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Photochemistry of Group 6 Fischer Carbene Complexes: Beyond the Photocarbonylation Reaction

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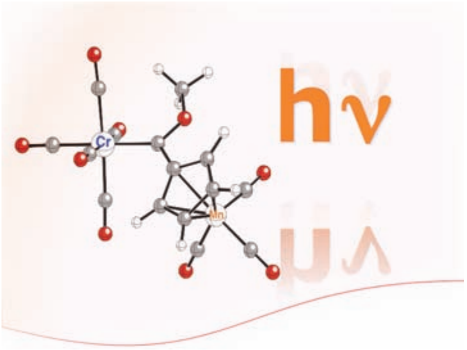

The seminal report by Hegedus in 1982, showing that alkoxychromium(0) carbenes reacted with imines under bright Colorado sunlight to yield β-lactams, marked the beginning of a key reaction in organometallic chemistry. Very little was known about the mechanism of this reaction. In fact, Hegedus proposed the reversible generation of a chromium-coordinated ketene, which would react with nucleophiles. This coordinated species would show all the advantages of ketenes without their shortcomings, namely, dimerization, formation of undesired adducts, and so forth. The quest for the detection of these species and the pursuit of the mechanism of the photocarbonylation (a reaction exclusive to Cr(0) and Mo(0) carbene complexes, not W(0) carbene complexes) remained unabated over the next 15 years. In fact, all attempts to experimentally determine the mechanism of this useful reaction have been fruitless. At the same time, the photocarbonylation of Cr(0) carbenes matured into a valuable synthetic reaction, allowing access to several families of organic compounds. Unfortunately, reactions other than photocarbonylation remained elusive.

We used a combination of experimental and computational methodologies to study the photocarbonylation of Cr(0) carbene complexes and the subsequent reaction of the photogenerated ketenes with nucleophiles. In parallel, we discovered new photochemical processes and succeeded in making photoreactive the so-called "unreactive" W(0) carbene complexes. In this Account, we discuss the disentangling of the mechanisms of these transformations, thereby *shedding some light* onto the photochemistry of group 6 metal (Fischer) carbene complexes.

The original designation of the electronic transitions of group 6 carbene complexes was reassigned, and the photocarbonylation step was analyzed again, resulting in the sequence $S_0-T_1-S_0$, which is far removed from conventional organic photochemistry. The T_1 species is a chromacyclopropanone; its unpaired electrons are primarily localized in the metal fragment and in the former carbene carbon atom. The T_1-S_0 intersystem crossing occurs with the participation of the solvent through an unusual loose-bolt radiationless mechanism. The photogenerated S_0 species reacts with imines to form the final β-lactams in a mechanism that resembles the organic Staudinger reaction, but here the metal is present during the entire reaction coordinate. The selectivity of these reactions is defined by the nucleophilic attack on the O-bonded metallaketene instead of the subsequent conrotatory ring closure, a distinct departure from the organic reaction. Appropriate modification of the substituents of the carbene ligand or in the coordination sphere of the complex results in new photoprocesses; these include 1,2-metalladyotropic rearrangements as well as α-fragmentations in which W(0) carbene complexes become photoreactive. Moreover, the inclusion of additional metal centers usually results in new reactions, such as the formation of fulvenes by $\eta^5 \rightarrow \eta^3$ photoslippage, or in the complete inhibition of the photoreactivity. The photochemistry of group 6 metal–carbene complexes thus offers unexplored territory for pursuing new reactions and reaction mechanisms.

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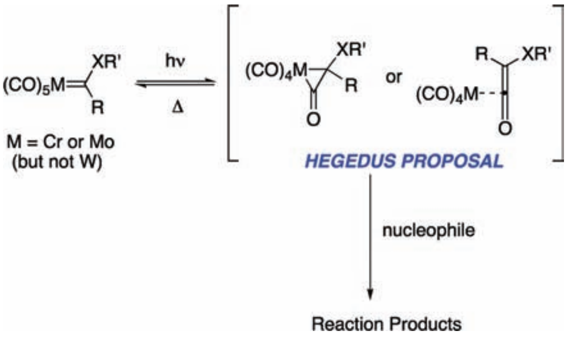
Introduction

The irradiation of group 6 (Fischer) metal–carbene complexes[1] with visible light in the presence of nucleophiles allows easy access to a wide variety of compounds (β-lactams, cyclobutanones, amino acids and peptides, polynuclear hydrocarbons, or β-lactones) in a process known as photocarbonylation reaction.[2] This rich and synthetically powerful photoreactivity has no parallel in the photochemistry of any other class of organometallic compounds. It competes in efficiency and exceeds in versatility with many well-established and synthetically useful photochemical organic reactions.[3]

Nevertheless, the synthetically useful photochemistry of chromium(0) and molybdenum(0) carbene complexes (but not tungsten(0) carbene complexes) relies exclusively on the reversible insertion of a *cis*-CO ligand into the M═C bond to yield ketene-like species. This mechanistic insight was reported by Hegedus et al. in 1988 who systematized the photochemistry of group 6 carbene complexes in the presence of nucleophiles (Scheme 1).[4] Despite the close parallelism of the ketenes derived from the irradiation of group 6 metal–carbene complexes and free ketenes, all the efforts directed toward the detection of these elusive intermediates have been fruitless so far.

SCHEME 1. Photocarbonylation Mechanism Proposed by Hegedus et al. in 1988 (see refs 2d and 4)



While the photocarbonylation of chromium(0) Fischer carbene complexes has been established as a versatile synthetic protocol, the intimacies of this fundamental transformation remained essentially unexplored for nearly 20 years. Furthermore, no other photoprocesses have been described for group 6 Fischer carbene complexes. Reported herein is a summary of the efforts carried out in our laboratories during the past decade to *shed some light* into the photochemistry of these complexes. The problem was sequentially (albeit not chronologically) addressed through the following steps.

Electronic Structure of Fischer Carbene Complexes

Group 6 metal–carbene complexes are strongly colored compounds, with their color ranging from pale yellow to dark red. The UV–visible spectra of Fischer metal–carbene complexes shows three well-defined absorptions: a spin-forbidden metal–ligand charge transfer (MLCT) absorption at around 500 nm, the spin-allowed and moderately intense ligand-field (LF) absorption in the range of 350–450 nm, and one additional LF transition in the range of 300–350 nm (Figure 1).[2d] The position of these bands strongly depends on the nature of the substituents attached to the carbene carbon atom. On the basis of early molecular orbital calculations,[5] the MLCT band was assigned to the promotion of an electron from the nonbonding metal-centered HOMO to the carbene–carbon p-atomic orbital centered LUMO, while the LF band was attributed to the more energetic transition to the metal centered LUMO+1.

