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The Electronic Structure and Photochemistry of Group 6 Bimetallic (Fischer) Carbene Complexes: Beyond the Photocarbonylation Reaction

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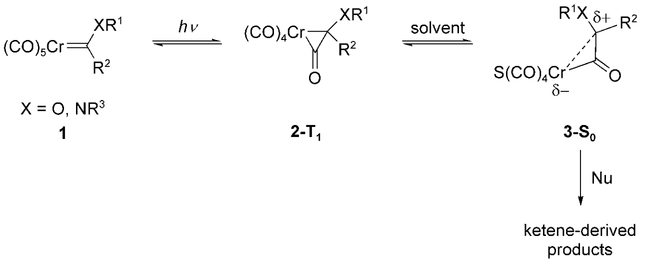
Abstract: The UV spectra of Group 6 metal carbene complexes bearing a $CpM(CO)_3$ (Cp = cyclopentadienyl) moiety bonded to the carbene carbon atom exhibit a redshift of the absorption maxima at higher wavelengths with respect to the parent monometallic complexes. This redshift is partly due to a higher occupation on the p_z atomic orbital of the carbene carbon atom. Time-dependent DFT calculations accurately assign this band to a metal-to-ligand charge-transfer transition, thus showing that the presence of a second metal center does not affect the nature of the transition. However, the photochemical reactivity of Group 6 metal carbene complexes bearing a $CpM(CO)_3$ moiety strongly depends on the nature of this metal fragment. A new photoslippage reaction leading to fulvenes occurs when Mn-derived products **11a**, **11b**, and **12a** are irradiated (both Cr and W derivatives), whereas Re-derived product **11c** behaves like standard Fischer complexes and yields the usual photocarbonylation products. A new photoreduction process occurring in the metallacyclopropanone intermediate is also observed for these complexes. Both computational and deuteration experiments support this unprecedented photoslippage process. The key to this differential photoreactivity seems to be the M–Cp back-donation, which hampers the slippage process for Re derivatives and favors the carbonylation reaction.

Keywords: bimetallic complexes · carbenes · density functional calculations · electronic structure · photochemistry

Introduction

The photocarbonylation reaction of Group 6 Fischer carbene complexes[1] competes in efficiency and exceeds in versatility many well-established synthetically useful photochemical organic reactions.[2] Both alkoxy- and aminochromium(0) carbene complexes photocarbonylate leading to an impressive array of ketene-derived products in the presence of nucleophiles. The mechanism of this photocarbonylation process and the ulterior reaction of the photogenerated ketenes have recently been clarified.[3] The irradiation of a chromium(0) (Fischer) carbene complex **1** (Scheme 1) generates the coordinatively unsaturated chromacyclopropanone structure **2-T₁** (with a biradical character) by intersystem crossing (ISC) from the lowest excited singlet state (S_1) to the lowest triplet state (T_1). The evolution of these metallacyclopropanone species occurs by a jump (spin inversion) to the S_0 hypersurface by coordination of a molecule of solvent, thus leading to ketene-derived products (from **3-S₀**) in the presence of ketenophiles, or reverting to the starting carbene complex in their absence (Scheme 1). In contrast, simple tungsten(0) carbene complexes are photochemically inert toward this process.



Scheme 1. Photocarbonylation reaction of Fischer carbene complexes. Nu = nucleophiles.

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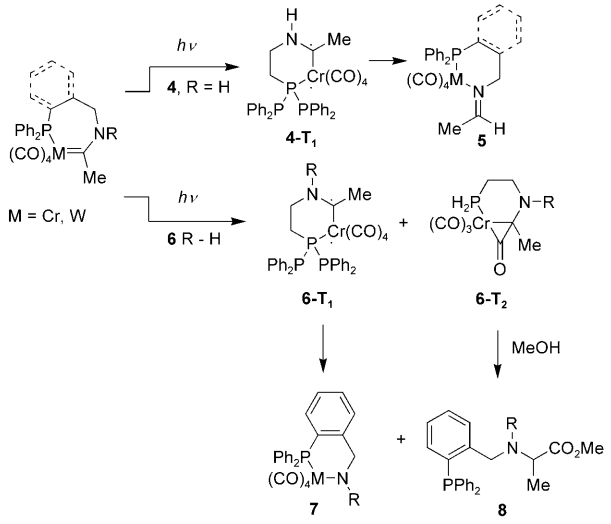
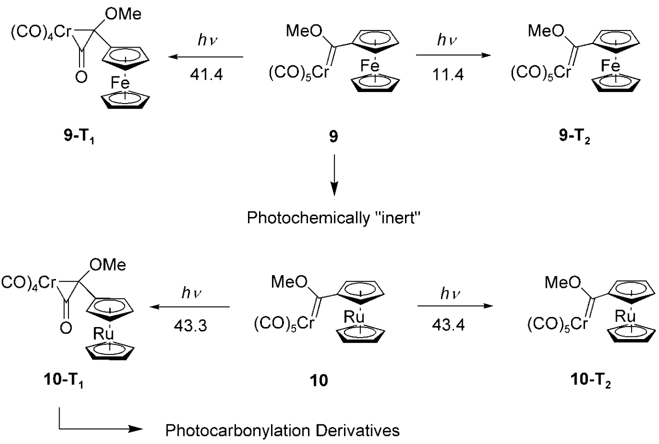
Nevertheless, during recent years reactions other than photocarbonylation have been achieved in both Cr^0 and W^0 Fischer carbene complexes by careful ligand tuning.[4,5] The modification of the coordination sphere of the metal results in the formation of new triplet species, which are usually lower in energy than the triplet excited state leading to photocarbonylation-derived products. Thus, complexes **4** experience type I dyotropic rearrangements from **4-T$_1$** to yield compounds **5** (Scheme 2). This process competes favorably with photocarbonylation. However, complexes **6** form fragmentation products **7** together with photocarbonylation products **8** through the triplet species **6-T$_1$** and **6-T$_2$**, respectively (Scheme 2).



Scheme 2. Photochemical reactivity of complexes **4** and **6**.



Scheme 3. Metal-dependent photoreactivity of metallocenyl-substituted carbene complexes. The numbers under the arrows correspond to computed energies [kcal mol^{-1}]. See reference [6].

We recently reported the unusual photochemical behavior of metallocene-substituted metal (Fischer) carbene complexes **9** and **10** (Scheme 3), which opens doors to new forms of metal-dependent photochemistry.[6] In these complexes, the difference in energies between a noncarbonylated (**9-T$_2$** and **10-T$_2$**) and metallacyclopropanone triplet species (**9-T$_1$** and **10-T$_1$**) determines the success or failure of the carbonylation process (Scheme 3). The strong metal-dependent reactivity observed for metallocenyl-substituted Fischer carbene complexes led us to perform a combined computational–experimental study of the behavior of cyclopentadienyl(metal)tricarbonyl-substituted Fischer carbene complexes, for which a totally new reactivity has been encountered.

