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Computational and Experimental Studies on the Mechanism of the Photochemical Carbonylation of Group 6 Fischer Carbene Complexes

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Dedicated to the memory of Dr. Juan C. del Amo killed in the terrorist attack in Madrid on March 11th, 2004

Abstract: The photocarbonylation reaction of Group 6 Fischer carbene complexes has been studied by DFT and experimental procedures. The process occurs by intersystem crossing (ISC) from the lowest excited singlet state (S_1) to the lowest triplet state (T_1), the latter structure being decisive for the outcome of the reaction. Methylenepentacarbonylchromium(0) complexes, alkoxypentacarbonylchromium(0)carbene complexes, and alkoxyphosphinetetracarbonylchromium(0) carbene complexes have coordinatively unsaturated chromacyclopropanone T_1 structures with a biradical character. The evolution of the metallacyclopropanone species occurs by a jump (spin inversion) to the S_0 hypersurface by coordination of a molecule of the solvent, leading to ketene-derived products in the presence of ketenophiles or reverting to the starting carbene complex in their absence. The T_1 excited states obtained from methylenephosphinetetracarbonylchromium(0) complexes and pentacarbonyltungsten(0)carbene complexes are unable to produce the carbonylation. The reaction with ketenophiles is favored in coordinating solvents, which has been tested experimentally in the reaction of alkoxypentacarbonylchromium(0) complexes and imines.

Keywords: carbene complexes · carbonylation · chromium · density functional calculations · photochemistry · reaction mechanisms

Introduction

Nowadays Fischer carbene complexes are reagents of general use in organic and organometallic chemistry.[1] The scope of the extremely rich thermal reactivity of these complexes has been recently widened by report from ourselves[2] and from other groups[3] on the possibility to effect the catalytic transmetalation from Group 6 metal–carbene complexes to other transition metals, opening opportunities to explore new reactivity based on these compounds. Our recently reported[4] photochemically induced dyotropic rearrangements of chromium(0) aminocarbene complexes, unambiguously demonstrate that there are also opportunities to discover new photo-processes of these complexes. However, despite the enormous amount of work dedicated to the chemistry of these complexes, their reaction mechanisms have received little attention. This is an important point, since even apparently simple processes such as the addition of nucleophiles to α,β-unsaturated carbene complexes have been recently shown to occur by pathways more complex than a simple addition to the metal.[1k,n,5]

The initial proposal by Hegedus and co-workers in 1988 that the irradiation of chromium(0) carbene complexes promotes a carbonylation process to produce ketene-like species,[6] systematized the photochemistry of Group 6 carbene complexes in the presence of nucleophiles, and opened gates to a varied and efficient entry to ketene-derived pro-

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Supporting information (cartesian coordinates (in Å) and total energies (in a. u., non-corrected zero-point vibrational energies included) of all the stationary points discussed in the text, and a figure with the chief geometrical data of complexes **9**) for this article is available on the WWW under http://www.chemeurj.org/ or from the authors.

ducts.[1d,h,j] In spite of the synthetic efficiency of these reactions, very little is still known about the intimacies of the mechanism of the main photochemical process. In this work, some light will be shed about this fundamental process of Group 6 metal–carbene complexes.

The UV/Vis spectra of Fischer metal–carbene complexes[7] show three well-defined absorptions: a forbidden metal–ligand charge transfer (MLCT) absorption around 500 nm, the allowed low-energy ligand-field (LF) absorption in the range of 350–450 nm, and the high-energy LF absorption in the range of 300–450 nm. The two LF absorptions generally overlap. These absorptions are attributable to electronic transitions from the higher nonbonding metal-centered b_2-occupied orbital to the empty carbene-centered $2b_1$ (MLCT), $2a_1$ (low energy LF), and $3a_1$ (high energy LF) orbitals, respectively (Figure 1).

Most of the mechanistic photochemical studies carried out on this kind of complexes focused on the irradiation on LF bands. These photo-processes usually result in the extrusion of a CO ligand. Thus, activation of the high-energy LF band of $[(CO)_5W{=}C(OMe)Ph]$ results in the dissociation of one of the four *cis*-CO ligands,[7] whereas the irradiation of the low-energy LF band provokes the loss of the *trans*-CO ligand.[8] CO-photoextrusion leads to a long-life intermediate having a tetracarbonylcarbene structure (Scheme 1, Equation (a)). It has been proposed that the free coordination site of these species is blocked by an agostic interaction with a C−H bond of the neighboring alkoxy group (curved arrow in Equation (a) in Scheme 1).[9] Matrix photolysis studies on the MLCT band of chromium and tungsten Fischer carbene complexes revealed the isomerization from the most stable *anti* isomer to the less stable *syn* isomer (Scheme 1, Equation (b)).[10] To date, none of these processes have found application in the chemical synthesis of relevant compounds.