With the help of TD-DFT calculations, we found interesting differences with respect to the earlier work. Thus, the HOMO → LUMO promotion is symmetry forbidden, and the MLCT band was ascribed to the promotion of one electron from the metal-centered HOMO-1 to the LUMO which is a π-extended orbital involving the p-atomic orbital of the carbene carbon atom (Figure 1). Similarly, the LF transition was assigned to the promotion of one electron from the HOMO-3 (centered in the π-system of the carbene ligand, Figure 1) to the LUMO.[6]

Both the LF and the MLCT bands have a remarkable $\pi-\pi^*$ character, which implies that the position of the wavelength maxima strongly depends on the occupation of the p_z-atomic orbital of the carbene carbon atom (mainly, the LUMO). This has been demonstrated by using different *p*-substituted styrylchromium(0) carbene complexes, where the position of the corresponding absorptions nicely correlates with the donor/acceptor nature of the substituent (measured with the respective Hammett–Brown σ_p^+ constants).[6] This accurate reassignment of the electronic spectroscopy of group 6 Fischer carbene complexes should have interesting consequences in the interpretation of the photochemistry of these and related compounds and constitutes the first step to fully understand the photochemistry of these compounds.

Photocarbonylation Process

As stated above, the photoinsertion of a *cis*-carbonyl ligand into the metal–carbene bond (process known as photocarbonylation) is undoubtedly the most important phototransformation

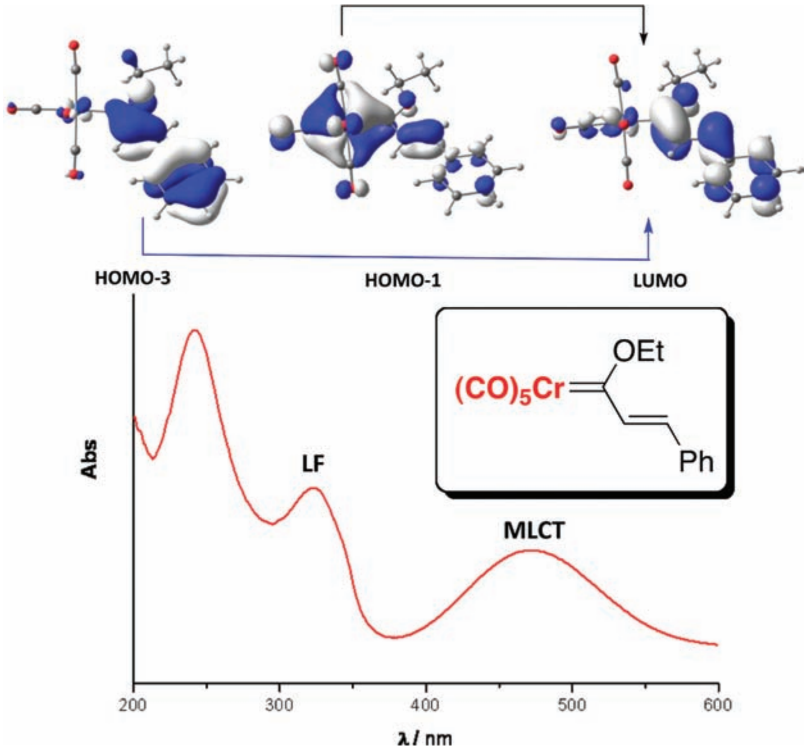


FIGURE 1. UV−vis spectrum and molecular orbitals of pentacarbonyl-ethoxystyrylchromium(0) carbene complex.

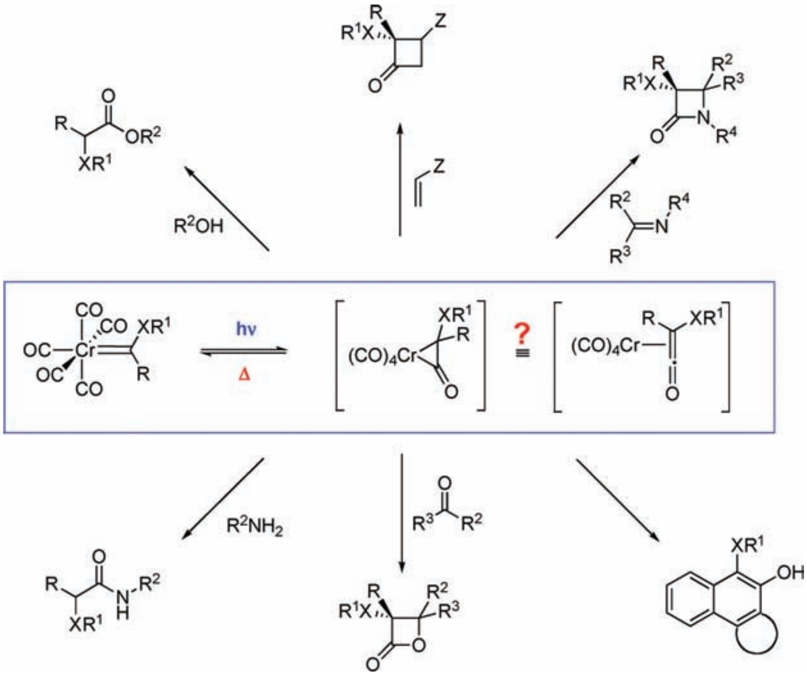
of Fischer carbene complexes.[2] The smooth ketene-like behavior of chromium(0) carbene complexes under these conditions confers them a tremendous potential as reagents in organic synthesis (Scheme 2). The reaction mechanism of this key transformation has attracted comparatively much less attention very likely due to experimental difficulties in detecting the intermediates involved in the process. Therefore, we decided to face this problem using a combination of experimental and computational (DFT) tools.[7,8]

