

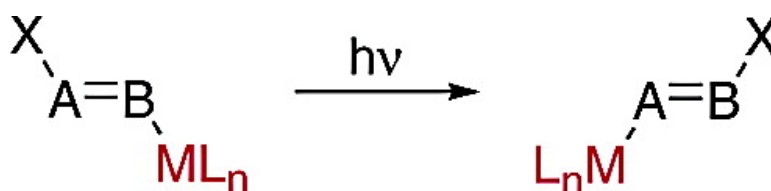
Communication

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 in a Chromium(0) Center: An Unprecedented Reaction Pathway**

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J. Am. Chem. Soc., **2003**, 125 (32), 9572-9573 • DOI: 10.1021/ja035614t • Publication Date (Web): 22 July 2003

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(M=Cr, X=H)

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Light-Induced Aminocarbene to Imine Dyotropic Rearrangement in a Chromium(0) Center: An Unprecedented Reaction Pathway

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Photochemistry of chromium(0)carbene complexes¹ is one of the fundamental pillars on which the synthetic versatility² of these compounds is based. The usefulness of the light-induced reactions of these complexes stems from their ability to reversibly generate ketene-like intermediates,³ initially postulated in 1988 by D'Andrea and Hegedus. Since then, the different efforts directed toward the detection of these elusive intermediates have been fruitless.^{4,5} Recently, we reported a theoretical-experimental study on the mechanism of the photoreaction of group 6 alkoxychromium(0)-carbene complexes with imines.⁶ Further work by our group resulted in the light-induced carbene transfer from group 6 carbene complexes to olefins.^{7,8} We have now studied the photochemistry of complexes **1** having the carbene heteroatom substituent tethered to the metal nucleus by a phosphine ligand and a carbon chain of variable length and rigidity. Reported herein is the discovery of a new photochemical aminocarbene to imine dyotropic rearrangement.

Complexes **1** were prepared by intramolecular ligand displacement on aminocarbene complexes **2** (boiling hexanes/benzene, 1:1 mixtures).⁹ These latter compounds were obtained by aminolysis of pentacarbonyl[methoxymethylcarbene]chromium(0), **3**, with the corresponding aminophosphines **4** (Figure 1).

Irradiation (450 W Hg-medium-pressure lamp, Pyrex filter, and Pyrex well) of complexes **1** in MeCN/MeOH solutions resulted in their smooth conversion to new organometallic compounds that lacked the carbene moiety (Scheme 1). A combination of 1D- and 2D-homonuclear (COSY and NOESY) and heteronuclear (¹H-¹³C HSQC, ¹H-¹³C HMBC, ¹H-³¹P HMBC, and ¹H-¹⁵N HSQC) experiments was performed to assign most of the ¹H, ¹³C, and ³¹P signals of compounds **5b** and **5c**. The structure of the reaction products was finally resolved by X-ray diffraction analysis⁹ carried out in a single monocrystal of **5c**. Thus, instead of the photocarbonylation process, a new carbene to imine rearrangement has occurred. The reaction occurs with tethers of different lengths (**4a,b**) and rigidities (**4c**), showing that the rearrangement process is general.

Experimental results above indicate that chromium(0)carbenes **1a–c** are transformed upon irradiation into N-metalated imines **5a–c** instead of the usually proposed ketenes.¹ This transformation is formally a 1,2-dyotropic rearrangement of type 1 according to the definition proposed by Reetz.¹⁰ Both C–Cr and N–H bonds migrate, and the Cr and H atoms interchange their positions, the C=N moiety (structure II contributes significantly to the description of the com-

