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Photochemical reactions of chromium imine–carbene complexes with heteroatom-containing double bonds

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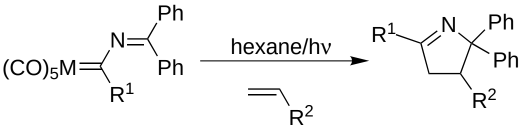
Abstract—The irradiation of chromium imine–carbene complexes in the presence of heteroatom-containing double bonds leads to the formation of azadienes through a metathesis process and/or heterocycles through a formal [3+2] cyclization. © 2001 Elsevier Science Ltd. All rights reserved.

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 which occurs with formation of a mixture of different products has been described.[2] We have previously reported the photochemical cyclopentannulation of imine–carbene complexes with alkenes and alkynes as a good method for the synthesis of 1-pyrroline and 2*H*-pyrrole derivatives (Scheme 1).[3]

In this case, we found that when the irradiation of the carbene complex **1a** was carried out without any unsaturated compound, the reaction yielded the metathesis compound between the carbene Cr=C bond and the imine N=C bond of the other carbene molecule (Scheme 2).[3] The formation of **2a** supposes an interaction between nitrogen and chromium atoms. Such an interaction was previously reported for metal-mediated imine metathesis.[4] Thus, we found it of interest to study the reaction between imine–carbene complexes and heteroatom-containing double bonds. Herein, we report our findings.



Scheme 1.

First, we analyzed the metathesis procedure. The yield for this reaction is concentration-dependent since two molecules of the imine–carbene complex are needed. Highest yields for 2-azadiene **2a** can be obtained for high concentrations of **1a** (2.5 mmol in 50 mL hexane) irradiated for a short time (40 min). Under these conditions, compound **2a** was isolated in 20% accompanied with the recovery of most of the starting carbene. A longer irradiation causes higher levels of polymerization due to the reactivity of the azadiene in the reaction conditions. Moreover, it is also possible to carry out the cross metathesis between two different carbene complexes (Scheme 3). In this case, all four compounds are formed almost equimolecularly in 19% total yield, together with polymeric material. The four different products were identified by GC/MS.

This metathesis reaction between two different carbene molecules prompted us to study the irradiation of the carbene complexes in the presence of imines. Thus, we irradiated the carbene complex **1a** with a 125 W medium-pressure mercury lamp using hexane as solvent with 10 equiv. of benzophenone imine until the total consumption of the starting carbene (2 h for 0.25 mmol of **1a**, monitored by TLC, hexane/CH_2Cl_2 1:1). We could check that the same metathesis compound **2a** was formed, although the yield increased to 29%. In a

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Keywords: chromium compounds; photochemistry; metathesis; cyclization.

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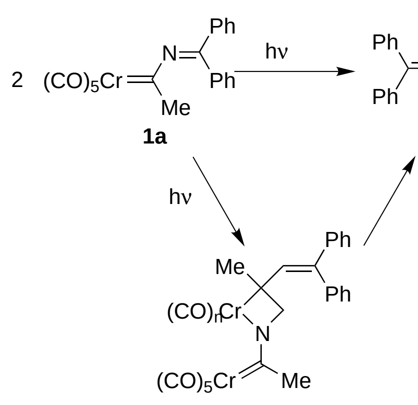
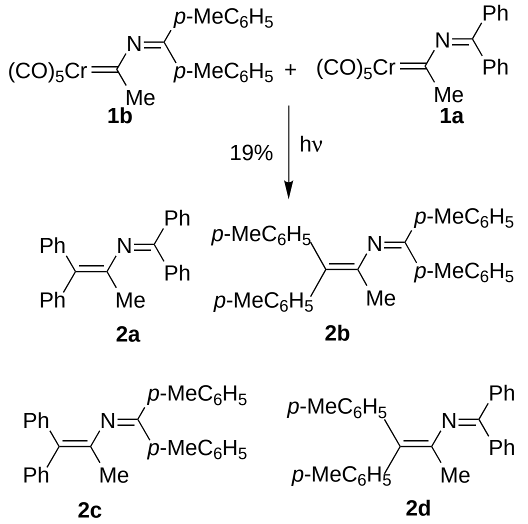


Scheme 2.



Scheme 3.

similar way, irradiation of **1a**, in the presence of 10 equiv. of a Schiff base derived from benzophenone, gave a 27% yield of the same product (Scheme 4). **2e** could be obtained from 3-pentanone imine and also from *N*-(diethylmethylidene)phenylamine (Scheme 4). This reaction leads to the preparation of 2-azadienes that have a high versatility in synthetic procedures.[5] The photochemistry of these compounds is under study in our research group.[6]

Next, we were interested in the photochemical behavior of carbene complexes in the presence of azocompounds which possess an N=N double bond. The irradiation of **1a** with 10 equiv. of azobenzene led to the formation of the 1,3-diaza-1,3-butadiene **3** in a 22% yield and the triazoline **4** in a 35% yield. In this case, the metathesis is not the only possible reaction path. The metathesis leads to the diazabutadiene, but the triazoline is obtained through a cycloaddition process analogous to the one previously reported by us[3] for the photoreaction of imine–carbene complexes with alkenes (Scheme 5).