Irradiation of alkoxychromium(0) carbene complexes, either in the LF band followed by relaxation to the MLCT band or directly in the MLCT band, results in the excitation of these complexes to the S_1 excited state, which readily decays to the triplet T_1 state by intersystem crossing (ISC) due to spin−orbit coupling.[9] These triplet species (**1(T_1)**) have a chromacyclopropanone structure whose unpaired electrons are mainly localized in the metal fragment and in the former carbene carbon atom. It is worth noting that *the triplet species **1(T_1)** corresponds with the chromacyclopropanone proposed by Hegedus and co-workers* to explain the reaction products obtained in the photochemical reaction of chromium(0) carbene complexes.[2d,4] These coordinatively unsaturated complexes change their multiplicity before evolving to the ketene-derived products (Figure 2). This is accomplished by filling the corresponding free coordination site with a molecule of a coordinating solvent in the apical position. To experimentally confirm the theoretical prediction, the photolysis of alkoxy-carbene **1** with the imine PhCH=N(p-OMeC$_6$H$_4$) was carried out in solvents with different coordinative ability. It was found the higher the donor number of the solvent (i.e., tetrahydrofuran or acetonitrile), the higher were the conversions of complex **1** into the corresponding β-lactam.[7]

The geometrical features and the NBO analysis carried out on these newly formed species (**2(S_0)**) show that they possess a structure which corresponds to a ketene species coordinated to chromium with a highly polarized Cr−C (former carbene carbon atom) bond. Therefore, complexes **2(S_0)** can be viewed as a acylchromate complexes from which ketene-derived products can now be formed in the presence of nucleophiles on the S_0 hypersurface, while in their absence these species revert to the starting carbene complex in a highly exothermic process (Figure 2).

The solvent-induced T_1−S_0 crossing of chromoketene **1(T_1)** to the acylchromate **2(S_0)** was further analyzed in detail.[10] Relaxed scans of this complex at different Cr−OH$_2$ distances, where the OH$_2$ ligand models an ethereal solvent (Figure 3), showed that the T_1 state exhibits a very shallow Morse-like curve, whose minimum is located at r = 3.746 Å, with r being the Cr−OH$_2$ distance (Figure 3). The harmonic analysis of this structure shows two low-frequency vibrations associated with stretching of the Cr−O interaction and

SCHEME 2. Photocarbonylation Reaction of Fischer Carbene Complexes and Its Applicability in Organic Synthesis



symmetrical bending of two carbonyls to achieve the octahedral coordination. This result, together with the negligible energy difference between both states at long Cr$-$OH$_2$ distances, indicates that the available thermal energy is enough for the molecule to go from the T$_1$ to the S$_0$ potential energy surface. This radiationless ISC does not take place through a narrow conical intersection (a photochemical funnel) but occurs at *r*-values larger than 4.0 Å along an energy plateau shared by both spin states. This process, which is called the loose-bolt effect in organic chemistry,[3c] has no known precedents in the photochemistry of metal complexes.

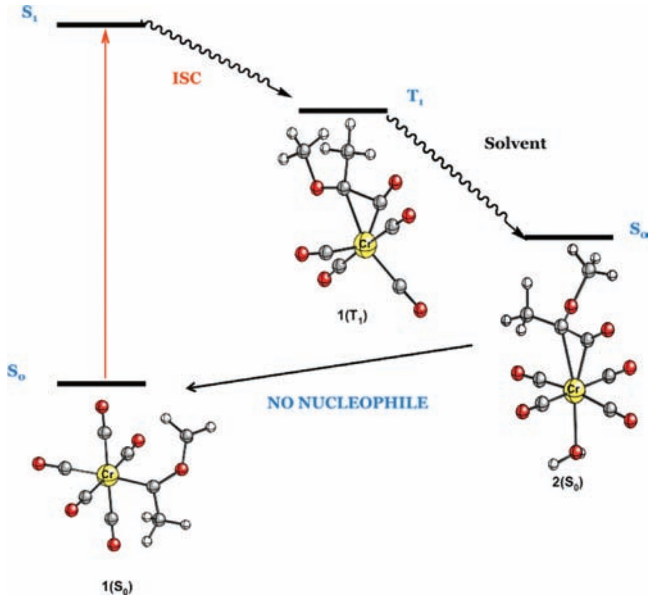


FIGURE 2. Photocarbonylation of chromium(0) carbene complexes.

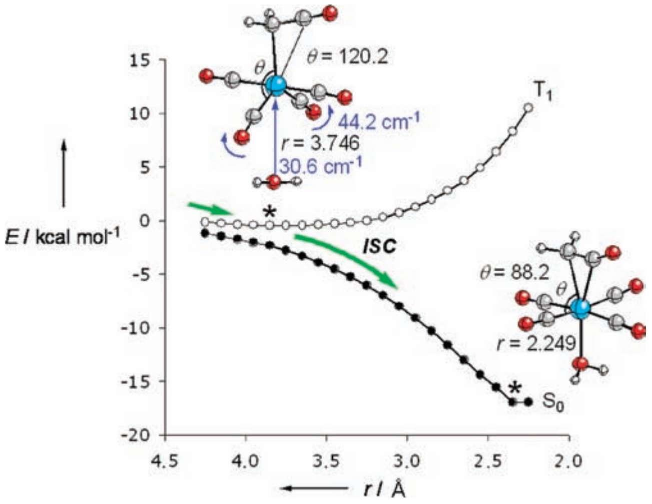
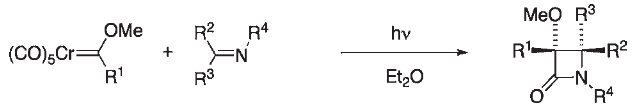


FIGURE 3. Fully relaxed scans for the model chromoketene **1** coordinated with a water molecule as a model for a coordinating ethereal solvent. The energies and geometries were computed at different Cr$-$OH$_2$ distances, denoted as *r*. Open and black circles indicate calculations for T$_1$ and S$_0$ states, respectively. Arrows indicate the stretching and bending vibrations associated with the T$_1-$S$_0$ radiationless intersystem crossing, represented by the bold arrows. Wavenumbers associated with these vibrations are given in cm^{-1}. All data have been computed at the (u)B3LYP/6-31G(d)&LANL2DZ level.