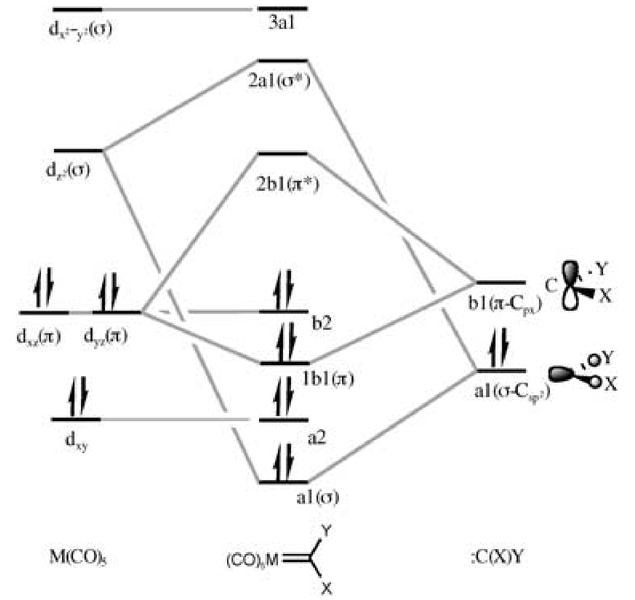
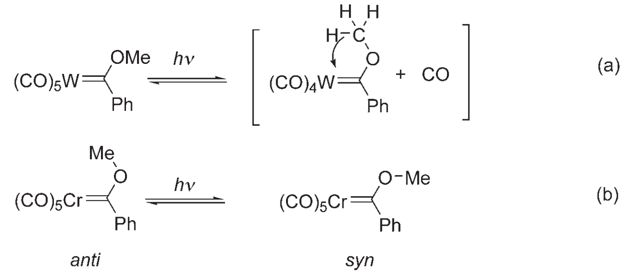


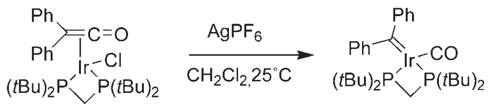
Figure 1. Canonical molecular orbitals corresponding to the octahedral structure of Fischer carbenes in the ground state.



Scheme 1.

The seminal finding by McGuire and Hegedus[11] that Cr and Mo (but not W) Fischer carbene complexes when exposed to sunlight in the presence of an imine formed a β-lactam in almost quantitative yield, turned out to be a general reaction. As stated above the intermediacy of ketene-like species formed by the reversible insertion of a *cis*-CO ligand into the M=C bond was postulated by Hegedus and co-workers in 1988 on the basis of indirect evidence.[6] This hypothesis is reasonable, since irradiation of the MLCT band should promote the transition of one electron from the metal-centered HOMO orbital to the carbene-carbon-centered LUMO orbital. Formally, this is a one-electron oxidation of the metal, which is known to facilitate the CO-insertion in M−C bonds.[12] However, and in spite of the synthetic usefulness of this process, many efforts directed to experimentally detect these ketene-like species have been fruitless up to date.[13] Strikingly, the reverse isomerization of metal-bonded ketene to carbene complex has been reported by Grotjahn and co-workers at an Ir nucleus (Scheme 2).[14]

Abstract in Spanish: *La reacción de fotocarbonilación de complejos de tipo Fischer del grupo 6 se ha estudiado mediante DFT y procedimientos experimentales. El proceso ocurre por cruce intersistémico (ISC) desde el estado excitado singlete (S_1) al estado triplete de más baja energía (T_1). La estructura de este triplete es decisiva para el resultado de la reacción. Los tripletes T_1 de los complejos metilenopentacarbonilcromo(0), alcoxipentacarbonilcromo(0)carbeno y alcoxifosfinotetracarbonilcromo(0)carbeno tienen estructuras de cromaciclopropanona coordinativamente insaturadas con un carácter birradicálico. La evolución de estas especies metalociclopropanónicas ocurre mediante el salto (inversión de espin) a la hipersuperficie S_0 por coordinación con una molécula de disolvente, produciendo productos derivados de cetenas, en presencia de cetenófilos o revertiendo al complejo metal-carbeno de partida en la ausencia de estos. Los estados excitados T_1 derivados de complejos metilenfosfinotetracarbonilcromo(0) y pentacarbonilwolframio(0) no carbonilan. La reacción con cetenófilos se favorece en disolventes coordinantes. Este hecho se ha comprobado experimentalmente en la reacción de complejos alcoxypentacarbonilcromo(0) e iminas.*



Scheme 2.

Our preliminary contribution to understand the mechanisms associated with the photochemical reactivity of chromium(0)carbene complexes and imines by using a combination of experimental and theoretical methods,[15] assumed as the starting point of the reaction to be a preformed metallaketene. DFT calculations carried out on three different model carbenes (methylene-, dihydroxymethylenepentacarbonyl-, and methylenephosphinetetracarbonylchromium(0) complexes) show that the effect of the ligands on the carbonylation process is a reasonable probe to study this fundamental organometallic reaction. Reported herein is a DFT study on the carbonylation of Group 6 metal–carbene complexes promoted by light. Experimental support for the main conclusions is presented, together with theoretical arguments that explain the difficulties in the experimental detection of the photogenerated intermediates.

Computational Details

All the calculations reported herein were carried out with the Gaussian 98 suite of programs.[16] Electron correlation was partially taken into account using the hybrid functional usually denoted as B3LYP[17] and the standard 6–31G* or 6-31+G* basis sets[18] for hydrogen, carbon, oxygen, and nitrogen, and the Hay–Wadt small-core effective core potential (ECP) including a double-ξ valence basis set[19] for chromium or tungsten (LANL2DZ keyword). We denote these basis sets schemes as LANL2DZ&6–31G(d) and LANL2DZ&6-31+G(d), respectively. Zero-point vibrational energy (ZPVE) corrections were computed at the same level and were not corrected. Excited states were located at the CIS level[20] and triplets were optimized at the uB3LYP level. Stationary points were characterized by frequency calculations[21] and have positive definite Hessian matrices. Transition structures (TSs) show only one negative eigenvalue in their diagonalized force constant matrices, and their associated eigenvectors were confirmed to correspond to the motion along the reaction coordinate under consideration. Bond orders and atomic charges were computed by using the natural bond order (NBO)[22] method.

