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A Theoretical−Experimental Approach to the Mechanism of the Photocarbonylation of Chromium(0) (Fischer)−Carbene Complexes and Their Reaction with Imines

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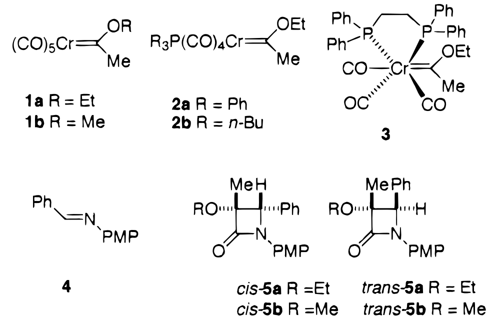
Irradiation of a chromium−carbene complex (visible light) is thought to promote the reversible insertion of a CO-ligand into the Cr−carbene bond to form a Cr−ketene complex.[1] This ketene-like behavior is one of the paradigmatic processes of these complexes[2] and has resulted in exceptionally efficient synthesis of compounds such as β-lactams, cyclobutanones, amino acids and peptides, polynuclear hydrocarbons, allenes, etc.[3] Despite the close parallelism between the photoreactivity of these complexes and free ketenes, the sole reported attempt made to directly detect the intermediacy of ketene species met with no success.[4] Moreover, a goodly number of questions associated with these synthetically useful processes remain unanswered. For example, although it is known that the reactivity of carbene complexes is strongly affected by the substitution at the carbene ligand, there are no data to establish the influence of ligands different from CO bonded to the chromium center. Thus, α,β-unsaturated chromium metal−carbene complexes and complexes having two heteroatoms bonded to the carbene carbon are listed as photochemically unreactive.[3a]

The behavior of chromium−carbene complexes having ligands different from CO in the photocarbonylation was studied first using their reaction with imines to form 2-azetidinones. The compounds employed in this study are collected in Chart 1. Compounds **2** were used as models for complexes having soft and strong σ-donor ligands, respectively.[5] Complex **3** was prepared from *diphos* and **1a** and used to study the additive effect of two σ-donors in the photocarbonylation reaction.

Irradiation (visible light) of complexes **1a** and **2a** in the presence of imine **4** gave the expected 2-azetidinones **5a**. Traces of compounds **5a** were obtained from complexes **2b** and **3**. Strikingly, β-lactam **5a** was obtained as a *cis*/*trans*-mixture in all cases, while the analogous reaction between complex **1b** and imine **4** was reported to yield a single *cis*-diastereomer.[6] We then effected the reaction of complex **1b** and imine **4** and consistently obtained a mixture of *cis*- and *trans*-2-azetidinones **5b**, independently of the reagent concentration used.[7] The *cis/trans* ratio of β-lactams **5** depends on the nature of the ligands attached to the metal center, and it is strongly affected by the reaction temperature. The presence of a strong σ-donor (Bu_3P) bonded to the chromium (complex **2b**) inhibits the photocarbonylation, while softer σ-donors (Ph_3P) are compatible with the reaction (complex **2a)**. Furthermore, the bonding of two σ-donor ligands (complex **3)** to the chromium center, results also in the almost complete inhibition of the process.

Chart 1



Due to the difficulties of experimental characterization of the possible reaction intermediates, we have studied several model compounds, by using computational tools.[8] All calculations have been performed at the B3LYP[9] level, using the standard 6-31G* basis set[10] for hydrogen, carbon, oxygen, and nitrogen, and the Hay−Wadt small-core effective core potential (ECP) including a double-ζ valence basis set[11] for chromium. Substitution of one CO unit in $(CO)_5$ Cr═CH_2, **7**, by PH_3 resulted in an enlargement of the C−Cr-L angle (from 90.0° for L = CO to 93.6° for L = PH_3) and in a larger HOMO−LUMO gap (E_g= 0.97 kcal/mol for L = PH_3, respect to L = CO). Assuming that this transition is involved in the photocarbonylation reaction, chromium−carbene complexes having trialkylphosphines should be much less reactive than their carbonylated analogues, as it was found for complex **2b**. Arylphosphine ligands in turn, should yield photoreactive complexes due to their larger -donor character, that should reduce the HOMO−LUMO gap. For *diphos*, we should be in the lower limit of reactivity with the additive effect of two arylphospines resulting in a more difficult carbonylation step.