The Reaction with Imines to Yield β-Lactams

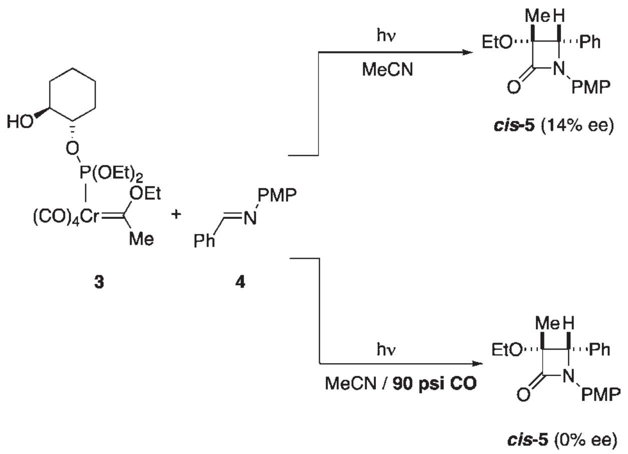
Having established a reasonable model for the photocarbonylation step in the photochemistry of chromium(0) carbene complexes, the addition of an imine to the coordinated ketene was studied next. This reaction forms 2-azetidinones in good yields, and it is usually free of byproduct (Scheme 3).[2d] The reaction is highly diastereoselective, since Fischer carbene complexes form β-lactams where the larger substituent of the ketene is placed *cis* to the *anti*-substituent of the imine. This contrasteric bias has been claimed to be due to the effect of the alkoxy-substituent during the cycloaddition.[2d]

SCHEME 3. Photolysis of Fischer Carbene Complexes with Imines to Produce 2-Azetidinones



The participation of the metal in the transformation of the chromium complex into the final products and not only in the first carbonylation step was demonstrated by irradiating the chiral complex **3** in the presence of imine **4**. This reaction yielded a mixture of *cis/trans*-β-lactams **5** in a 4.0:1 ratio with 66% conversion (Scheme 4).[12] Both diastereoisomers were separated by column chromatography, and the enantiometric excess (ee) for diastereomer ***cis*-5** (14%) was measured by ^{1}H NMR in the presence of Eu(hfc)$_3$. Even with the observed low ee, due probably to the fact that the inducing center is located far away from the emerging chiral centers, the formation of chiral products is compatible with a mechanism in which the metal is present in the enantio-discriminating step, namely, the conrotatory ring closure of the zwitterion.[11] Nevertheless, there is a possibility of organocatalysis by the free chiral phosphine which would be responsible for the observed ee.[13] To safely disregard this process, we ensured the removal of the metal moiety from the reactive system by working under moderate CO pressures (90 psi). Thus, the irradiation of complex **3** and imine **4** in MeCN under 90 psi of CO (to ensure the decomplexation of the metal moiety as Cr(CO)$_6$) gave the mixture of *cis/trans*-β-lactams **5** in a 3.8:1 ratio and in 70% isolated yield (Scheme 4). Similarly, the isomers were separated and the compound ***cis*-5** was analyzed again by ^{1}H NMR in the presence of Eu(hfc)$_3$. The ee was 0% within the experimental error, thus confirming that no asymmetric induction was obtained if the metal moiety is removed from the reactive system.

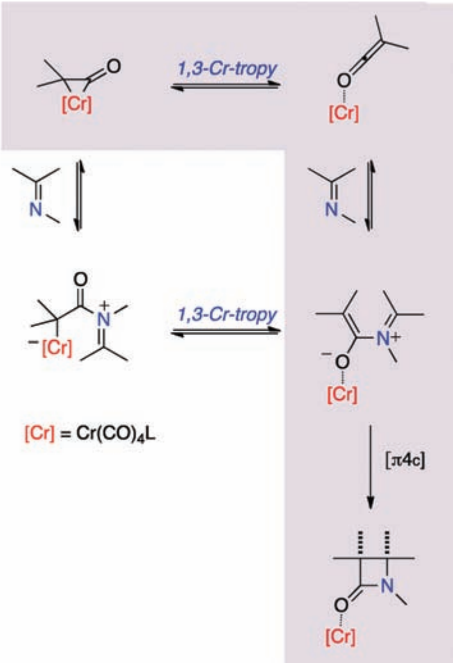
SCHEME 4. Photolysis of Chiral Complex **3** with Imine **4**



Two related reaction mechanisms can be envisaged for this transformation: (i) the nucleophilic attack of the lone pair of the nitrogen atom of the imine to the carbonyl group of the acyl-chromate **2(S$_0$)** followed by a 1,3-metallotropic process forming a chromium enolate–iminium zwitterionic complex which produces the final cycloadduct through a conrotatory ring closure or, alternatively, (ii) the 1,3-metallotropic process can occur first from the acyl-chromate to produce the corresponding O-coordinated ketene, which produces the final cycloadduct after nucleophilic attack of the imine and subsequent four electron conrotatory electrocyclation, following the standard mechanism for the Staudinger reaction (Scheme 5).[11] Using a combined experimental–computational study,[12] we confirmed the experimental result, namely the metal moiety is present during the whole reaction coordinate, and subsequently found that the 1,3-metallotropy must occur before the nucleophilic attack of the imine. This rearrangement, albeit slightly endergonic (see Figure 4), takes place due to a more favorable HOMO(imine)–LUMO+1(oxygen-coordinated ketene) interaction which constitutes the driving force of the transformation.

The stereochemical outcome of reaction should be biased to the formation of *cis*-β-lactams for (*E*)-imines attacking the oxygen-coordinated ketene in an exo-face approach. The effect of the metal moiety in the four electron conrotatory electrocyclation was compared to the process with the classical nonmetallic pathway. No significant differences between metalla- and classical reaction pathways were observed. Thus, the formation of the *cis*-β-lactams lactams is strongly favored in both cases, and therefore, it was concluded that the metal moiety has no effect in the outcome of the ring closure of the zwitterionic species (Scheme 5). However, the experimental results indicate that Fischer carbene complexes afford a significant amount of trans-β-lactams (even up to 1.4:1 *cis/trans* ratio). This fact seems to indicate that the stereochemical discrimination in the metalated reaction should occur in the nucleophilic addition of the imine nitrogen atom to the sp-hybridized carbon atom of the oxygen-coordinated ketene. This addition leads to two zwitterions derived from the *endo/exo* nucleophilic addition of the (*E*)-imine to the metalated ketene. The differences in energies between the *endo* and the *exo* attacks were consistent with the *cis/trans*-isomer ratio experimentally observed. Therefore, the estereodiscrimination in the reaction of O-metalated ketenes probably derived from the facial selectivity of the ketene (namely, the *endo/exo* ratio) and not from the final conrotatory cyclization step. The complete reaction profile for the reaction of complex **1** and MeHC=Me to form the final 2-azetidinone is shown in Figure 4.