Results and Discussion

Model complex **1a** was used to tune our theoretical model. The different excited states of complex **1a** were computed by using the configuration interaction method at the CIS level. The S_0 geometry of complex **1a** was optimized at the B3LYP/LANL2DZ&6-31+G(d) level. The most stable excited state of complex **1a** is a triplet (T_1) that has a vertical excitation energy of 24.4 kcal mol^{-1}, with the first singlet (S_1) resting 32.7 kcal mol^{-1} above T_1. The structure of this first triplet was optimized at the UB3LYP/LANL2DZ&6-31+G(d) level, leading to the structure **2a** which lies 21.9 kcal mol^{-1} above S_0. An additional S_0 stationary point denoted as **1a′** was also optimized. In this case the methylene moiety is coplanar with two colinear equatorial CO groups, whilst **1a** has the CH_2 moiety bisecting the plane defined by two adjacent equatorial CO groups. According to our results, **1a′** has an imaginary frequency associated with the rotation of the CH_2 fragment around the Cr–C bond, and lies only 0.3 kcal mol^{-1} above **1a**. Distortion of the symmetry group of **1a′** coupled to the optimization of the resulting triplet state, produced structure **3a**. Triplet **3a** is 17.4 kcal mol^{-1} more stable than **2a** (the triplet derived from **1a**) and is only 4.6 kcal mol^{-1} above the S_0 state of **1a** (Figure 2). It is worth noting that the triplet **3a** corresponds with the chromacyclopropanone (or chromium-coordinated ketene) proposed by Hegedus and co-workers to explain the reaction products obtained in the photochemical reaction of chromium(0) carbene complexes.[6]

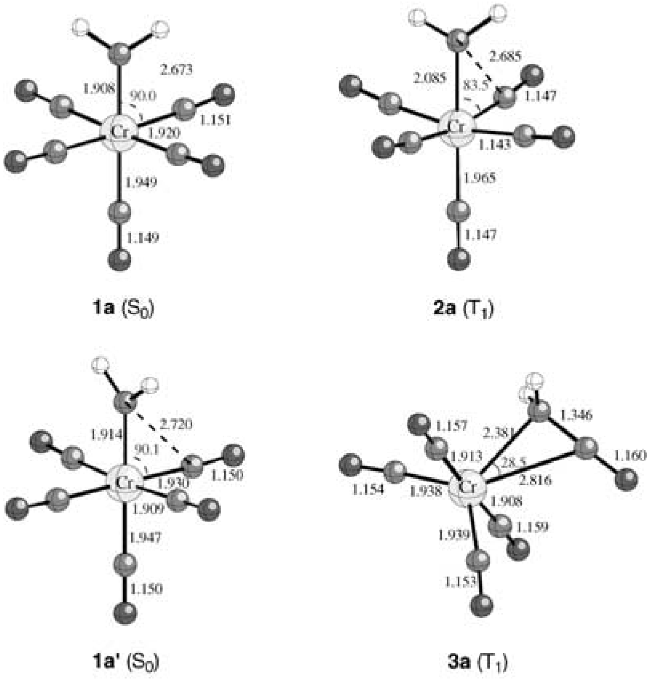


Figure 2. Ball-and-stick representations of complexes **1a,a′–3a**. S_0 and T_1 denote the ground and first triplet states, respectively. All S_0 and T_1 structures (bond lengths [Å] and angles [°]) correspond to fully optimized B3LYP/LANL2DZ&6-31+G(d) and UB3LYP/LANL2DZ&6-31+G(d) geometries, respectively.

The results obtained with the model compound **1a** encouraged us to study complex **1b**. A theoretical study of the structure and conformational behavior of this complex was recently reported by us.[10c] According to our results, compound **1b** may exist in two conformers *anti*-**1b** and *syn*-**1b,** *anti*-**1b** being 1.8 kcal mol^{-1} more stable than the *syn* conformer. Both isomers have the [C(OMe)Me] moiety bisecting the plane defined by two contiguous equatorial CO ligands. The CIS method was again used to determine the different excited states of both isomers of **1b**. The most stable excited state of *anti*-**1b** is a triplet with a vertical excitation energy of 65.7 kcal mol^{-1}, whilst the first singlet S_1 is 27.0 kcal mol^{-1} above this T_1 state. These results agree with the order of energy levels that is characteristic of a d^6 metal in a strong ligand field.[23] The geometry of the triplets derived from both isomers of **1b** was computed again at the UB3LYP/LANL2DZ&6–31G(d) level and converged to the corresponding cyclopropanone chromium complexes **3b** (from *anti* -**1b**) and **3c** (from *syn*-**1b**) (Figure 3). The species **3c** is 37.9 kcal mol^{-1} higher in energy than *syn*-**1b**, whereas the species **3b** is 41.8 kcal mol^{-1} higher in energy than *anti*-**1b**. Therefore, **3c** is 2.1 kcal mol^{-1} more stable than **3b**, which is the opposite order of stability found for both isomers in the S_0 state.

