10^{-3} M) and methyl vinyl ketone (15 mmol, 10 equiv) was prepared in deoxygenated hexane (300 mL). Aliquots of this solution (40 mL) were irradiated for 15 min through a Pyrex glass with a 125 W medium-pressure mercury lamp after the addition of different amounts of quencher: 0, 0.5, 0.75, 1, 3, 5, and 7 equiv (0, 12, 18, 25, 74, and 178 mmol). After the irradiation, the solutions were monitored by GC/MS with an internal standard of biphenyl (ca. 10^{-3} M).

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