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Metal-Tuned Photochemistry of Metallocene-Substituted Chromium(0)–Carbene Complexes

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The use of transition metals in photochemical reactions[1] allows the performance of new and efficient transformations, since they allow the tuning of photochemical reactivity and the switching between different reaction pathways.[2] Furthermore, the photochemical behavior of isostructural metal complexes is strongly metal-dependent. A good example for this assertion is found in the photocarbonylation reaction of Group 6 metal (Fischer)–carbene complexes.[3] Both alkoxy- and aminochromium(0)–carbene complexes photocarbonylate leading to ketene-derived products in the presence of nucleophiles. In contrast, tungsten(0)–carbene complexes are usually photochemically inert.[4]

Within this context, we have reported the ligand-tuned photoreactivity of Group 6 Fischer aminophosphine-bridged carbene complexes **1**. These complexes produce two coexisting triplet states **1M-Cr(T_1)** and **1M-Cr(T_2)**, from which ketene derivatives (**2**), type I dyotropic rearrangements (**3a**) and fragmentation (**3b**) occur (Scheme 1).[5] By using the appropriate ligands, even the "photoinert" tungsten(0)–carbene complexes were made reactive.[5b,c]

The variety of available electronic excited states that these complexes may exhibit prompted us to study the photochemical behavior of metallocene (Fe and Ru)-substituted metal–carbene complexes,[6] a feature which to our knowledge remains unaddressed in the chemical literature so far. We have already shown that the photoreaction of chromium(0)–carbene complex **4** and ferrocenyl–imines **5** was productive, leading to the corresponding β-lactams **6**, whereas ferrocenyl–carbene **7** was photochemically inert (Scheme 2).[7]

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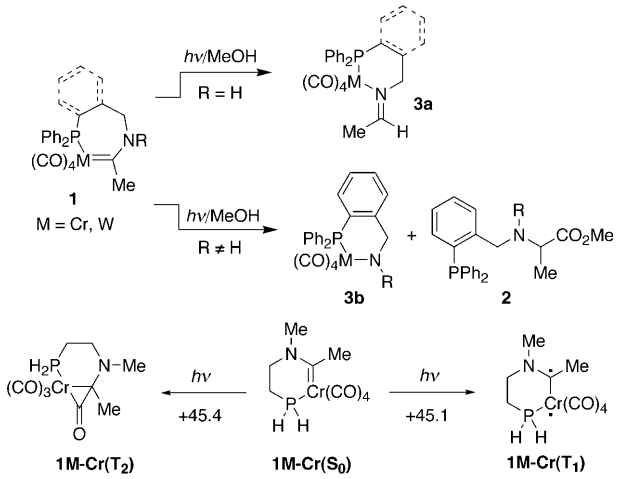
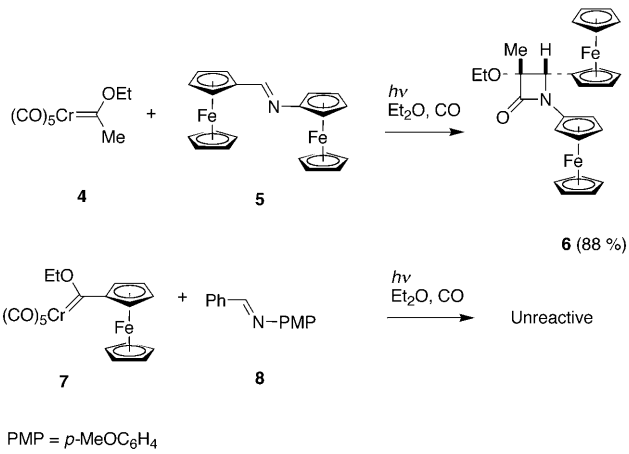
To explain this reactivity the S_0 geometry of complex **9** was optimized at the B3LYP/def2-SVP level.[8] The most stable excited state of complex **9** is a triplet (**9T_1**) (excitation



Scheme 1.



Scheme 2.

energy of 12.1 kcal mol^{-1}) and its optimized structure is not the expected chromacyclopropanone.[3] In fact, the chromacyclopropanone structure corresponds to the second most stable triplet state ($\mathbf{9T_2}$; excitation energy of 41.4 kcal mol^{-1}) (Figure 1). Thus, the excitation of complex **9** should lead to the first singlet state $\mathbf{9S_1}$, which would readily decay to the most stable triplet $\mathbf{9T_1}$ by ISC due to spin–orbit coupling. Therefore, no carbonylative photochemistry is expected for chromium(0)–carbene complexes with ferrocene motifs attached to the carbene carbon.