Once having defined the structural requisites for the carbonylation process to occur, we turned our attention to the structure of the complex derived from the carbonylation of **7**. Since previous experimental work[3] indicates that the stereochemistry of [2 + 2] cycloadditions involving these ketene-like compounds

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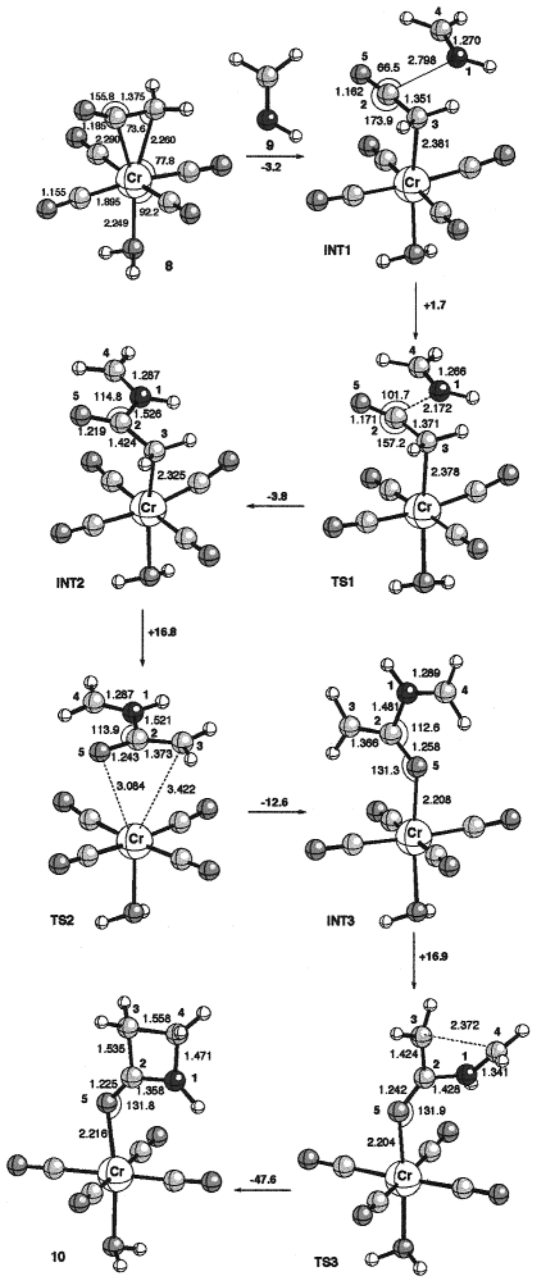

Figure 1. Stationary points found in the interaction between complex **8** and methanimine **9** to yield cycloadduct **10**. Bond distances and angles are given in Å and degrees, respectively. Numbers over the arrows correspond to the relative energies between the corresponding structures. Zero-point vibrational energy corrections have been included (kcal/mol).

is identical to that found in the equivalent thermal nonmetalated cycloadditions, the calculations on **7** and on following stationary points were performed in the S_0 state. Thus, the octahedral 18-electron complex **8**, with the ketene and the solvent in the axial positions, was obtained.

The reaction between complex **8** and methanimine $CH_2{=}NH$ **9**, to yield the cycloadduct **10** (Figure 1) was studied next. As in the classical Staudinger reaction between ketenes and imines,[12,13] a stepwise mechanism was obtained instead of the $[_{\pi}2_s + {}_{\pi}2_a]$ or $[_{\pi}2_s+({}_{\pi}2_s+{}_{\pi}2_s)]$ pathways. We have located the orientation complex **INT1** before the formation of the C−N bond. The first transition structure (**TS1** in Figure 1) lies only 1.72 kcal/mol above **INT1**. The C1···N2 distance is quite large in this saddle point, as would be expected for an early transition state. The next reaction intermediate is **INT2**, in which the C1−N2 bond is already formed and the C3 atom is bound to the chromium center. We have found another reaction intermediate denoted as **INT3**, which is 4.15 kcal/mol less stable than **INT2**. In this local minimum, the O5 atom is bound to chromium and in consequence, the C2−C3 and N1−C2 bond distances are shorter than in **INT2**. Therefore, **INT3** can be considered as a chromium enolate−iminium zwitterionic complex. Since formation of the C3−C4 bond is required to complete the reaction, a 1,3-chromium shift has to occur to form the cycloadduct.[14] We have located the saddle point **TS2** which connects **INT2** and **INT3**, the corresponding energy barrier being ~15 kcal/mol larger that that associated with formation of the N1−C2 bond. The next transition structure **TS3** corresponds to the formation of the C3−C4 bond. The geometry and the harmonic analysis of this saddle point indicate that it corresponds to a conrotatory ring closure and therefore is subjected to torquoelectronic effects.[15] **TS3** connects **INT3** with the reaction product **10**, which is ~33 kcal/mol more stable than the separate reagents. It is expected, being that the chromium is bonded to the reagents during the whole reaction, the effect of ligand changes would be reflected in the reaction selectivity, probably by influence over the charge distribution and steric effects in **TS1** and in **INT3**.

In conclusion, theoretical models to explain the photocarbonylation of chromium−carbene complexes and their reaction with imines have been developed. The theoretical results are fully consistent with the experimental data about these reactions, including the influence of the chromium ligands and substituents at the carbene carbon in the reactivity. Efforts to fully develop a general theoretical model and to gain a deeper experimental insight into these amazing processes are now underway.

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Supporting Information Available: Text describing the full experimental procedure, the preparation of complexes **2** and **3**, the characterization of 2-azetidinones **5**, energies (*E*, hartree), zero-point vibrational energies (ZPVE, hartree/particle) and Cartesian coordinates (Å) of stationary points reported in Figure 1 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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