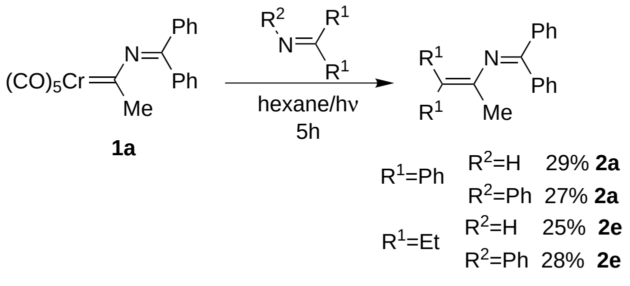
Then, in order to assess the necessity of a nitrogen atom in the unsaturated compound, we paid attention to the reaction with ketones. In this case, there were no traces of the metathesis reaction but the irradiation yielded oxazolines. Ketones with both aliphatic and aromatic substituent can be used (Scheme 6). The products were fully characterized by their spectroscopic data (^{1}H and ^{13}C NMR) and mass spectrometry. The configuration assignment of compound **5a** was made on the basis of X-ray diffraction (Fig. 1). The main side product of these reactions was benzophenone from the carbene complex decomposition.

When we tried to carry out this reaction in the presence of aldehydes, the corresponding heterocycle could be detected in the reaction crude by GC/MS, but all the efforts made to separate failed.

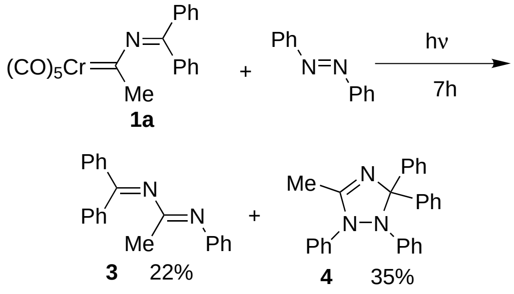
In conclusion, we have reported the photochemical metathesis reaction of imine–carbene complexes to yield azadienes when irradiated in the presence of compounds with C=N or N=N double bonds. The irradiation in the presence of ketones and azocompounds yielded cycloaddition products.

Carbene complexes irradiation. The carbene complex **1a** (2 mmol) or a mixture of **1a** (1 mmol) and **1b** (1 mmol) was dissolved in 50 mL of deoxygenated hexane and irradiated at room temperature under an argon atmosphere, through Pyrex glass with a 125 W medium-pressure mercury lamp. After 40 min, the solvent was removed with a rotary evaporator, and the products were purified by column chromatography (silica gel, hexane/Et$_2$O).

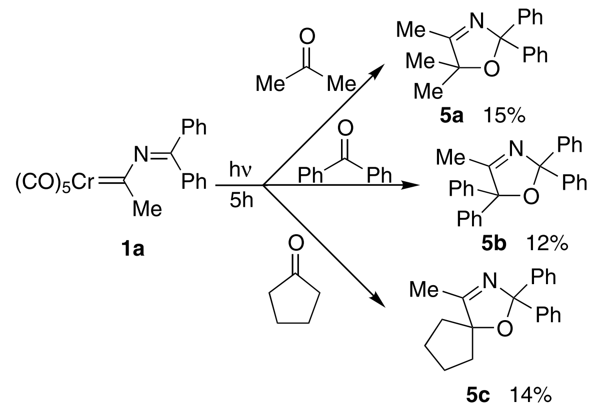
General procedure for irradiation in the presence of unsaturated compounds. The carbene complex **1a** (0.25 mmol) was dissolved in 50 mL of deoxygenated hexane. Ten equivalents of the unsaturated compound were added, and the mixture was irradiated at room temper-



Scheme 4.



Scheme 5.



Scheme 6.

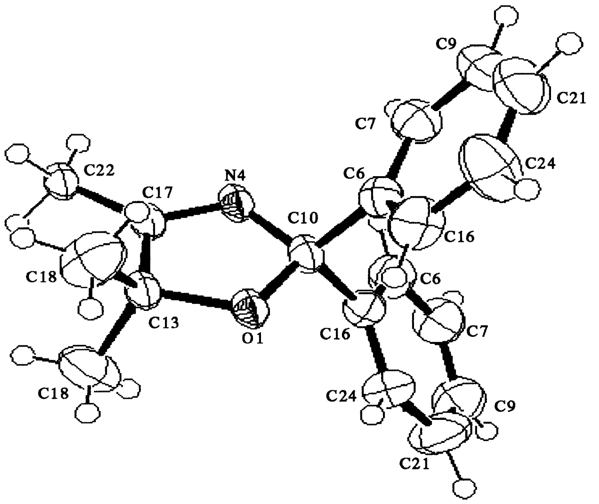


Figure 1. ORTEP diagram for compound **5a**.[7]

ature under an argon 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 product was purified by column chromatography (silica gel, hexane/Et_2O).

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7. Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 167120. The compound **5a** was purified by recrystallization in hexane/CH_2Cl_2 (mp 103–105°C). A colorless crystal of **5a** ($C_{18}H_{19}NO$, MW = 265.36) was transferred to the goniostat. The data were collected at room temperature with an Enraf Nonius apparatus with Kappa geometry and an electronic CCD detector. It was determined a monoclinic symmetry with a *Pm* space group. Unit cell parameters are $a=6.4824$, $b=14.9596$, $c=8.3545$ Å, $\beta=112.052°$, and $D_{\text{calcd}}=1.174$ g/cm^3 for $Z=2$. A total of 3036 unique data were collected for $0.99\geq 2\theta\geq 27.49°$. The structure was solved by direct methods using SHELX-97 with a GOF = 1.543. Final residuals are $R(F)=0.085$ and $R_w(F)=0.2284$.