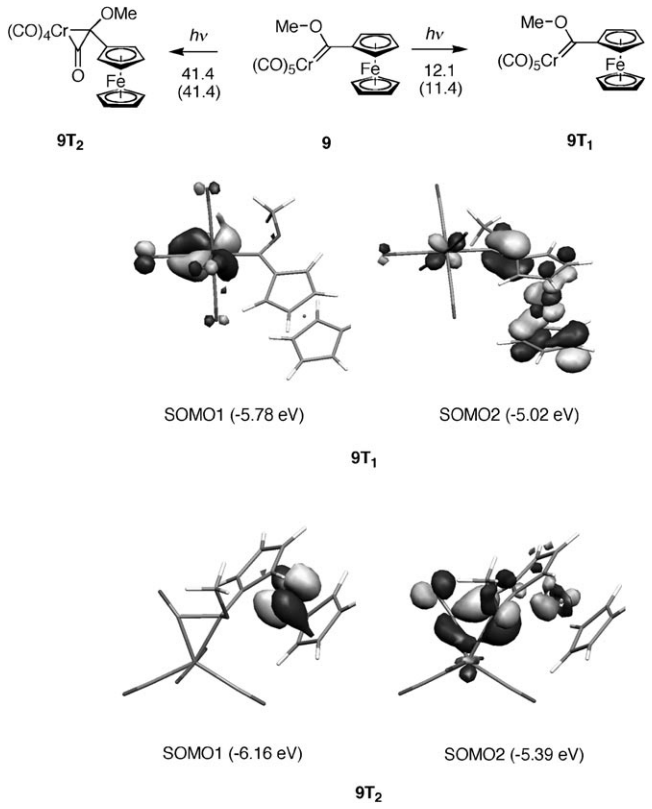


Figure 1. Triplet states of complex **9**. Energies (kcal mol^{-1}) under the arrows were computed at the B3LYP/def2-SVP level. In parenthesis, those computed at the B3LYP-PCM/def2-SVP//B3LYP/def2-SVP level.

Due to the strong metal–ligand dependency of the photoreactivity of these metal complexes, the photochemical behavior of the [pentacarbonyl(methoxyruthenocenyl)carbene]chromium(0) **10** was addressed next. B3LYP/def2-SVP calculations showed the coexistence of two nearly degenerated triplets $\mathbf{10T_1}$ and $\mathbf{10T_2}$, with vertical excitation energies of 42.4 and 42.8 kcal mol^{-1}, respectively. Interestingly, $\mathbf{10T_2}$ has a chromacyclopropanone structure, whereas $\mathbf{10T_1}$ is a noncarbonylated species. The excitation of complex **10** should form any of the close energy triplets $\mathbf{10T_1}$ or $\mathbf{10T_2}$ by ISC. Then, $\mathbf{10T_2}$ will decay to the singlet hypersurface by coordination of one molecule of solvent, and should react with nucleophiles to produce ruthenocenyl-substituted photocarbonylation products, which are difficult to obtain by conventional synthetic procedures (Figure 2).[3,9]