Computational Details

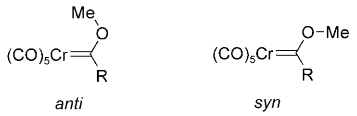
All the calculations reported herein were obtained with the Gaussian 03 suite of programs.[7] Electron correlation was partially taken into account by using the hybrid functional usually denoted as B3LYP[8] with the double-ξ quality plus polarization def2-SVP basis set for all atoms.[9] All stationary points were confirmed by vibrational analysis:[10] for equilibrium structures, all normal modes have real frequencies, whereas transition states have one normal mode with an imaginary frequency. Calculations of absorption spectra were accomplished by using the time-dependent density functional theory (TD-DFT)[11] method at the same level. The assignment of the excitation energies to the experimental bands was performed on the basis of the energy values and oscillator strengths. The B3LYP Hamiltonian was chosen because it was proven to provide accurate structures and reasonable UV/Vis spectra for a variety of chromophores.[12] Despite the known deficiencies of TD-DFT for long-range charge-transfer states,[11,12] this method has proven to be very promising for many transition-metal complexes.[13] The selected method was recently shown to provide very good results for Fischer carbene complexes.[14]

The atomic orbital occupations and donor–acceptor interactions were computed by using the natural bond orbital (NBO) method.[15] The energies associated with these two-electron interactions were computed according Equation (1):

$$\Delta E^{(2)}_{\phi\phi*} = -n_{\phi} \frac{\langle \phi^* | \hat{F} | \phi \rangle^2}{\varepsilon_{\phi*} - \varepsilon_{\Phi}}$$

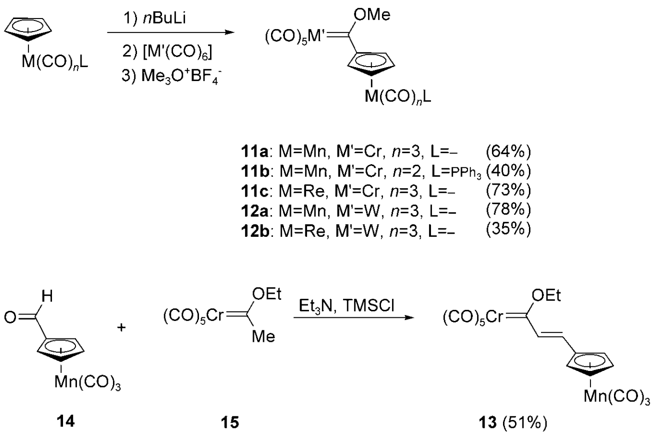
in which $\hat{F}$ is the DFT equivalent of the Fock operator and ϕ and ϕ^* are two filled and unfilled NBOs having ε_{ϕ} and $\varepsilon_{\phi*}$ energies, respectively; n_{ϕ} stands for the occupation number of the filled orbital.

Geometry optimizations (B3LYP/def2-SVP level) were carried out starting with the *anti* form of Fischer alkoxycarbenes (an orientation in which the methyl group of the alkoxy substituent is directed toward the pentacarbonylmetal moiety). These species are the most stable isomers in the gas phase and in the solid state.[16]



Results and Discussion

Pentacarbonyl(ethoxy)phenylchromium(0) carbene complex **1a**[17] and bimetallic carbene complexes **11** and **12** were prepared in moderate to very good yields by following the standard alkyllithium addition–alkylation sequence reported by Fischer,[18] whereas α,β-unsaturated complex **13** was obtained following the Aumann procedure,[19] by reaction of pentacarbonyl(ethoxy)methylchromium(0) carbene (**15**)[18] and aldehyde **14**[20] (Scheme 4).



Scheme 4. Synthesis of complexes **11**–**13**.

Bimetallic carbene complexes **11**–**13** are strongly colored compounds, their color ranging from red to deep red. The UV/Vis spectra of all complexes show a well-defined absorption around 400 nm (Figure 1), which can be ascribed to a metal-to-ligand charge transfer (MLCT) in accordance with our previous findings on related Fischer carbene complexes.[14]

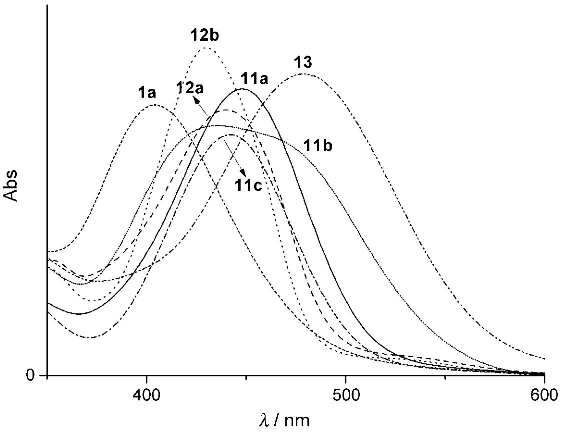


Figure 1. Room-temperature UV/Vis spectra of complexes **1a** and **11**–**13** in pentane (in all cases the concentration of the sample was ca. 10^{-4} mol L^{-1}).

Pentacarbonyl(ethoxy)phenylchromium(0) carbene complex **1a** was used as the reference to study the effect of the second metal center on the electronic properties of complexes **11**–**13**. As depicted in Figure 1, the MLCT band is redshifted in the bimetallic complex **11a** by approximately 45 nm with respect to complex **1a**. It has been suggested that, in Fischer alkoxycarbenes, the occupation of the p_z orbital of the carbene carbon atom is related to the position of the MLCT. Thus, a higher occupation of the p_z orbital usually translates into the red displacement of this MLCT absorption.[14] Indeed, the computed NBO p_z occupation in **11a** is 0.61 e whereas it is reduced in the phenyl-substituted carbene complex **1a** (0.58 e). This higher occupation is partly due to a stabilizing two-electron interaction between an occupied d atomic orbital of the Mn atom and the p_z atomic orbital of the carbene carbon atom (associated second-order energy of -0.54 kcal mol^{-1}, Figure 2).

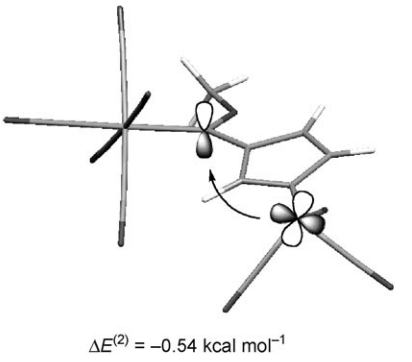


Figure 2. Two-electron stabilization (and associated second-order perturbation energy) in complex **11a**.

TD-B3LYP/def2-SVP calculations were carried out to accurately assign the vertical transitions responsible for the observed spectra of these compounds. The data compiled in Table 1 (which includes the calculated oscillator strengths of the main absorptions) show a very good agreement between the calculated vertical excitation energies (in the gas phase) and the wavelengths of the absorption maxima in the experimental UV/Vis spectra (recorded in pentane). The deviation of the calculated from the experimental values is in the range of 20–40 nm (the calculated data are always blueshifted compared to the experimental measurements). TD-DFT calculations assign the absorption around 450 nm of complex **11a** to the promotion of one electron from the HOMO-1, which is centered in the chromium center, to the LUMO, a π-extended orbital involving the p_z atomic orbital of the carbene carbon atom (Figure 3). This situation is identical to that calculated for monometallic Fischer carbene complexes.[14] Therefore, it can be concluded that the presence of the $Mn(CO)_3$ fragment, albeit clearly provoking a redshift of the absorption at higher wavelengths with respect to the monometallic complex **1a**, does not alter the nature of the transition (namely, a MLCT band).