SCHEME 5. Possible Reaction Pathways for the Addition of Imines to Photogenerated Acylchromates from Fischer Carbene Complexes



Beyond the Photocarbonylation Process

The photocarbonylation reaction can be altered or even completely inhibited by modifying the electronic structure of the initial carbene complex. Thus, it is well-known that chromium(0) carbene complexes having either two heteroatoms or alkenyl and alkynyl groups bonded to the carbene carbon, as well as tungsten(0) complexes do not undergo this transformation.[2d] The exception is the so-called "photo-Dötz" reaction reported by Merlic and co-workers.[14] Similarly, we found that the replacement of a carbonyl ligand by a soft σ-donor ligand (PPh_3) in the coordination

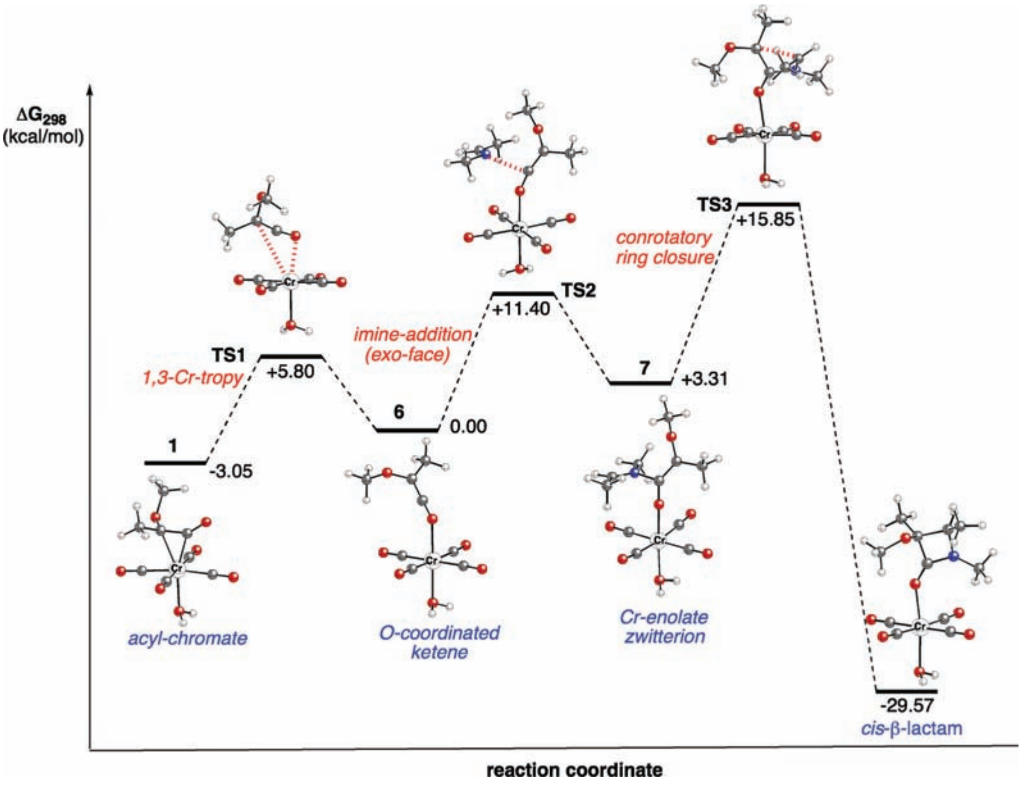
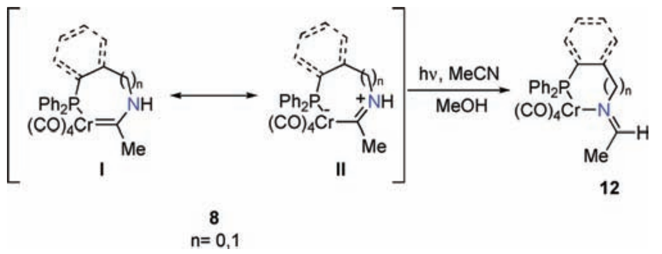


FIGURE 4. Computed reaction profile for the reaction of complex **1** and MeHC=NMe. All data have been computed at the B3LYP/6-31G(d)&LANL2DZ level.

sphere of the metal hampered the photocarbonylation reaction while strong σ-donor ligands (like PBu_3) completely inhibit the process.[7,12] In all cases, either the diminished or absent photocarbonylation is very likely due to the high occupation of the p_z atomic orbital of the carbene carbon atom, which avoids the photoinsertion of a CO ligand into the metal-carbene carbon bond.

Taking these facts into account, we prepared the amino−phosphino complexes **8** characterized by a high p_z occupation (in fact, structure II in Scheme 6 contributes significantly to the description of the complex). Irradiation of these complexes in the presence of methanol yields *N*-coordinated imines **12** without any photocarbonylation derivatives.[15] The transformation of complex **8** into imines **12** can be viewed as a formal 1,2-dyotropic rearrangement according to the original definition by Reetz.[16]

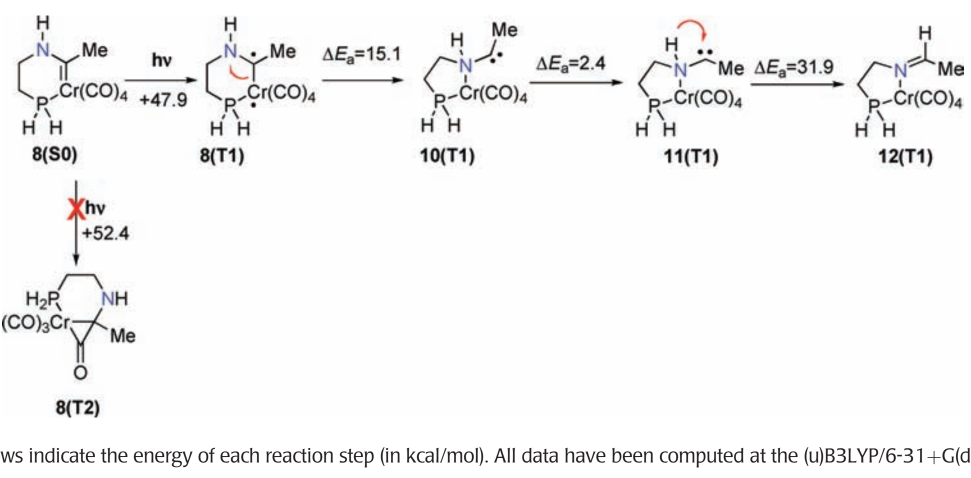
SCHEME 6. Photoreaction of Amino-Carbenes **8** to Produce Complexes **12**