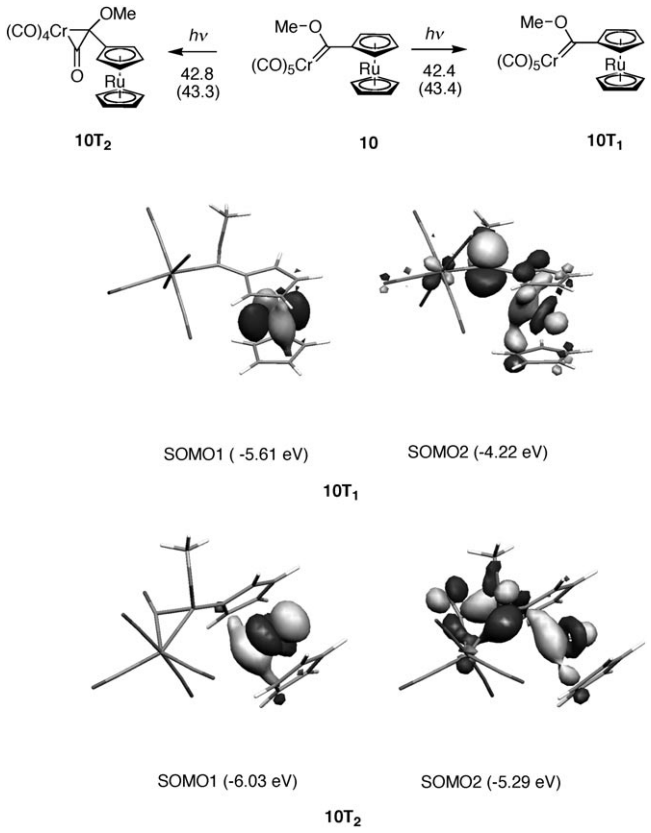
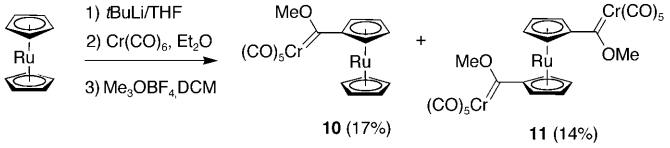


Figure 2. Triplet states of complex **10**. Energies (kcal mol^{-1}) under the arrows were computed at the B3LYP/def2-SVP level. In parenthesis those computed at the B3LYP-PCM/def2-SVP//B3LYP/def2-SVP level.

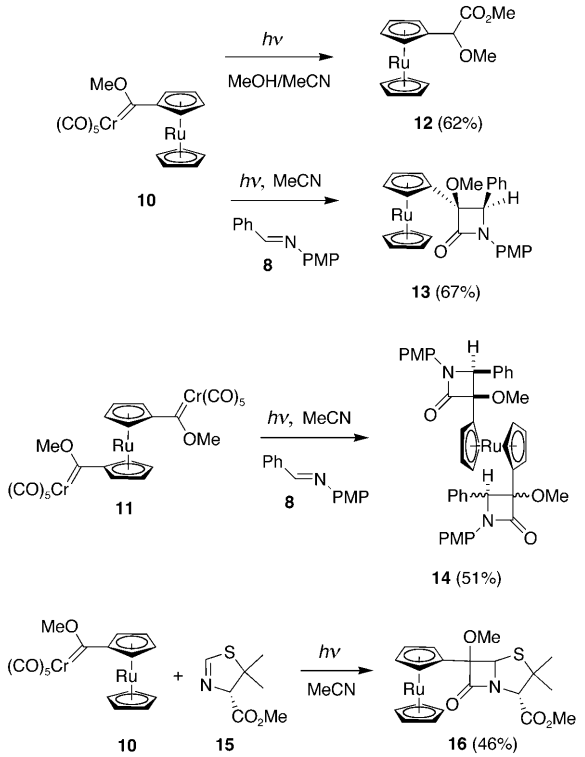
To validate the theoretical results, ferrocene-substituted complex **7** was irradiated in the presence of MeOH (see Supporting Information) and recovered unaltered. In parallel, ruthenocenylcarbene complex **10** was prepared (Scheme 3) and irradiated as above, yielding ester **12** in



Scheme 3.

62% yield. This result confirms the theoretically predicted photoreactivity for this complex. Furthermore, the irradiation of complex **10** and imine **8** produced β-lactam **13** in 67% yield. This is the first example of a 2-azetidinone bearing a metallocene directly attached to the C3 of the four-membered ring. Finally, biscarbene complex **11** also formed the corresponding bis-β-lactam **14** by irradiation in the presence of imine **8** (Scheme 4).

The synthesis of unknown metallapenicillin derivatives was pursued next. Thiazoline **15** was irradiated in the pres-



Scheme 4.