The more electron-rich $Mn(CO)_2(PPh_3)$ and $Re(CO)_3$ fragments (complexes **11b** and **11c**, respectively) have no

Table 1. Comparison of main UV/Vis excitation energies λ_{max} [nm] and the corresponding oscillator strengths (in parentheses) for complexes **1a** and **11**–**13**.

Entry	Complex	λ_{exptl} (MLCT band)[a]	λ_{calcd}[b]
1	**1a**	403	387 (0.177)
2	**11a**	448	407 (0.184)
3	**11b**	434	
4	**11c**	442	403 (0.256)
5	**12a**	439	
6	**12b**	431	
7	**13**	480	451 (0.440)

[a] Experimental data, recorded at room temperature in pentane with a concentration of approximately 1×10^{-4} mol L^{-1}. [b] Computed TD-B3LYP/def2-SVP gas-phase vertical excitation energies.

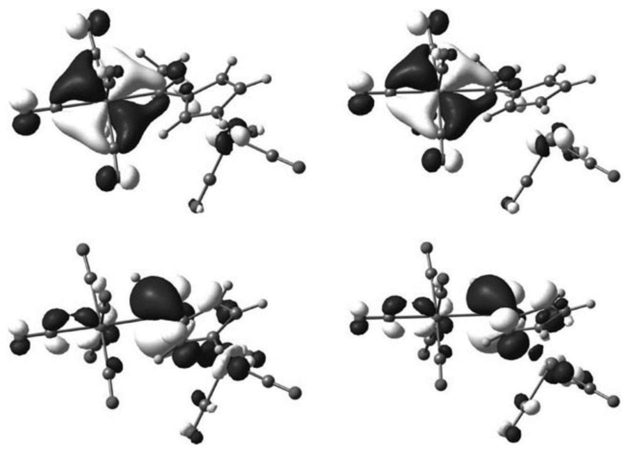


Figure 3. Molecular orbitals HOMO−1 (top) and LUMO (bottom) of complexes **11a** (left) and **11c** (right) calculated at the B3LYP/def2-SVP level (isosurface value of 0.035).

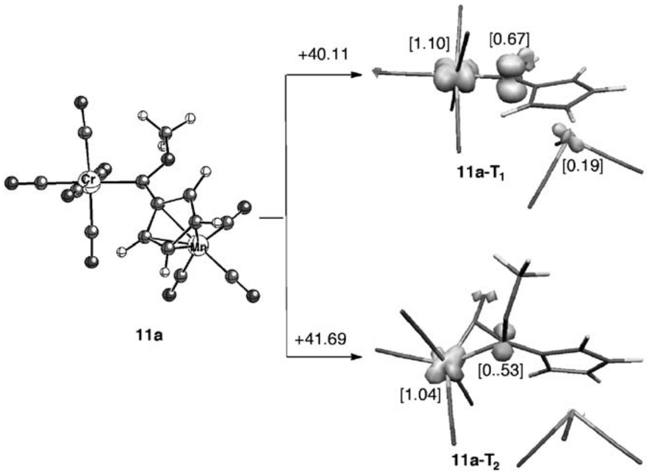


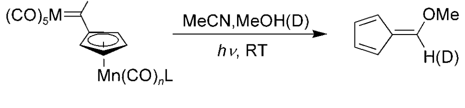
Figure 4. Triplet states of complex **11a**. Energies (in kcal mol^{-1}) and spin densities (in brackets) were computed at the uB3LYP/def2-SVP level.

significant effect on the position of the absorption maxima of the MLCT band. A small blueshift is observed (6–14 nm with respect to complex **11a**; Figure 1 and Table 1). The difference between the computed NBO p_z occupation of the carbene carbon atom on the complexes **11b** and **11c** (0.61 e in both cases) and complex **11a** is negligible. Analogously, TD-DFT calculations for complex **11c** assign the corresponding vertical transition to a HOMO-1→LUMO transition. The shape of the molecular orbitals involved in the absorption in these complexes is similar to that obtained for complex **11a**. The assignment of this transition as a MLCT absorption is therefore reliable (Figure 3). The highest p_z occupation is computed for the α,β-unsaturated complex **13** (0.64 e) due to π conjugation. This is reflected in a strong redshift of complex **13** compared to complex **11a** (480 vs. 448 nm, Table 1) of the corresponding MLCT band (HOMO-1→LUMO vertical transition).

The fact that the MLCT band is similar in monometallic carbene complexes (such as complex **1a**) and bimetallic compounds **11** might suggest a similar photoreactivity for both types of complexes. However, we have previously demonstrated that the photoreactions of carbene complexes strongly depend on the structure and relative energy of the triplet excited state formed by an ISC process after the initial photoexcitation of the complex to the singlet excited state.[3] In fact, changes in the electronic structure of the complexes due to the presence of different ligands in the carbene substituent or in the coordination sphere of the metal can provoke the formation of different triplet excited states, which lead to new reaction channels.[4–6]

For that reason, we first computationally studied (uB3LYP/def2-SVP level) the most stable triplet excited states of the parent carbene complex **11a**. The calculations show that the most stable excited state of cyclopentadienyltricarbonyl(Mn) carbene complex **11a** is the triplet state **11a-T$_1$** (Figure 4). The computed spin densities for **11a-T$_1$** indicate that the unpaired electrons are located on both the chromium center and the former carbene carbon atom, with significant participation of the manganese moiety (Cr = 1.1, C_{carb} = 0.67, Mn = 0.19 a.u., respectively). This makes biradical **11a-T$_1$** different from the species formed in both the photocarbonylation[3d] and dyotropic processes[4] of monometallic chromium(0) Fischer carbene complexes, in which the unpaired electrons are located exclusively on the chromium and former carbene carbon atoms. This fact makes new phototransformations potentially possible. Additionally, a higher-lying triplet (**11a-T$_2$**) was also located. This species, which has a typical metallacyclopropanone geometry, is analogous to those leading to ketene-derived products in the standard photochemistry of Cr-metal carbene complexes.[3d]

To test the above-mentioned possibility of the existence of new reaction pathways, complex **11a** was submitted to the usual photochemical conditions. Irradiation of complex **11a** (400 W medium-pressure Hg lamp, Pyrex filter) in MeCN/MeOH surprisingly yielded fulvene **16** as the single reaction product (100 % conversion according to NMR spectroscopy) (Scheme 5). Fulvene **16** was also formed when using THF/MeOH as the solvent. However, isolation of compound **16** proved to be difficult due to extensive decomposition,[21] and only a 28 % yield of pure fulvene **16** could be isolated after fast filtration through silica gel. The use of CD_3OD in the irradiation of complex **11a** resulted in quantitative incorporation of deuterium on the exocyclic double



11a: M = Cr, n=3, L= –
12a: M = W, n=3, L= –
11b: M = Cr, n=2, L= PPh_3

16 (28%)[a]
[$^2H_1$]-**16**

[a] Compound **16** was unstable. See text.

Scheme 5. Photochemical reactions of complexes **11a**, **11b**, and **12a**.

bond, which yielded compound [$^2H_1$]-**16** as the only reaction product. Note that the results were identical when tungsten(0) carbene complex **12a** was submitted to the above-mentioned photochemical conditions (Scheme 5). This is thus one of the few existing examples in which "photochemically inert" tungsten(0) carbene complexes are made reactive.[4b,c] These transformations are a clear indication that the photochemical reactivity of Fischer carbene complexes is strongly dependent on the electronic effects exerted by the substituents attached to the carbene carbon atom.