Computational tools showed that this process occurs stepwise and in the triplet hypersurface starting from the biradical intermediate **8(T1)** (which is 4.5 kcal/mol more stable than the corresponding triplet metallacyclopropane **8(T2)** which would lead to the photocarbonylation products). This biradical is transformed into carbene **10(T1)**, via the migration of the metal moiety from the carbene carbon atom to the nitrogen atom. The final reaction product **12(T1)** is formed after isomerization to carbene **11(T1)** and subsequent migration of the hydrogen atom from the nitrogen to the carbene carbon atom (Scheme 7). This transformation constitutes *the first photoreaction different from photocarbonylation* described for group 6 Fischer carbene complexes. Furthermore, the tungsten(0) carbene analogues to **8** also undergo this transformation.[17] This means that complexes which were traditionally considered as photoinert complexes[2d] can indeed be reactive upon irradiation with the appropriate modifications in their electronic structures. No significant differences between chromium(0) and tungsten(0) Fischer carbene complexes were observed in the computed pathways.[18]

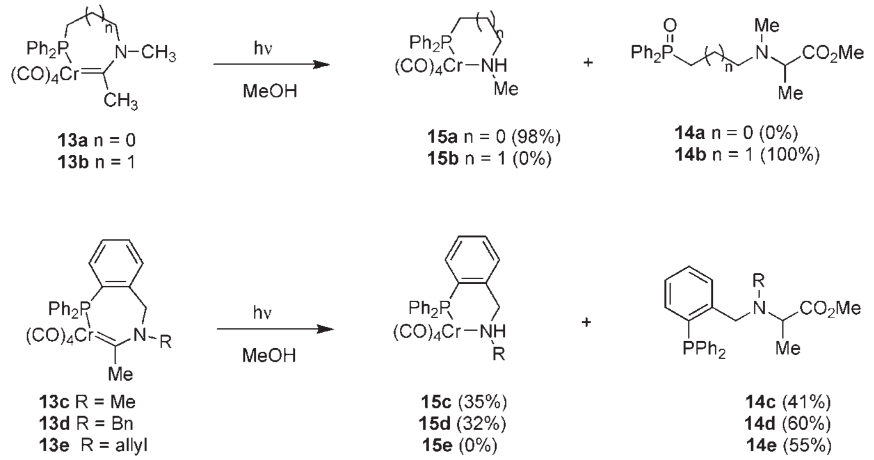
This new photodyotropic process highly depends on the structure of the carbene complex. The transformation is inhibited by replacing the hydrogen atom attached to the nitrogen by an alkyl group (very likely due to the different migratory ability of these substituents compared to the hydrogen atom). Thus, irradiation of the new series of complexes **13**, produced by alkylation of complexes **8**, leads either to mixtures of photocarbonylation products **14** and *N*-coordinated amines **15** or exclusively to one of both reaction products, depending on the structure of the starting carbene complex (Scheme 8).[18] Again, the formation of these new complexes **15** can be considered as a new photoreaction different from photocarbonylation or photodyotropy. Indeed, our calculations suggest that a new α-fragmentation process produces complexes **15** where the cleavage of the $C_{carbene}$−N bond occurs in the triplet-excited state. This process is analogous to the α-photofragmentation of amides,[19] which are the isolobal analogues of aminocarbene complexes **13**.[20]

SCHEME 7. Computed Reaction Profile for the Transformation of Aminocarbene **8** to Complex **12**[a]



[a]Numbers close the arrows indicate the energy of each reaction step (in kcal/mol). All data have been computed at the (u)B3LYP/6-31+G(d)&LANL2DZ level.

SCHEME 8. Photoreactions of Complexes **13** to Produce Complexes **15** and Esters **14**

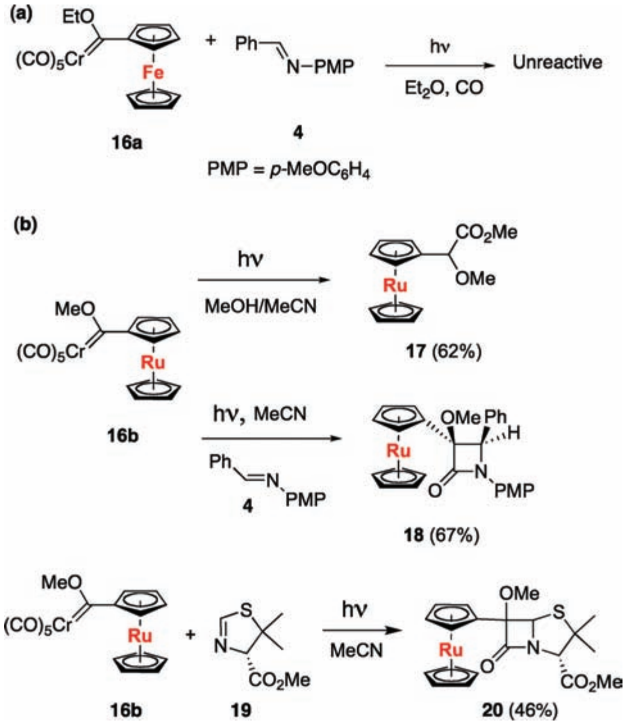


Tuning the Photoreactivity: The Case of Bimetallic Complexes

From the above findings, it is clear that small modifications in the electronic structure of the carbene complex may lead to great changes in its photoreactivity. Thus, we decided to study the effect of a second metallic fragment attached to the carbene ligand.

The importance of the electronic nature of the initial complex can be clearly seen in the photolysis of ferrocenyl-substituted carbene complex **16a** that was recovered unchanged in its reaction with imine **4**. Neither β-lactams nor other photoproduct were observed even after long irradiation times (Scheme 9a).[21]

SCHEME 9. Photolysis of Metallacene–Carbene Complexes **16**



Strikingly, the ruthenocenyl-carbene analogue **16b** does undergo the standard photocarbonylation process and produces photocarbonylation derivatives in good yields.[22] In this way, we succeeded in preparing the first example of a 2-azetidinone bearing a metallocene directly attached to the C3 of the four-membered ring and the 6-ruthenocenyl penicillin derivative **20**, which might exhibit potential biological activity.

The reasons for this differential behavior between ferrocene and ruthenocene derived chromium(0) carbene complexes are found in the structure of the corresponding triplet excited states. Our computational results show the coexistence of a very low-energy noncarbonylated triplet for complex **16a** and a high-energy metallacyclopropanone triplet. This implies that irradition of complex **16a** leads to the formation of a triplet species, which does not possess the structure required to react with nucleophiles (Figure 5a). In sharp contrast, two nearly degenerated triplet states coexist in its ruthenocene counterpart **16b**. Simple visual inspection of the corresponding SOMOs of T1 species (Figure 5) indicates appealing differences in the electronic structures of ferrocenyl- and ruthenocenyl-substituted carbenes, which are translated to a differential photoreactivity. One of these two triplets is a carbonylated metallacyclopropanone species (similar to **1(T1)** in Figure 2), which can react toward nucleophiles forming the observed photocarbonylation products.[22] This simple study confirms that the formation of the metallacyclopropanone species in the triplet excited state is decisive for the photocarbonylation to occur.