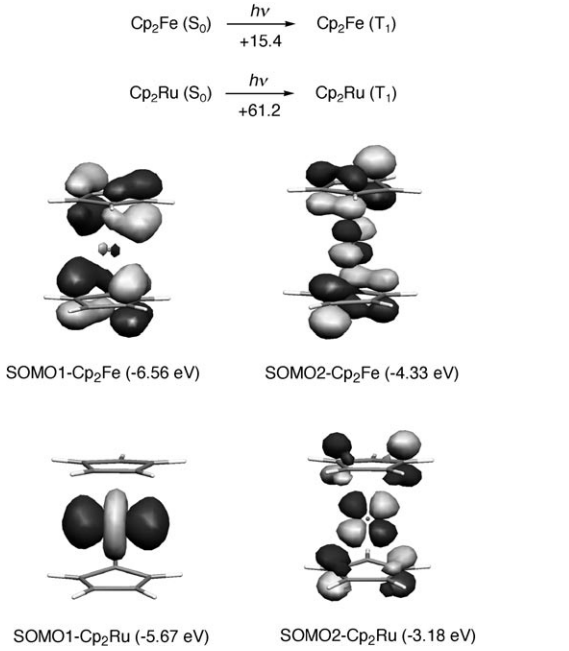


Figure 3. Triplet states of ferrocene and ruthenocene. Computed vertical excitation energies (in kcal mol^{-1}) under the arrows.[5]

ence of complex **10** affording penicillinate **16** as a mixture of diastereomers in an overall 46% yield (Scheme 4). Leaving aside the lack of stereochemical control (which was already predictable on the basis of the known mechanism of the Staudinger reaction)[10] this approach is the first reported entry to 6-ruthenocenyl-substituted penicillins.

Next we looked for an explanation for the differential photochemical behavior of ferrocene- and ruthenocene-substituted chromium(0)–carbene complexes. To rule out the role of ferrocene as a quencher of the photocarbonylated triplet $\mathbf{9T_2}$, the photoreactive complex [pentacarbonyl(methoxymethyl)carbene]chromium(0) was irradiated in the presence of imine **8** and one equivalent of ferrocene. The corresponding 2-azetidinone (66% yield) was obtained.

The orbital distribution of complexes $\mathbf{9T_1}$/$\mathbf{9T_2}$ and $\mathbf{10T_1}$/$\mathbf{10T_2}$ (Figures 1 and 2) was considered next. The most appealing difference between $\mathbf{9T_1}$ and $\mathbf{10T_1}$ is that the SOMO1-$\mathbf{9T_1}$ is ligand centered (in the $(CO)_5Cr$ fragment), while the corresponding SOMO1-$\mathbf{10T_1}$ is centered in the ruthenocene moiety. This difference is analogous to that found in the SOMO1 orbitals of the most stable T_1 states of ferrocene and ruthenocene (Figure 3). Moreover, the SOMO2 of $\mathbf{9T_1}$ and $\mathbf{10T_1}$ are similar and analogous to the corresponding SOMO2 of the parent metallocenes. The SOMOs of $\mathbf{9T_2}$ and $\mathbf{10T_2}$ are, in contrast, comparable both in energy and orbital distribution. Interestingly, the first triplet of ferrocene also lies at 14.4 kcal mol^{-1}, while the first triplet of ruthenocene lies at 61.2 kcal mol^{-1}.[11] We can conclude that the presence of the ferrocene moiety in complex **9** forms a low-lying ligand-centered triplet inhibiting the photo-insertion of a CO ligand in the Cr–carbene bond and thus leading to the observed lack of photoreactivity. In the case of Ru–carbene complex **10**, both triplet-excited states are quasi-isoenergetic and their coexistence leads to the observed carbonylative reaction.

In conclusion, we have disclosed an unknown metal-dependent photochemistry of metallocene-substituted chromium(0)–carbene complexes **9**, **10**, and **11**. The computational results show the coexistence of a low-energy non-carbonylated triplet for complex **9** with a high-energy metallacyclopropanone triplet, explaining its photoinertia. In strong contrast, two nearly degenerated triplet states coexist in ruthenocene derivatives. One of the two triplets is a carbonylated metallacyclopropanone species reactive towards nucleophiles. These theoretical predictions have been demonstrated experimentally by the development of a synthesis of 3-ruthenocenyl-2-azetidinones and the preparation of a 6-ruthenocenylpenicillin derivative for the first time. Efforts to study other metal-dependent organic photochemistry as well as the synthesis of natural products that contain unusual metallocene-derived structures are currently underway in our laboratories.

Experimental Section

Detailed experimental procedures and characterization of compounds **10**, **11**, **12**, **14**, **15**, and **16** are included as Supporting Information.

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