To explain the new transformation of carbene complex **11** to fulvene, computational studies were carried out at the uB3LYP/def2-SVP level. Initially, species **11a-T$_1$** evolves to complex **II(T$_1$)** through the transition state **TS1** (computed activation barrier of 15.1 kcal mol^{-1}) in the triplet hypersurface (Figure 5). This process can be considered as a photochemically induced slippage of the η^5-Mn(CO)$_3$ fragment to the η^3-Mn(CO)$_3$, which involves the formation of a new Mn–C (former carbene carbon atom) bond. The computed spin densities on **II(T$_1$)** indicate that both unpaired electrons are localized on the Mn atom (1.8 a.u.). We have not been able so far to locate and characterize a transition structure that connects **II(T$_1$)** with a new intermediate, which would lead to the observed fulvene in the triplet potential energy hypersurface. Instead, we found that bimetallic complex **II(S$_0$)**, formed by exothermic decay of **II(T$_1$)** via a new ISC process (reaction energy of −12.7 kcal mol^{-1}), easily evolves to complex **III(S$_0$)** through **TS2** (activation barrier of 10.4 kcal mol^{-1}) in the singlet state. Complex **III(S$_0$)** can be viewed as a Mn–fulvenyl complex, weakly bonded to the Cr(CO)$_5$ moiety (Mn–Cr and Cr–C bond lengths of 3.146 and 2.603 Å, respectively), in which the cyclopentadienyl (Cp) substituent is not attached directly to the metal.

Analogously to the mechanisms described for transmetalation[22] and photocarbonylation[3c,d,f] processes, the presence of a coordinating solvent is essential for this reaction to occur, since (CO)$_5$Cr(NCMe)[23,24] is formed releasing Mn complex **IV(S$_0$)** through a highly exothermic process. This complex readily evolves to the observed reaction products **16** in the presence of MeOH, through a process favored by the highly unsaturated nature of intermediate **IV(S$_0$)** (Figue 5). This transformation may occur through coordination of MeOH to the Mn center followed by intramolecular H transfer and concomitant decoordination to yield the observed fulvene **16**, as previously described in the literature for similar systems.[25] Obviously, the use of CD$_3$OD would lead to [$^2H_1$]-**16** by deuterium intramolecular transfer in this last step.

Once the mechanism for this new reaction pathway was clear, the influence of the metal in the Cp moiety was addressed. Calculations on Re complex **11c** showed that the most stable excited state was a triplet (**11c-T$_1$**), the unpaired electrons of which were located almost exclusively on the Cr and the carbene carbon atoms (Cr = 1.1, Re = 0.05, C_{carb} = 0.68 a.u, respectively), unlike complex **11a-T$_1$**. This structure points to complex **11c** behaving like its mononuclear counterparts. A more energetic metallacyclopropanone species **11c-T$_2$** was also located, thus making the photocarbonylation process potentially possible (Figure 6).

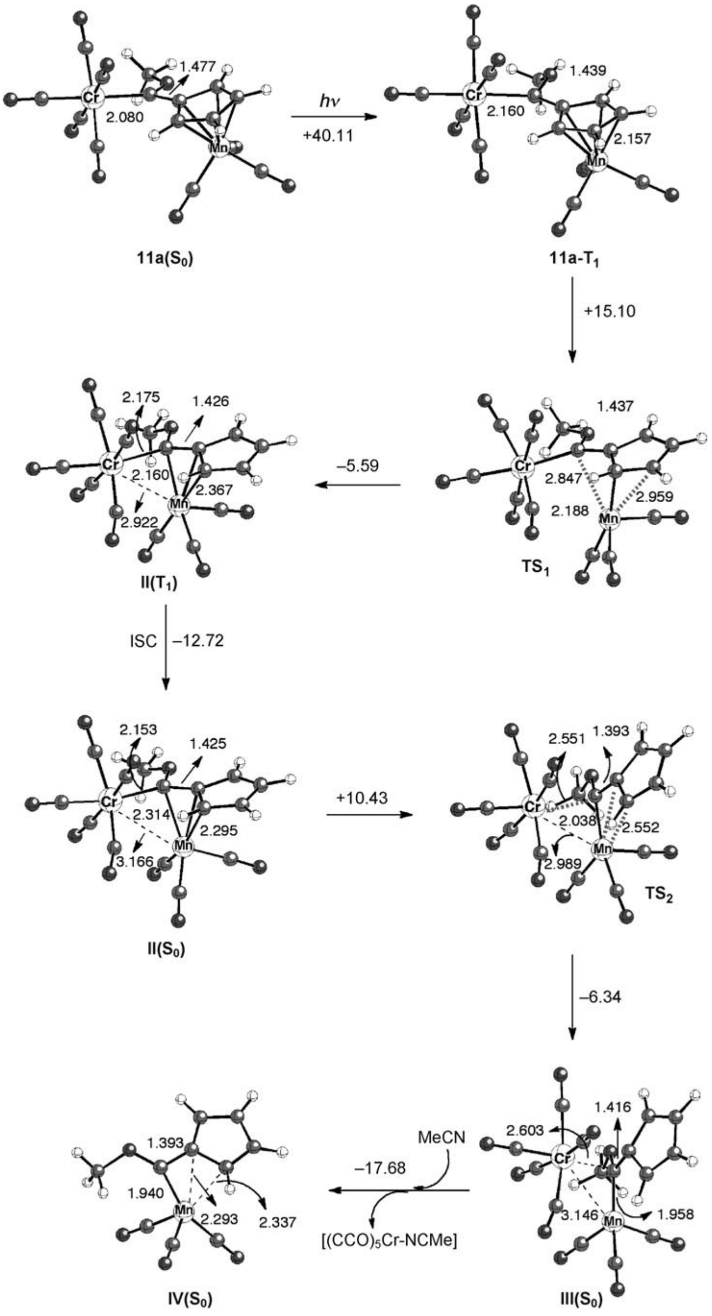


Figure 5. Computed reaction pathway ((u)B3LYP/def2-SVP level) for photochemical reaction of complex **11a**. Energy values are given in kcal mol^{-1} and bond lengths in Å.

Compound **11c** was irradiated under identical conditions to those described above. In this case, the carbonylation product **17** was obtained in 20 % yield together with 31 % of ester **18**, which arose from oxidation of the starting material. When the reaction was carried out in THF/MeOH, **17** was obtained in considerably improved yield (41 %), again with ester **18** (4 %) and a new product **19** (4 %). The reaction of W-derived complex **12b** yielded only aldehyde **20** (11 %)[26] (Scheme 6).