The photoreactivity of half-sandwich Fischer carbene complexes having a CpM(CO)$_3$ (M = Mn, Re) in their structure was next addressed.[23] Similarly to the ferrocenyl group,[6] the presence of the cyclopentadienyl–tricarbonylmetal moiety provokes a red-shift of the MLCT band without altering the

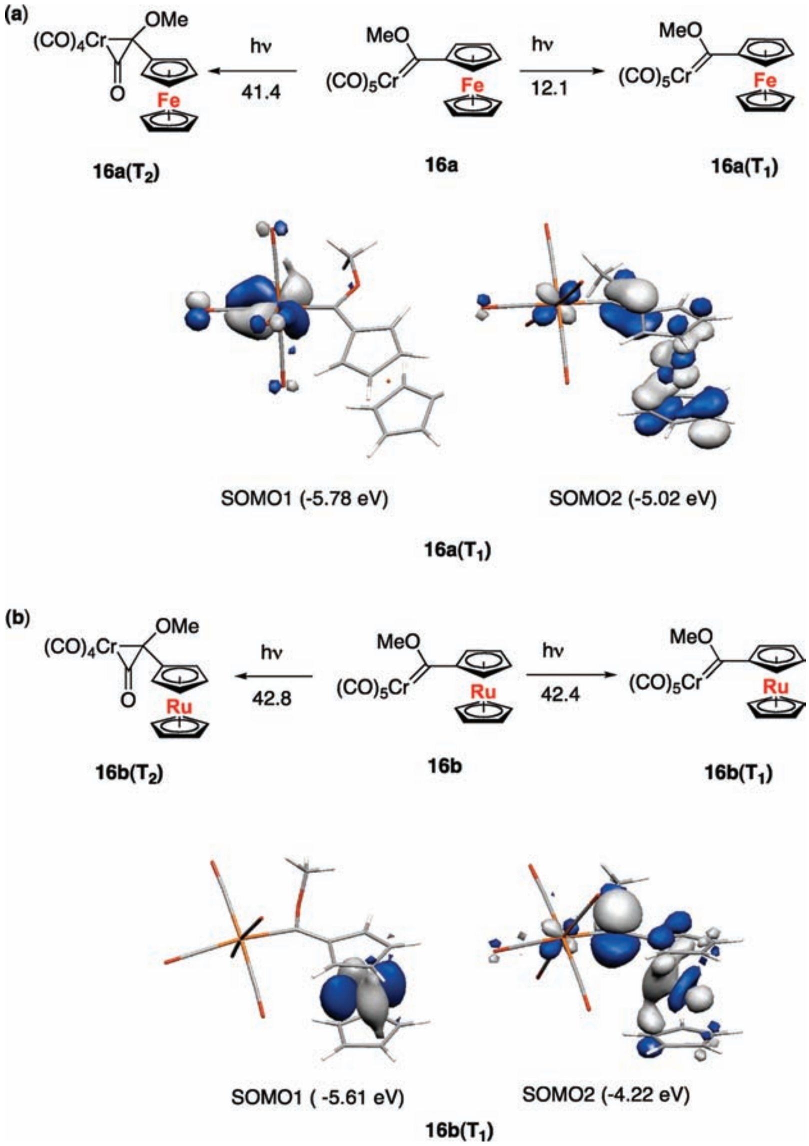


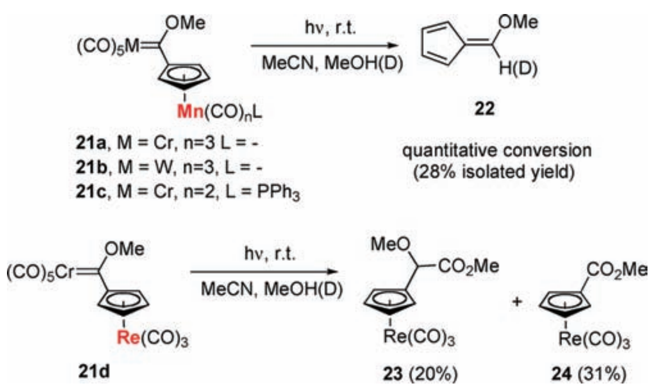
FIGURE 5. Most stable triplet excited states for carbenes **16**. Numbers close to the arrows indicate the energy of each reaction step (in kcal/mol). All data have been computed at the (u)B3LYP/def2-SVP level.

HOMO-1 → LUMO nature of this transition. This effect is mainly due to the role of the additional metal fragment attached to the carbene ligand as π-donor group, which increases the electronic occupation of the "empty" p_z atomic orbital of the carbene carbon atom.

The most stable triplet species for both Mn(I) and Re(I) complexes were computationally located. Similarly to metallocene-substituted complexes **16**, two coexistent triplet complexes (the carbonylated metallacyclopropanone and the noncarbony lated species) were found for half-sandwiched complexes **21**. By contrast, both triplet species derived from Mn(I) or Re(I) complexes are nearly degenerate, which opens doors to the possible formation of photocarbonylation products. While Re(I) complexes mainly lead to products derived from a photocarbonylation process upon irradiation in the presence of MeOH, Mn(I) carbene complexes (either Cr(0) or W(0) derivatives) quantitatively evolve to methoxyfulvenes **22** (Scheme 10).

The transformation of half sandwich carbenes **21** into fulvenes is a new photoreaction of Fischer carbene complexes (Figure 6). A plausible reaction mechanism involving a $\eta^5 \rightarrow \eta^3$ photoslippage process of the cyclopentadienyl fragment in the triplet hypersurface, starting from the biradical intermediate **21a-T1**, was proposed based on computational (DFT) grounds. After a new ISC process, intermediate **II(S0)** is transformed into a Mn−fulvenyl complex (weakly bonded to the $Cr(CO)_5$ moiety), which smoothly evolves to the highly unsaturated complex **IV(S_0)** in a solvent-assisted process. Finally, complex **IV(S_0)** can coordinate a MeOH molecule to form the observed fulvene

SCHEME 10. Photoreactions of Carbene Complexes **21**



through an intramolecular H-transfer and concomitant decoordination, as previously described in the literature for similar systems.[24] The key to the differential photoreactivity between Mn(I) and Re(I) complexes **21a** and **21d** seems to be the metal–Cp back-donation, which hampers the slippage process for Re derivatives, thus favoring the carbonylation reaction. To test this hypothesis, we irradiated complex **21c**, where a CO ligand was replaced by a σ-donor PPh_3 ligand (increasing the back-donation ability of the metal moiety), and found that the photochemical reaction proceeds much slower (and with lower conversion) than in complexes **21a,b**, leading to fulvene **22** together with some unidentified impurities.