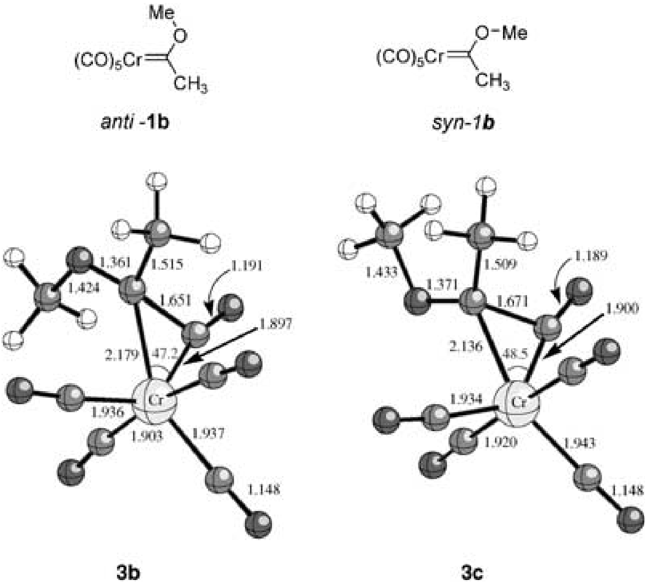


Figure 3. Fully optimized structures (UB3LYP/LANL2DZ&6–31G(d) level of theory, see text) of the first excited triplet states of Fischer carbenes *anti*- and *syn*-**1b** (Structures **3b** and **3c**, respectively). See Figure 2 caption for additional details.

It can be reasoned from the above results that the irradiation of alkoxychromium(0) carbene complexes, either in the LF band followed by relaxation to the MLCT band,[23] or directly in the MLCT band, results in the excitation of these complexes to the S_1 state, which readily decays to T_1 by intersystem crossing (ISC) due to spin-orbit coupling. This is a general phenomenon in Group 6 metal carbonyl complexes.[24] The calculated spin densities for Cr are 0.95 au for **3b** and 0.96 au for **3c**, whereas the calculated spin densities for the carbene-C atom are 0.43 au for **3b** and 0.46 au for **3c**, respectively. These values indicate that the chromacyclopropanone triplet species **3b** and **3c** have biradical character.

We have previously proposed[15] that the reaction of photogenerated chromacyclopropanone species and nucleophiles to form ketene-derived products occurs on the S_0 hypersurface. Therefore, species **3** should change their multiplicity prior to evolving to the ketene-derived products. This may be accomplished by filling the free coordination site of species **3** with a molecule of solvent (water in our model, as a computational equivalent of a coordinating solvent such as diethyl ether) in the apical position. The optimization of the geometry of this new structure in its S_0 state was effected from **3b** and **3c**, leading in both cases to the structure **4**, in which the methoxy group is outside the carbonyl plane (Figure 4).

To gain insight into the mechanism of the solvent-induced T_1–S_0 crossing of chromoketene **3a**, we have performed relaxed scans of this complex at different Cr–OH$_2$ distances.[25] The results obtained at the (U)B3LYP/LANL2DZ&6–31G(d) S_0 and T_1 potential energy surfaces are summarized

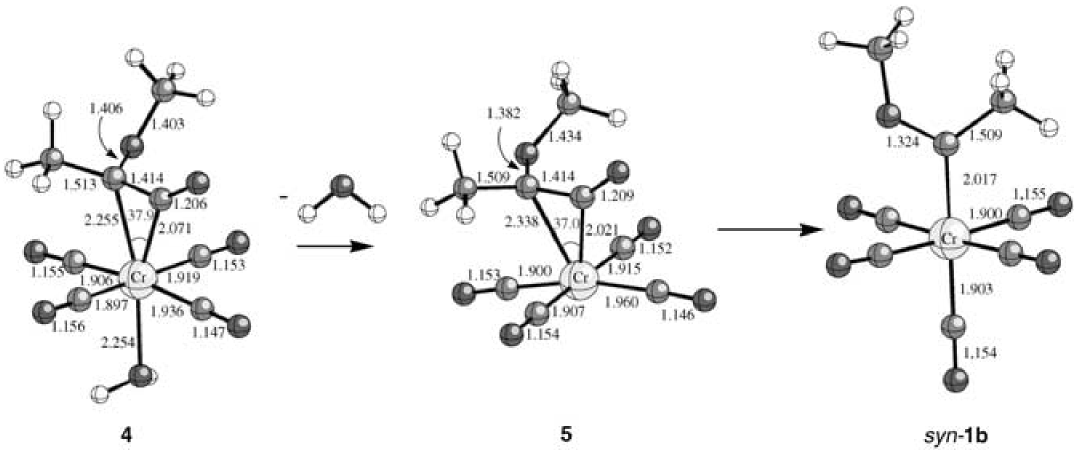


Figure 4. Fully optimized geometries (B3LYP/LANL2DZ&6–31G(d) level, see text) for the stationary points associated with the **4** →*syn*-**1b** transformation on the S_0 energy hypersurface. See Figure 2 caption for additional details. Structural data for *syn*-**1b** were taken from reference [10c].

in Figure 5. According to our results, the T_1 state of **3a** exhibits a very shallow Morse-like curve whose minimum is located at $r = 3.746$ Å, r being the Cr–OH_2 distance (Figure 5).