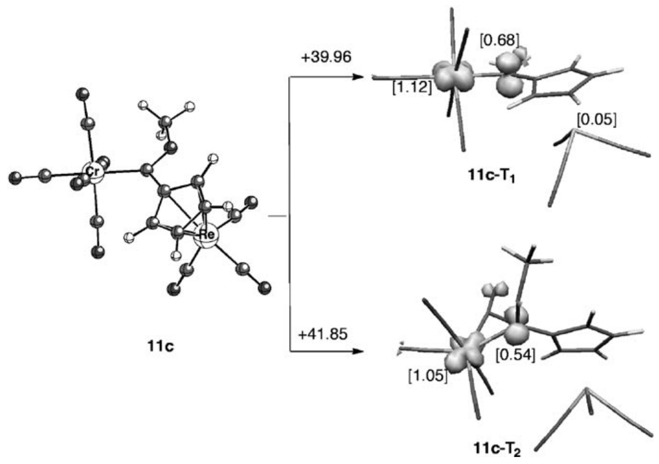
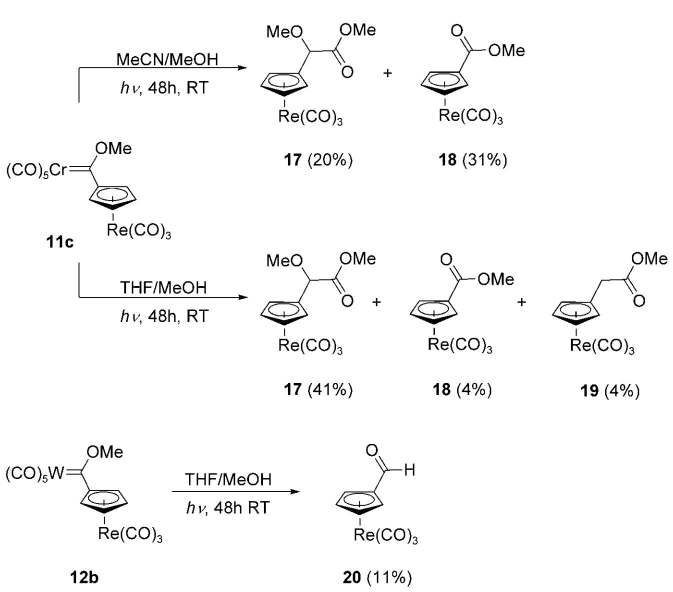
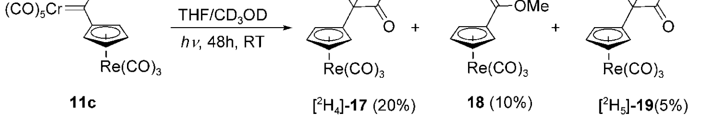


Figure 6. Triplet states of complex **11c**. Energies (in kcal mol^{-1}) and spin densities (in brackets) were computed at the uB3LYP/def2-SVP level.



Scheme 6. Photochemical reactions of complexes **11c** and **12b**.

The formation of derivative **19** is unprecedented in this chemistry and represents a hydrogen transfer to the putative carbonylation intermediate, since compound **17** is not the precursor of compound **19**.[27] Although we are aware of the low yield in which compound **19** is formed, it is, however, substantial proof for a new mechanistic pathway. Furthermore, the reaction of complex **11c** in THF/CD$_3$OD resulted in a double incorporation of deuterium in [^{2}H$_5$]-**19**, which was obtained together with compound [^{2}H$_4$]-**17** (Scheme 7).



Scheme 7. Photochemical reaction of complex **11c**.

Although at this time hypothetical, it is appealing to conclude that the metallacyclopropanone intermediate in these processes (depicted as **11c-T$_2$** in Figure 6), with a strong biradical character,[3d] could be reduced by accepting H radicals from the solvent, with concomitant MeO elimination. Evidently, this reduction has to occur on this species, otherwise the final product would be compound **17** bearing a MeO group next to the Cp ring. The second deuterium atom on [^{2}H$_5$]-**19** should arise from standard protonation of the enolate resulting from the reaction of the ketene and CD$_3$OD.

Interestingly, the two triplet species derived from complexes **11a** and **11c**, which lead to the photoslippage pathway, are lower in energy than the corresponding metallacyclopropanone species. However, no fulvene **16** or related products were observed for Re-derived complexes **11c**. This different behavior could be explained in terms of the strong back-donation of the Re to the Cp ring, which may hamper the initial slippage step in the **II(T$_1$)** species, therefore allowing bimolecular attack to the cyclopropanone species to occur. To prove this hypothesis, complex **11b** was prepared from CpMn(CO)$_2$PPh$_3$ by following the standard procedure described above (Scheme 4). For this complex, the photochemical reaction proceeds much slower (and with lower conversion) than in complexes **11a** and **12a**, and leads to fulvene **16** together with some unidentified impurities[28] (Scheme 5). It may then be concluded that the stronger Mn–Cp bonding due to the higher back-donation from the Mn to the Cp ring in complex **11b** slows down the photoslippage process, which is in clear accordance with the experimental results obtained for Re derivative **11c**.

Conclusion

The UV spectra of Group 6 metal carbene complexes bearing a CpM(CO)$_3$ moiety bonded to the carbene carbon atom have been studied. These complexes exhibit a shift of the absorption at higher wavelengths with respect to the parent monometallic complex **1a**, partly due to a higher occupation of the p$_z$ atomic orbital of the carbene carbon atom. DFT calculations accurately assign this band to a MLCT transition, thus showing that the presence of a second metal center does not affect the nature of the transition. Furthermore, both Mn- and Re-derived complexes exhibit an analogous behavior, which confirms that the nature of the band does not depend on the introduction of a second metal center.

In contrast, the photochemical reactivity of these complexes strongly depends on the nature of this metal fragment. Thus, a new photoslippage reaction leading to fulvenes occurs when Mn-derived products **11a**, **11b**, and **12a** are irradiated (both Cr and W derivatives). Computational and deuteration experiments support this unprecedented photoslippage process. However, Re-derived product **11c** behaves like standard Fischer complexes, yielding the usual photocarbonylation products and a new photoreduction process that occurs in the metallacyclopropanone intermediate. The key to this differential photoreactivity seems to be the metal–Cp back-donation, which hampers the slippage process for Re derivatives, thus favoring the carbonylation reaction. The search for novel reaction pathways in other bi- and polymetallic carbene complexes is currently under way in our laboratories.

Experimental Section

General procedures: All reactions were carried under an argon atmosphere. All solvents used in this work were purified with a Pure Solv PS-MD-5 system. Flame-dried glassware and standard Schlenk techniques were used for moisture-sensitive reactions. Purification of the crude reaction products was performed by flash column chromatography on silica gel (Merck, 230–400 mesh), and the identification of products was achieved by thin-layer chromatography (Kieselgel 60F-254). UV light (λ = 254 nm) and 5% phosphomolybdic acid solution in 95% EtOH were used to develop the plates. NMR spectra were recorded at 25 °C in $CDCl_3$ or CD_3CN, on Bruker Avance DPX 300 (300 MHz for ^1H, 75 MHz for ^{13}C), Bruker Avance 500 (500 MHz for ^1H, 125 MHz for ^{13}C), or Bruker Avance III 700 (700 MHz for ^1H, 175 MHz for ^{13}C) instruments. Chemical shifts are given in ppm relative to $CDCl_3$ (7.27 ppm for ^1H; 77.0 ppm for ^{13}C) or CD_3CN (1.94 ppm for ^1H; 118.7 ppm for ^{13}C). IR spectra were obtained on a Bruker Tensor 27 (MIR 8000–400 cm^{-1}) spectrometer as solid films (obtained by slow evaporation of the solvent: CH_2Cl_2, $CDCl_3$, or CD_3CN) through the attenuated total reflectance (ATR) technique. EIMS experiments were carried out on a MAT95 XP spectrometer at 220 °C. Elemental analyses were conducted on a LECO CHNS-932 apparatus. All commercially available products were used without further purification. UV measurements were recorded on a Varian (Cary 50) spectrometer in a solution of dry hexanes or CH_2Cl_2, at the concentration indicated for each case. Alkoxycarbene complexes **1a**,[17] **11**, and **12** were prepared by following the standard alkyllithium addition–alkylation sequence reported by Fischer.[18] $CpMn(CO)_2PPh_3$ was prepared and identified by comparison to analytical data previously described in the literature.[29]