Conclusions and Outlook

The availability of modern computers and sophisticated computational routines allowed the combination of experiment and theory in disentangling mechanistically complex processes involving organometallic compounds. The photocarbonylation of chromium(0) carbene complexes and the subsequent reaction of the photogenerated ketenes with nucleophiles was one of these processes. The synergy between computation and experiment allowed not only the understanding of this fundamental reaction but also the discovery of new photochemical transformations. This includes the making of the photochemically "unreactive" tungsten(0) carbene complexes reactive. The new methodologies developed during this work resulted in substantial changes in the way we look at the photochemistry of group 6 metal-carbenes (Fischer). These changes span from the reassignation of the electronic transitions of group 6 carbene complexes to new photochemical reactions and mechanisms, far away from conventional organic and organometallic photochemistry. We believe that the contents of this report represent a methodological way of understanding organometallic photochemistry and may be the basis for future work in metal–carbene and other organometallic complexes.

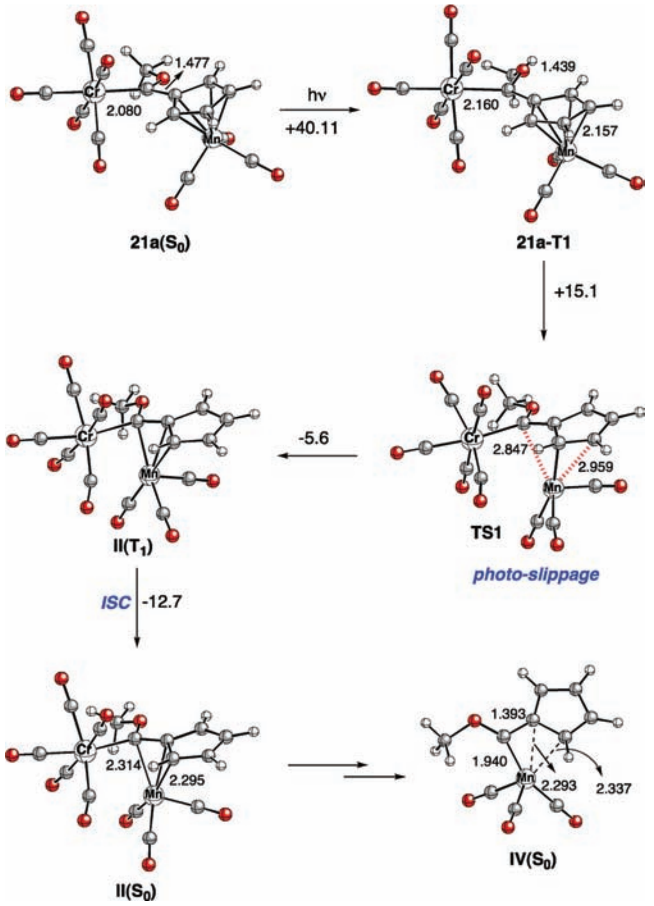


FIGURE 6. Photoinduced slippage in complex **21a**. Numbers close to the arrows indicate the energy of each reaction step (in kcal/mol). All data have been computed at the (u)B3LYP/def2-SVP level.

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BIOGRAPHICAL INFORMATION

Israel Fernández (Madrid, 1977) enjoyed studying Chemistry at the Universidad Complutense of Madrid (UCM). In 2005, he earned his Ph.D. in Chemistry at the UCM under the supervision of Prof. Miguel A. Sierra (with honors), receiving the Lilly-Young Researcher Award. After that, he joined the Theoretical and Computational Chemistry group of Prof. Gernot Frenking at the Philipps Universität Marburg as a postdoctoral researcher studying the bonding situation and reaction mechanisms of organic and organometallic compounds. In 2009, he received the Young-Researcher Award from the Spanish Royal Society of Chemistry. At present, I.F. is a Ramón y Cajal fellow at the UCM. His current research includes the computational study of the bonding situation and reaction mechanisms of organic, organometallic, and bio-organic compounds with special interest in C−C bond forming processes.

Fernando P. Cossío studied chemistry at the Universidad de Zaragoza (Spain) and received his Ph.D. in 1986 at the University of the Basque Country (UPV/EHU, Spain, Prof. C. Palomo). After a postdoctoral stay at CNRS (Talence, France, Dr. J.-P. Picard), he joined the UPV/EHU as Profesor Titular in 1988 and Catedrático in 2002. He has served as Dean of the Faculty of Chemistry (1999−2001) and as Vice-rector for Research of the UPV/EHU (2001−2003). In 1994, after a short stay at UCLA in the laboratories of Prof. K. N. Houk, he decided to combine theoretical and experimental organic chemistry to investigate the origins of selectivity in chemical reactions. His research interests include pericyclic reactions, C−C bond-forming reactions, and medicinal chemistry (design and chemical synthesis of inhibitors of integrins and epigenetic enzymes). He is also one of the founders of the spin-off company *Ikerchem S. L.* and since 2009 is the President of the Executive Committee of *Ikerbasque*, the Basque Foundation for Science.

Miguel A. Sierra was born in Villamiel (Toledo), studied Chemistry at the UCM (Madrid), and received his Ph.D. in 1987 (Honors). After a postdoctoral stay at Colorado State University (Prof. Louis Hegedus), he was promoted to Profesor Titular in 1990 and Catedrático in 2005 (UCM). He is consultor of the NBQ and Energetic Materials laboratories of the Spanish Defense Ministery, the Secretary of the Spanish Organic Section of the Spanish Chemical Society and a member of its Board. Among other awards, he received (2002) the Military Cross (white ribbon) for his work for the Organization for the Prohibition of Chemical Weapons (OPCW). His research encompasses the development of new processes based on transition-metal complexes, the study of organometallic reaction mechanisms, the preparation of new bioorganometallic compounds, and the design and synthesis of new energetic materials.

FOOTNOTES

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Dedicated to Professor Rafael Suau, a pioneer of photochemistry in Spain and a friend. In memoriam.

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