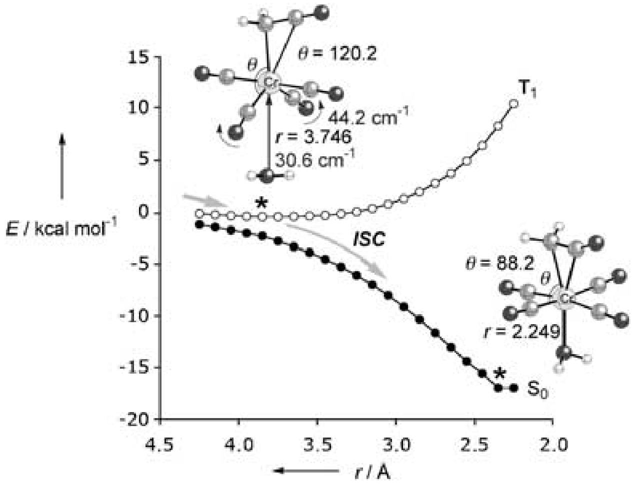


Figure 5. Fully relaxed scans for the chromoketene **3a** coordinated with a water molecule as a model for a coordinating ethereal solvent. The energies and geometries were computed at different Cr–OH_2 distances, denoted as r. Open and black circles indicate calculations for T_1 and S_0 states, respectively. Arrows indicate the stretching and bending vibrations associated with the T_1–S_0 radiation-less intersystem crossing, represented by the bold arrows. Wavenumbers associated with these vibrations are given in cm^{-1}.

This structure is almost identical to that shown in Figure 2 and does not show any significant interaction between the chromium atom and the oxygen atom of the model solvent. The harmonic analysis of this structure shows two low-frequency vibrations associated with the stretching of the Cr–O interaction and the symmetrical bending of two carbonyl groups to achieve the octahedral coordination. The energies corresponding to these vibrations are only 8.7×10^{-2} kcal mol^{-1} and 12.6×10^{-2} kcal mol^{-1}, respectively. This result, together with the negligible energy difference between both states at large Cr–OH_2 distances, indicates that the available thermal energy is sufficient for the molecule to pass from the T_1 to the S_0 potential energy surface. This radiationless intersystem crossing does not take place through a narrow conical intersection[26] but occurs at r values larger than 4.0 Å along a large energy plateau shared by both spin states.

From **4**, ketene-derived products can now be formed in the presence of ketenophiles, while in their absence, species **4** should revert to the starting complex **1b**. It is well known that alkoxychromium(0) complexes are photochemically stable for days in the absence of nucleophiles. Furthermore, this ketene-chromium to carbene-chromium complex reversion[27] has to occur on the S_0 hypersurface. The reversion of **4** to *syn*-**1b** is strongly exothermic[28] ($\Delta E = -30.6$ kcal mol^{-1}) on this hypersurface and occurs through the 16-electron intermediate **5** formed by elimination of the solvent molecule (in this case H_2O). Intermediate **5** evolves to give complex *syn*-**1b** by breaking of the carbene–CO bond (Figure 4). So far we have been unable to find a transition state connecting **4** to **5** or **5** to **1b**. Therefore, it is likely that this process occurs without any measurable energy of activation, which is in agreement with the computed exothermicity of the reaction.

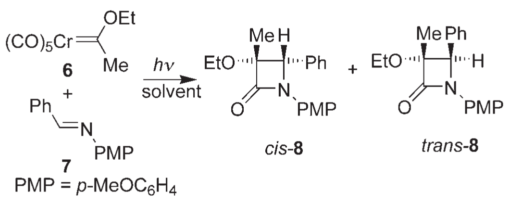
The structures of the metallacyclopropanone species **3** and **4** deserve further analysis. The T_1 species **3a–c** have elongated Cr–$C_{carbene}$ bonds (up to 0.12 Å) compared to those in the starting carbene complex **1b**. The [Cr–C]=O bond lengths are around 1.9 Å, and the C=O bond of the inserted CO ligand is about 0.03 Å longer than the CO bond in **1b**, which makes this a true C=O bond. The new bond formed between the former carbene-carbon atom and the inserted CO group is approximately 1.65 Å, which makes the species **3** true metallacyclopropanones. However, in the S_0 complex **4** the distance between Cr and the former carbene-carbon atom and the [Cr–C]=O moiety is elongated with respect to those in their corresponding T_1 structures **3b,c**. Similarly, in **4** the [C–C]=O distance has a value of 1.414 Å, which is considerably shorter than those in **3b** or **3c**. Therefore, the structure of the S_0 ketene complexes of chromium corresponds to a ketene species coordinated to chromium with a highly polarized Cr–C (former carbene-C) bond. NBO calculated bond orders for complexes **3b,c** and **4** validate the above discussion (Table 1). In fact, NBO analyses carried out on **4** give a charge value of -0.962 au for the chromium atom and $+0.158$ au for the carbene-C atom. Therefore, the S_0 saturated species **4** has, as expected, a significant acylchromate character, whereas **3b** and **3c** are more likely metallacyclopropanones (Table 1).