General procedure for preparation of cyclopentadienyl(tricarbonyl)-metal-substituted complexes 11 and 12: *n*BuLi (1 equiv) was added dropwise at −78 °C to a solution of the corresponding $CpM(CO)_3$ (M = Mn, Re; 1 equiv) in THF (10 mL mmol^{-1}). The reaction mixture was then stirred at this temperature for 45 min, after which it was warmed to −5 °C and the corresponding $M(CO)_6$ (M = Cr, W; 1 equiv) was added in one portion. The resulting solution was stirred for another hour, the solvent was evaporated in vacuo, the residue was dissolved in water (10 mL mmol^{-1}), the solution was cooled to 0 °C, and $Me_3O^+BF_4^-$ (1.74 equiv) was added. The mixture was stirred for 30 min, the resulting slurry was extracted with Et_2O, and then the organic layer was dried over $MgSO_4$, filtered, and the solvent evaporated in vacuo. The solid thus obtained was purified by flash column chromatography (SiO_2, argon pressure) with hexane as eluent.

Pentacarbonylmethoxy[cyclopentadienyl(tricarbonyl)manganese]carbene-chromium(0) (11a): Following the general procedure described above, cyclopentadienylmanganese(I) tricarbonyl (1 g, 4.9 mmol), *n*BuLi (3 mL of a 1.6 M solution in hexanes), $Cr(CO)_6$ (1 g, 4.9 mmol), and $Me_3O^+BF_4^-$ (1.26 g, 8.5 mmol) were reacted. The resulting crude product was then purified to yield a dark red solid identified as complex **11a** (1.3 g, 64%). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 4.81 (s, 3H; OCH_3), 4.95, (m, 2H; CH_{Cp}), 5.52 ppm (m, 2H; CH_{Cp}); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 66.5 (OCH_3), 84.0, 87.3, 106.7 (C_{Cp}), 216.3 (CO *cis*), 222.5 (CO *trans*), 222.8 (CO_{Mn}), 333.3 ppm (C=Cr); IR (ATR): $\tilde{\nu}$ = 2063, 2024, 1916, 1253, 1231, 1213, 650, 626 cm^{-1}; elemental analysis calcd (%) for $C_{15}H_7CrMnO_9$: C 41.12, H 1.61; found: C 41.63, H 1.82.

Pentacarbonylmethoxy[cyclopentadienyl(dicarbonyl)(triphenylphosphine)manganese]carbenechromium(0) (11b): *t*BuLi (0.5 mL of a 1.7 M solution in pentane) was added dropwise at −78 °C to a solution of $CpMn(CO)_2PPh_3$ (170 mg, 0.39 mmol) in THF (4 mL). The reaction mixture was stirred for 45 min, after which it was warmed to −5 °C and $Cr(CO)_6$ (86 mg, 0.39 mmol) was added in one portion. After stirring for a further hour, the solvent was evaporated under vacuum, the resulting residue was dissolved in water (10 mL), the solution was cooled to 0 °C, and $Me_3O^+BF_4^-$ (100 mg, 0.68 mmol) was added in one portion. After 30 min, the crude reaction product was extracted with Et_2O and the organic layer was dried over $MgSO_4$, filtered, and the solvent removed in vacuo to yield, after purification (SiO_2, argon pressure, hexanes), a dark red solid identified as complex **11b** (70 mg, 40%). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 4.20 (m, 2H; CH_{Cp}), 4.76 (s, 3H; OCH_3), 5.32 (m, 2H; CH_{Cp}), 7.42 ppm (m, 15H; ArH); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 66.1 (OCH_3), 86.3, 87.3, 104.1 (C_{Cp}), 128.4 (d, *J*(C,P) = 33.0 Hz, C_{Ar}), 129.9 (C_{Ar}), 132.8 (d, *J*(C,P) = 41.4 Hz, C_{Ar}), 136.8 (d, *J*(C,P) = 166 Hz, C_{Ar}), 216.8 (CO *cis*), 222.9 (CO *trans*), 230.1, 230.4 (CO_{Mn}), 301.9 ppm (C=Cr); IR (ATR): $\tilde{\nu}$ = 2927, 1928, 1858, 730, 695 cm^{-1}; elemental analysis calcd (%) for $C_{32}H_{22}CrMnO_8P$: C 57.16, H 3.30; found: C 57.40, H 3.40.

Pentacarbonylmethoxy[cyclopentadienyl(tricarbonyl)rhenium]carbene-chromium(0) (11c): Cyclopentadienylrhenium(I) tricarbonyl (500 mg, 1.5 mmol), *n*BuLi (0.9 mL of a 1.6 M solution in hexanes), $Cr(CO)_6$ (328 mg, 1.5 mmol), and $Me_3O^+BF_4^-$ (383 mg, 2.6 mmol) were reacted following the general procedure described above. The crude product was then purified to yield **11c** as a red solid (623 mg, 73%). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 4.76 (s, 3H; CH_3), 5.46 (m, 2H; CH_{Cp}), 6.08 ppm (m, 2H; CH_{Cp}); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 66.4 (OCH_3), 85.5, 88.7, 110.7 (C_{Cp}), 191.4 (CO_{Re}), 216.4 (CO *cis*), 222.2 (CO *trans*), 326.6 ppm (C=Cr); IR (CH_2Cl_2): $\tilde{\nu}$ = 2062, 2026, 1994, 1911, 1265, 1243, 1227, 1210, 664, 641 cm^{-1}; elemental analysis calcd (%) for $C_{15}H_7CrO_9Re$ (569.41): C 31.64, H 1.24; found: C 31.26, H 1.03.

Pentacarbonylmethoxy[cyclopentadienyl(tricarbonyl)manganese]carbene-tungsten(0) (12a): Cyclopentadienylmanganese(I) tricarbonyl (500 mg, 2.4 mmol), *n*BuLi (1.5 mL of a 1.6 M solution in hexanes), $W(CO)_6$ (862 mg, 2.4 mmol), and $Me_3O^+BF_4^-$ (630 mg, 4.3 mmol) were reacted according to the general procedure described above. After purification of the crude product, complex **12a** was obtained as a bright red solid (1.1 g, 78%). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 4.62 (s, 3H; OCH_3), 4.98 (m, 2H; CH_{Cp}), 5.52 ppm (m, 2H; CH_{Cp}); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 68.9 (OCH_3), 84.2, 88.5, 108.8 (C_{Cp}), 196.9 (CO *cis*), 201.8 (CO *trans*), 222.6 (CO_{Mn}), 306.2 ppm (C=W); IR (ATR): $\tilde{\nu}$ = 2070, 2024, 1904, 1260, 1230, 1211, 656, 626 cm^{-1}; elemental analysis calcd (%) for $C_{15}H_7MnO_9W$: C 31.61, H 1.24; found: C 31.30, H 1.12.

Pentacarbonylmethoxy[cyclopentadienyl(tricarbonyl)rhenium]carbene-tungsten(0) (12b): Cyclopentadienylrhenium(I) tricarbonyl (300 mg, 0.9 mmol), *n*BuLi (0.6 mL of a 1.6 M solution in hexanes), $W(CO)_6$ (313 mg, 0.9 mmol), and $Me_3O^+BF_4^-$ (229 mg, 1.55 mmol) were reacted as described above. After purification of the resulting crude product, compound **12b** was obtained as a bright red solid (470 mg, 35%). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 4.58 (s, 3H; OCH_3), 5.50 (m, 2H; CH_{Cp}), 6.08 ppm (m, 2H; CH_{Cp}); ^{13}C NMR (75 MHz, $CDCl_3$, 22 °C): δ = 68.8 (OCH_3), 85.8, 89.9, 113.1 (C_{Cp}), 191.5 (CO_{Re}), 197.0 (CO *cis*), 201.5 (CO *trans*), 299.4 ppm (C=W); IR (ATR): $\tilde{\nu}$ = 2072, 2028, 1904, 1255, 1224, 1155, 778 cm^{-1}; elemental analysis calcd (%) for $C_{15}H_7O_9Re$: C 25.69, H 1.01; found: C 25.30, H 1.20.

Formylcymantrene (14): *n*BuLi (0.6 mL of a 1.6 M solution in hexanes) was added dropwise at −78 °C to a solution of cymantrene (200 mg, 0.98 mmol) in THF (10 mL). The reaction mixture was stirred at this temperature for 45 min, after which DMF was added in one portion. The reaction was maintained at −78 °C for 40 min and afterwards warmed to 0 °C and stirred for an additional 30 min. The reaction mixture was then quenched with water, extracted with Et_2O, and the organic layer was washed with water, dried over $MgSO_4$, and the solvent evaporated under vacuum to yield, without further purification, compound **14**.[20] ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 4.95 (m, 2H; CH_{Cp}), 5.47 (m, 2H; CH_{Cp}), 9.63 ppm (CHO).

Pentacarbonyl{1-methoxy-3-[cyclopentadienyl(tricarbonyl)manganese]-2-propenylidenecarbene}chromium(0) (13): Et_3N (0.5 mL, 3.44 mmol) was added to a solution of pentacarbonyl(ethoxy)methylchromium(0) carbene (**15**; 211 mg, 0.86 mmol) and formylcymantrene **14** (200 mg, 0.86 mmol) in Et_2O (4.5 mL). Then, TMSCl (0.35 mL, 2.52 mmol) was added. Immediate HCl(g) evolution was observed. A slow flow of argon was passed through the reaction mixture until no more gas evolution occurred. The crude reaction product was stirred at room temperature for 1 h, after which it was isolated by filtration through a short pad of silica gel and dried under vacuum. The crude product thus obtained was purified by flash column chromatography (SiO_2, argon pressure, hexanes/ethyl acetate 10:1) to yield complex **13** as a dark red solid (208 mg, 51 %). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 1.68$ (t, $^3J(H,H) = 6$ Hz, CH_3), 4.86 (m, 2H; CH_{Cp}), 5.09 (q, $^3J(H,H) = 6$ Hz, OCH_2), 5.20 (m, 2H; CH_{Cp}), 6.50 (d, $^3J(H,H) = 15$ Hz, $CH{=}CH$), 7.54 ppm (d, $^3J(H,H) = 15$ Hz, $CH{=}CH$); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 15.2$ (CH_3), 76.3 (OCH_2), 83.4, 85.5 (CH_{Cp}), 93.1 (C_{Cp}), 123.1, 139.4 ($CH{=}CH$), 216.5 (CO *cis*), 223.6 (CO_{Mn}), 224.2 (CO *trans*), 329.7 ppm ($C{=}Cr$); IR (ATR): $\tilde{\nu} =$ 2963, 2058, 2022, 1919 (CO), 1591, 659, 631 cm^{-1}; elemental analysis calcd (%) for $C_{17}H_9CrMnO_9$: C 43.99, H 1.95; found: C 43.60, H 1.70.

General procedure for photochemical reactions: Photochemical reactions were conducted with a 400 W medium-pressure Hg lamp through a Pyrex filter. All reactions were carried out in dry degassed MeCN or THF by using standard Schlenk techniques. In a typical experiment, a solution of the carbene complex (0.11 mmol) in solvent (15 mL) was irradiated (all reactions were monitored by TLC until the disappearance of the starting material). The solvent was removed in vacuo and the crude product analyzed and purified as indicated for each case.

Photochemical reaction of complex 11a; synthesis of fulvenes 16[31]/[$^2H_1$]-16: The photochemical reaction of complex **11a** was studied in different solvents:

1) THF/MeOH: Following the general procedure described above, a solution of complex **11a** (150 mg, 0.34 mmol) in THF (46 mL) and MeOH (15 mL) was irradiated for 6 h. The solvent was then evaporated in vacuo, and the resulting crude product analyzed by ^1H NMR spectroscopy. This showed the presence of fulvene **16**, together with some minor impurities. The crude material was filtered through Celite to yield fulvene **16** as a colorless oil (10 mg, 28 %). (This product showed extensive decomposition when exposed to air, acid, or bases.) ^1H NMR (500 MHz, CD_3CN, 25 °C): $\delta = 3.95$ (s, 3H; OCH_3), 6.28 (m, 1H; CH), 6.34 (m, 1H; CH), 6.42 (m, 1H; CH), 6.51 (m, 1H; CH), 7.11 ppm (m, 1H; CH); ^{13}C NMR (125 MHz, CD_3CN, 25 °C): $\delta = 68.7$ (OCH_3), 117.2 (CH), 125.3 (CH), 127.1 (C), 127.7 (CH), 131.0 (CH), 158.1 ppm (CH).

2) MeCN/MeOH: According to the general procedure, complex **11a** (200 mg, 0.46 mmol) was dissolved in MeCN (62 mL), MeOH (21 mL) was added, and the solution was irradiated for 2 h 45 min. The solvent was then removed under vacuum, and the crude product analyzed by NMR spectroscopy. The ^1H NMR spectrum showed only the presence of fulvene **16**.

3) THF/[D_4]MeOH: [D_4]MeOH (2 mL) was added to a solution of complex **11a** (150 mg, 0.34 mmol) in THF (45 mL), and the resulting mixture was irradiated following the general procedure. After 24 h, the crude product showed the formation of fulvene [$^2H_1$]-**16**. This compound also showed extensive decomposition and could not be isolated from the crude mixture. ^1H NMR (700 MHz, CD_3CN, 25 °C): $\delta = 3.95$ (s, 3H; OCH_3), 6.28 (m, 1H; CH), 6.35 (m, 1H; CH), 6.42 (m, 1H; CH), 6.51 ppm (m, 1H; CH); ^{13}C NMR (175 MHz, CD_3CN, 25 °C): $\delta = 68.4$ (OCH_3), 116.9 (CH), 124.9 (CH), 126.2 (C), 127.4 (CH), 130.6 (CH), 157.6 ppm (t, $^3J(C,D) = 106$ Hz, CD).

Photochemical reaction of complex 12a: A solution of complex **12a** (200 mg, 0.35 mmol) and MeOH (15 mL) in THF (45 mL) was irradiated for 6 h following the general procedure. After removal of the solvent, the crude product was analyzed by NMR spectroscopy, which indicated the formation of fulvene **16** as the only reaction product. When the irradiation was effected in the presence of [D_4]MeOH, the reaction went to completion in 8.5 h, and fulvene [$^2H_1$]-**16** was obtained as the only reaction product.