Table 1. Selected bond lengths (r(X–Y)), angles, and bond orders (B(X–Y), in a.u., in parentheses) for complexes **1b** and intermediates **3b,c** and **4**.

	anti-**1b**[a]	*syn*-**1b**[a]	**3b** (T_1)	**3c** (T_1)	**4** (S_0)
r(Cr–C) [Å]	2.060	2.017	2.179 (0.38)	2.136 (0.40)	2.254 (0.40)
r(Cr–C=O) [Å]	1.904	1.900	1.897 (0.68)	1.900 (0.66)	2.071 (0.52)
r(C–C=O) [Å]	2.739	2.753	1.651 (0.75)	1.671 (0.71)	1.414 (1.22)
r(C=O) [Å]	1.153	1.155	1.191 (1.87)	1.189 (1.88)	1.206 (1.85)
C–Cr–C(=O) [°]	87.3	89.3	47.2	48.5	37.9

[a] See reference [10c].

According to the theoretical model developed above, the reaction of complex **6** (Scheme 3) with imines in different solvents would be a good probe to test the sequence carbene complex (S_0)→chromacyclopropanone (T_1)→acylchromate (S_0). In fact, de-insertion of CO from ketene complexes **4** (through unsaturated complexes **5**) is disfavored by strongly coordinating ligands. Furthermore, these strongly coordinating ligands favor the decay of the T_1 species **3** to S_0 species **4**, which is necessary for the subsequent reaction with nucleophiles. Therefore, the yield of the reaction between a carbene complex such as **6** and imine **7** (Scheme 3) must be dependent on the nucleophilicity of the solvent used. A series of experiments were carried out using a variety of solvents ranging in polarity from hexane to MeCN. A clear relationship between the donor number (DN) of the solvent and the yield of the reaction was found, as predicted by our model. Thus, good coordinating solvents such as THF or MeCN gave very high yields of the mixture of *cis*- and *trans*-β-lactams **8**, but the yields are poorer in noncoordinating solvents such as hexane or benzene (Table 2, Scheme 3). Formation of β-lactams **8** in noncoordinating solvents may be explained by deactivation of the T_1 chromacyclopropanone **3** by coordination with the lone pair of the imine nitrogen atom.[29]



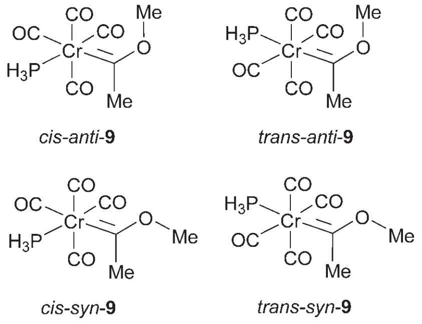
Scheme 3.

Table 2. Photochemical reactions of complex **6** and imine **7** in different solvents.

Entry[a]	Solvent[b]	DN[c]	Conversion[d]	*cis*-**8**/*trans*-**8**[e]
1	hexanes	–	32	7.3:1
2	benzene	–	55	3.2:1
3	CH_2Cl_2	0.00	69	4.4:1
4	THF	0.52	85	1:1
5	MeCN	0.36	90	6.3:1

[a] All the experiments were carried out using a 10^{-2} M concentration of solvent. [b] The temperature inside of the light box (monitored by using an external probe) was in the range of 26–30 °C for each case. [c] Values for donor number (DN)[30] are referenced to 1,2-dichloroethane. [d] The value of conversion is calculated based on the amount of unreacted imine observed after irradiation for 8 h (monitored by ^{1}H NMR spectroscopy). All the experiments were effected simultaneously to ensure identical reaction conditions, and repeated twice. The given values are the average of both experiments. [e] Determined by integration of the signals corresponding to H4 in the NMR spectra of the crude reaction mixtures.

As stated above, we have previously reported on the effect of the substitution of one or two CO ligands of the pentacarbonylchromium(0) carbene complexes by phosphines on the photochemical reaction with imines.[15] With a model for the carbonylation of alkoxypentacarbonylchromium(0) carbene complexes in hand, we studied the far more complicated situation of PH_3-substituted complexes. In this case, the number of possible starting situations for a determined complex is higher, since the PH_3 ligand can be either *cis* or *trans* to the carbene ligand, and for each isomer two possible *syn* and *anti* isomers of the carbene ligands are also likely (Scheme 4).



Scheme 4.

Calculations were pursued with the two more stable forms of both complexes, namely the *cis-syn*-**9** and *trans-anti*-**9** isomers (in both cases the [C(OMe)Me] fragment bisects the plane defined by the two equatorial CO ligands, like their analogous complexes **1b**). The optimization of the corresponding T_1 structures on the respective hypersurfaces was effected at the UB3LYP/LANL2DZ&6–31G(d) level as described above, and the structures **10** and **11** were obtained in both cases. The species **10** is 36.9 kcal mol^{-1} higher in energy than *trans-anti*-**9**, while **11** is 33.8 kcal mol^{-1} higher in energy than *cis-syn*-**9**. Both T_1 species show the chromacyclopropanone structure analogous to **3** (Figure 6). As for species **3**, the calculated spin density for the Cr atom in **10** is 1.02 au and for the former carbene-carbon atom is 0.42 au (the spin density values for **11** are 1.06 au and 0.52 au, respectively). Therefore, both **10** and **11** have biradical character.

Geometric data for complexes **9**–**12** are collected in Table 3. The presence of a PH_3 ligand in alkoxychromium(0) carbene complexes has no effect on the nature of the structures on the T_1 hypersurface, with the exception of the nar-

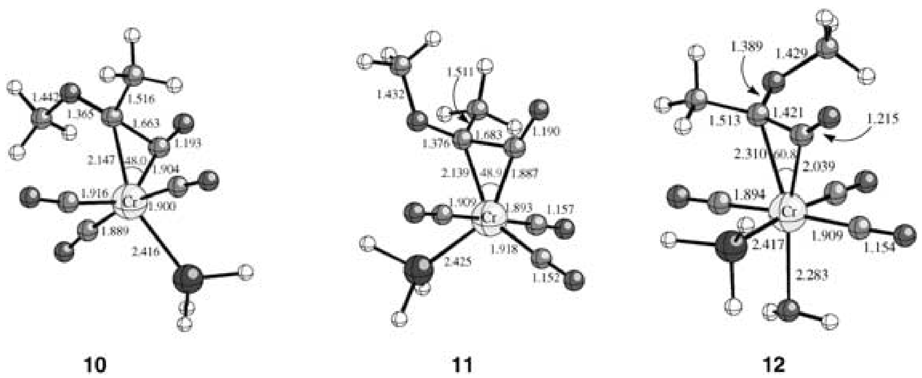


Figure 6. Fully optimized triplet structures **10** and **11** (UB3LYP/LANL2DZ&6–31G(d) level) and fully optimized structure **12** for the S_0 state (B3LYP/LANL2DZ&6–31G(d) level). See Figure 2 captions for additional details.

Table 3. Selected bond lengths (r(X–Y)), angles, and bond orders (B(X–Y), in a.u., in parentheses) for complexes **9** and intermediates **10, 11**, and **12**.

	cis-syn-**9**	*trans-anti*-**9**	**10**	**11**	**12**
r(Cr–C) [Å]	1.991	2.003	2.147 (0.25)	2.139 (0.39)	2.310 (0.77)
r(Cr–C=O) [Å]	1.899	1.858	1.904 (0.31)	1.887 (0.73)	2.039 (0.57)
r(C–C=O) [Å]	2.676	2.704	1.663 (0.81)	1.683 (0.70)	1.421 (1.20)
r(C=O) [Å]	1.157	1.160	1.193 (2.23)	1.190 (1.86)	1.215 (1.81)
r(Cr–P) [Å]	2.381	2.382	2.416 (0.26)	2.425 (0.36)	2.417 (0.38)
C–Cr–C(=O) [°]	86.9	88.8	48.0	48.9	37.5

rowing of the S_0–T_1 gap. Both T_1 structures **10** and **11** were deactivated to the S_0 hypersurface by coordination with a molecule of water as a model for an ethereal solvent. The S_0 active species **12** (Figure 6) is analogous to that obtained from pentacarbonylchromium(0) carbene complexes **4**. NBO analysis of **12** gives values of -0.881 au for Cr and $+0.194$ au for the former carbene-carbon atom. Again, **12** is a highly polarized species with significant acylchromate character. The Cr–C (former carbene) distance is larger than that of its analogue **4** due to the donor effect of the phosphine ligand, which makes the metal less prone to accept charge from the ketene ligand (Table 3, Figure 6).[31]

Finally, our model was tested against alkoxytungsten(0) carbene complexes that, until today, have proven inert towards photocarbonylation. We carried out calculations on pentacarbonyl(methoxymethylcarbene)tungsten(0) **13**. The geometry and conformational behavior of this complex have been previously calculated by us.[10c] Calculations carried out at the CIS level on the more stable *anti*-**13** conformer revealed a stable triplet state having a vertical excitation energy of 83.0 kcal mol^{-1}. However, in this case, S_1 is located only 5.3 kcal mol^{-1} higher in energy than T_1. The geometry of both triplets derived from *anti*-**13** and its isomer *syn*-**13** were optimized at the UB3LYP/LANL2DZ&6–31G(d) level. The optimization resulted in complexes **14** and **15**, respectively. Complex **14** is 54.0 kcal mol^{-1} higher in energy than *anti*-**13**, whereas *syn*-**13** is 51.3 kcal mol^{-1} lower in energy than **15**. Both triplets **14** and **15** differ only by 0.1 kcal mol^{-1}. Contrary to the behavior of their chromium counterparts **3b** and **3c**, neither **14** nor **15** have a tungstenacyclopropanone structure. Thus, the bond lengths between carbene-C atoms and the closest CO groups are 2.716 Å and 2.567 Å, respectively, without any measurable bond order between both atom pairs. Therefore, no ketene-like species are formed by excitation of an alkoxypentacarbonyltungsten(0) carbene complex (Figure 7). Hence, our model is in good accord with the experimentally observed lack of photochemical reactivity tungsten(0) carbenes.

Based on the calculations effected above we can attribute the inertia of tungsten(0)–carbene complexes to a stronger W–C(=O) bonding with respect to Cr–C(=O), together with a decrease in the nucleophilicity of the carbene-carbon atom in the excited state. Thus, NBO calculated bond orders range from 0.81–0.82 for *cis*-[W–C(=O)] in complexes **13** and from 0.71–0.74 for *cis*-[Cr–C(=O)] in complexes **1b**.