Photochemical reaction of complex 11c: The photochemical reaction of complex **11c** was studied in different solvents:

1) THF/MeOH: A mixture of complex **11c** (190 mg, 0.34 mmol) and MeOH (15 mL) in THF (45 mL) was irradiated for 50 h following the general procedure. After removal of the solvent, the ^1H NMR spectrum of the crude product showed the presence of three different products (**17**–**19**) that were isolated by flash column chromatography (SiO_2, hexanes/CH_2Cl_2 2:1).

Compound **17** (light yellow oil, 62.5 mg, 41 %). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 3.46$ (s, 3H; OCH_3), 3.82 (s, 3H; CO_2CH_3), 4.49 (m, 1H; *CH*OMe), 5.29 (m, 2H; CH_{Cp}), 5.56 (m, 1H; CH_{Cp}), 5.65 ppm (m, 1H; CH_{Cp}); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 52.6$ (OCH_3), 58.5 ($COOCH_3$), 76.7 (*C*HOCH$_3$), 83.0, 83.8, 85.0, 85.4 (CH_{Cp}), 102.1 (C_{Cp}), 170.0 (*C*O$_2$CH$_3$), 193.3 ppm (CO_{Re}); IR (ATR): $\tilde{\nu} = 2022$, 1909, 1752, 1271, 1224, 1201 cm^{-1}; MS (EI): *m/z* (%): 438 (91) [M^+], 410 (100) [$M^+ - CO$], 380 (17) [$M^+ - CO - OMe$], 352 (50) [$M^+ - 2CO - OMe$], 324 (90) [$M^+ - 3CO - OMe$], 294 (94) [$M^+ - 3CO - 2OMe$]; elemental analysis calcd (%) for $C_{12}H_{11}O_6Re$: C 32.95, H 2.53; found: C 32.70, H 2.38.

Compound **18**[32] (white solid, 5.6 mg, 4 %). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 3.82$ (s, 3H; OCH_3), 5.37 (m, 2H; CH_{Cp}), 6.02 ppm (m, 2H; CH_{Cp}).

Compound **19** (colorless oil, 5 mg, 4 %). ^1H NMR (500 MHz, $CDCl_3$, 25 °C): $\delta = 3.45$ (s, 2H; CH_2), 3.74 (s, 3H; OCH_3), 5.30 (m, 2H; CH_{Cp}), 5.46 ppm (m, 2H; CH_{Cp}); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): $\delta = 33.7$ (CH_2), 52.3 (OCH_3), 83.9, 85.1 (CH_{Cp}), 100.4 (C_{Cp}), 170.5 (*C*OOCH$_3$), 193.7 ppm (CO_{Re}); IR (ATR): $\tilde{\nu} = 2021$, 1908, 1740, 1436 cm^{-1}; MS (EI): *m/z* (%): 408.0 (89) [M^+], 380 (100) [$M^+ - CO$], 352 (84) [$M^+ - CO - OMe$], 322 (69) [$M^+ - 2CO - OMe$], 294 (98) [$M^+ - 3CO - OMe$]; elemental analysis calcd (%) for $C_{11}H_9O_5Re$: C 32.43, H 2.23; found: C 32.20, H 2.13.

2) MeCN/MeOH: Following the general procedure, a solution of complex **11c** (150 mg, 0.26 mmol) and MeOH (11 mL) in THF (34 mL) was irradiated for 24 h. After removal of the solvent, the NMR spectrum of the crude product showed the presence of compounds **17** and **18**, which were isolated by flash column chromatography (SiO_2, hexanes/CH_2Cl_2 2:1). Yields: compound **17** (23.5 mg, 20 %), compound **18** (31.5 mg, 31 %).

3) THF/[D_4]MeOH: Compound **11c** (175 mg, 0.31 mmol) was irradiated for 48 h in the presence of [D_4]MeOH (2 mL) according to the general procedure described above. After removal of the solvent, the NMR spectrum of the crude product showed the formation of compounds [$^2H_4$]-**17**, **18**, and [$^2H_5$]-**19** together with unreacted starting material (17.5 mg). The crude material was purified by flash column chromatography (SiO_2, hexanes/CH_2Cl_2 2:1). Yields are based on recovered starting material.

Compound [$^2H_4$]-**17** (light yellow oil, 24.9 mg, 20 %). ^1H NMR (500 MHz, $CDCl_3$, 22 °C): $\delta = 3.46$ (s, 3H; CDCOC*H*$_3$), 5.29 (m, 2H; CH_{Cp}), 5.57 (m, 1H; CH_{Cp}), 5.64 ppm (m, 1H; CH_{Cp}); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): $\delta = 51.9$ (sept, $^1J(D,C) = 90$ Hz, CO_2CD_3), 58.4 (OCH_3), 76.4 (t, $^1J(D,C) = 90$ Hz, *C*DOCH$_3$), 83.0, 83.8, 85.0, 85.5 (CH_{Cp}), 102.0 (C_{Cp}), 170.1 (*C*O$_2$CD$_3$), 193.3 ppm (CO_{Re}); IR (ATR): $\tilde{\nu} = 3116$, 2955, 2924, 2854, 2021, 1909, 1747 cm^{-1}; MS (EI): *m/z* (%): 442 (95) [M^+], 414 (100) [$M^+ - CO$], 380 (86) [$M^+ - CO - OMe$].

Compound **18** (10.6 mg, 10 %).

Compound [$^2H_5$]-**19** (tan solid, 6.1 mg, 5 %). For this compound a small quantity of the nondeuterated product was observed on the ^1H NMR (3.43 ppm (s, 1H; CH_2)) and ^{13}C NMR (53.4 ppm (CH_2)) spectra. ^1H NMR (700 MHz, $CDCl_3$, 25 °C): $\delta = 5.30$ (m, 2H; CH_{Cp}), 5.46 ppm (m, 2H; CH_{Cp}); ^{13}C NMR (175 MHz, $CDCl_3$, 25 °C): $\delta = 33.3$ (sept, $^1J(D,C) = 105$ Hz, CD_3), 51.6 (q, $^1J(D,C) = 91$ Hz, *C*D$_2$CO), 84.0, 85.1 (CH_{Cp}), 100.4 (C_{Cp}), 170.5 (*C*OOCD$_3$), 193.8 ppm (CO_{Re}); IR (ATR): $\tilde{\nu} = 2020$, 1906, 1753 cm^{-1}; MS (EI): *m/z* (%): 413 (78) [M^+], 385 (98) [$M^+ - CO$], 357 (72) [$M^+ - 2CO$], 323 (27) [$M^+ - 2CO - OCD_3$].

Photochemical reaction of complex 12b: Following the general procedure described above, complex **12b** (175 mg, 0.25 mmol) was dissolved in THF (31 mL) and irradiated in the presence of MeOH (10 mL) for 24 h. After removal of the solvent, the crude product was analyzed by NMR spectroscopy and purified (SiO_2, hexanes/CH_2Cl_2 2:1), to yield compound **20**[31] as a tan solid (10 mg, 11 %). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 5.47$ (m, 2H; CH_{Cp}), 6.02 (m, 2H; CH_{Cp}), 9.60 ppm (s, 1H; CHO). For this reaction an unidentified mixture of compounds was also observed.

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