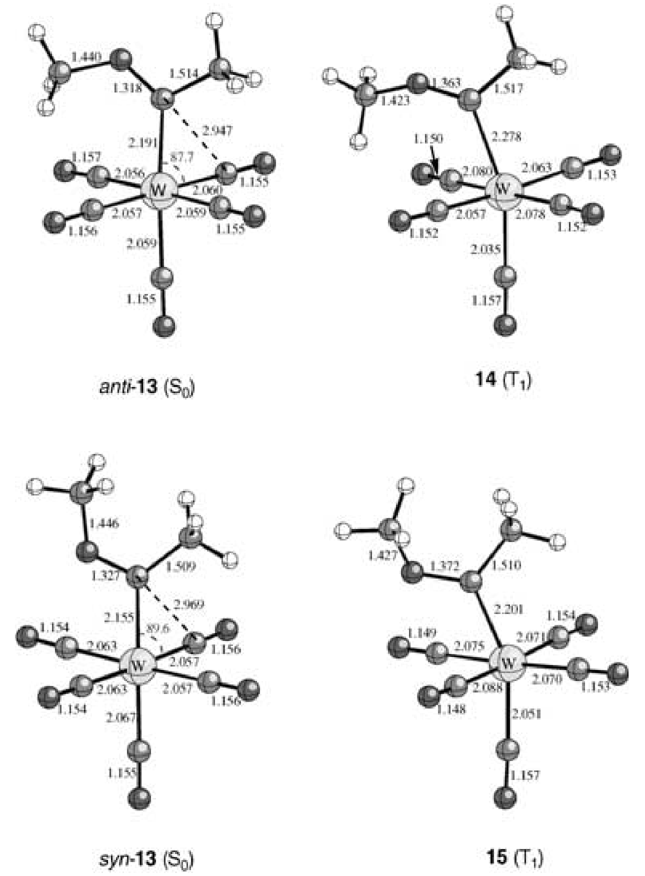


Figure 7. Fully optimized (B3LYP/LANL2DZ&6–31G(d) level) structures of tungsten(0) carbenes *syn*- and *anti*-**13** at their ground state. The corresponding excited T_1 structures **14** and **15**, optimized at the UB3LYP/LANL2DZ&6–31G(d) level, are also shown. See Figure 2 caption for additional details.

Conclusion

The photocarbonylation reaction of Group 6 Fischer carbene complexes was studied by DFT and experimental procedures. The process occurs by ISC from the lowest excited singlet state (S_1) to the lowest triplet state (T_1). The structure of the triplet is decisive for the outcome of the reaction. Methylenepentacarbonylchromium(0) complexes, alkoxypentacarbonylchromium(0) carbene complexes, and alkoxyphosphinetetracarbonylchromium(0) carbene complexes have coordinatively unsaturated chromacyclopropanone T_1 structures with significant biradical character. The evolution of these species takes place by an additional ISC to the S_0 hypersurface (spin inversion) by coordination of a molecule of the solvent. In the presence of ketenophiles, ketene-derived products are formed, however, in their absence, the reversion to the carbene complex takes place. This step is highly exothermic and is responsible for the experimentally observed *anti* → *syn* isomerization of chromium(0) carbene complexes in the absence of nucleophiles. On the contrary, pentacarbonyltungsten(0) carbene complexes do not carbonylate. Thus, the photoreactivity of Group 6 carbene complexes is strongly related to the coordinating ability of the solvent. Coordinating solvents facilitate the reaction by favoring the deactivation of the T_1 species. This prediction has been tested experimentally in the reaction between alkoxypentacarbonylchromium(0) complexes and imines.

Experimental Section

Photochemical reactions: general procedure: All photochemical reactions were conducted by using a 450-W medium-pressure mercury lamp fitted with a Pyrex filter. All the reactions were carried out in the specified solvent, dried and degassed (vacuum-Ar, four cycles) in a rubber septum-sealed Pyrex tube filled with argon. For all cases pentacarbonyl[(ethoxy)-(methyl)carbene]chromium(0) (**6**) was allowed to react with *N*-(4-methoxylphenyl)benzylideneimine (**7**). In a typical experiment a solution of the carbene complex (53 mg, 0.20 mmol) and imine **7** (42 mg, 0.20 mmol) in the indicated solvent (20 mL) was irradiated for 8 h. The solvent was removed in vacuo and the residue was dissolved in a mixture of hexane/AcOEt (1:1) and then exposed to direct sunlight until a clear solution was obtained. The solution was filtered through a short pad of celite, then the solvent was eliminated, and the isomeric composition of the β-lactam mixture was checked by ^{1}H NMR spectroscopy (see text). The conversion for the reaction was estimated by integration of well-resolved signals of the imine proton at $\delta = 8.4$ ppm. The ratio of isomers was determined by comparison of the integrals for the signals at $\delta = 4.85$ and 5.01 ppm for compound *trans*-**8** and with those at $\delta = 4.78$ and 5.03 ppm for *cis*-**8**.

Hexanes: following the general procedure, 48 mg of the reaction mixture was obtained. The *cis/trans*-β-lactam **8** ratio was 7.3:1.

Benzene: following the general procedure, 52 mg of the reaction mixture was obtained. The *cis/trans*-β-lactam **8** ratio was 3.2:1.

Dichloromethane: following the general procedure, 56 mg of the reaction mixture was obtained. The *cis/trans*-β-lactam **8** ratio was 4.4:1.

Tetrahydrofuran: following the general procedure, 59 mg of the reaction mixture was obtained. The *cis/trans*-β-lactam **8** ratio was 1:1.

Acetonitrile: following the general procedure, 60 mg of the reaction mixture was obtained. The *cis/trans*-β-lactam **8** ratio was 6.3:1.

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