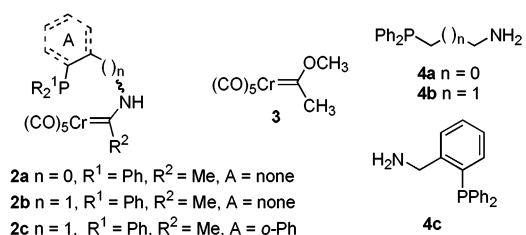
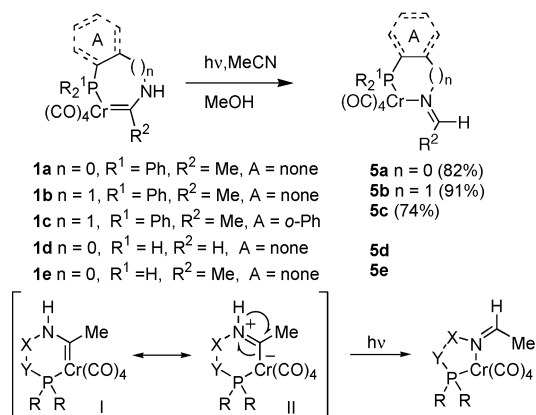


Figure 1.

plex) being the static scaffold. Computational studies^{11–13} on the transformation of model chromium(0)carbene **1d** into coordinated imine **5d** showed that the **1d** → **5d** reaction is exothermic by 14.7 kcal/mol at the ground state S₀. Because in the experimentally studied imines **5a–c** the methyl group is always syn to the chromium atom (R² = Me, Scheme 1), we have calculated the structures and energies of both *syn*- and *anti*-**5e**. Our calculations indicate that the *syn* stereoisomer is 0.8 kcal/mol more stable than its anti analogue.⁹ Therefore, both the 1,2-dyotropic transformations and the double inversion stereochemistry are thermodynamically favored processes.

Scheme 1



We have found¹⁴ that the lowest energy excited state of **1d** is a triplet, with a vertical excitation energy of 2.66 eV (465.5 nm). The first excited singlet state S₁ lies 0.80 eV above the triplet. It can be assumed that the dyotropic reaction starts with a short-lived triplet state T₁, formed after initial photoexcitation of the singlet ground state S₀ to the excited singlet state S₁.^{15,16} The triplet state of **1d** has a C–Cr distance ca. 0.2 Å larger than that found at the S₀ state. In addition, the spin densities of both centers are 0.582 and 1.675 au, respectively, thus indicating that in this excited state there is a significant contribution of the biradical structure depicted in Scheme 2.

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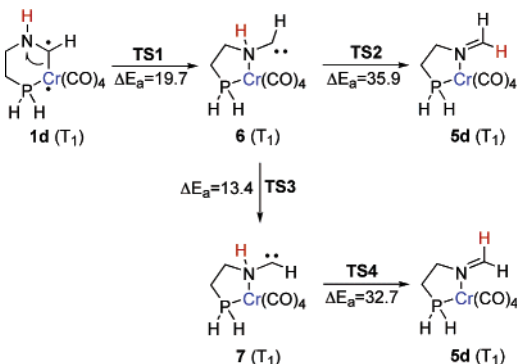
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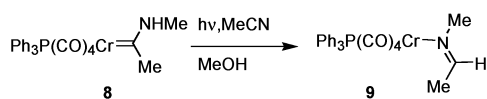
Scheme 2



We have not been able so far to locate and characterize a concerted transition structure that connects **1d** and **5d** in either the S_0 or the T_1 potential energy hypersurfaces. Instead, we have found a stepwise mechanism whose first transition structure (**TS1** in Scheme 2) is associated with the 1,2-migration of the chromium atom from the carbene to the nitrogen, with an activation energy of 19.7 kcal/mol. Efforts to locate **TS1** in the S_0 manifold meet with no success. An intrinsic reaction coordinate (IRC)¹⁷ study from **TS1** at the T_1 state led to the uncoordinated triplet carbene **6**, in which the spin density of the carbene center is 1.887 au. This carbene can be transformed into **5d** at the T_1 state by means of **TS2** (a saddle point associated with the migration of the hydrogen atom from the nitrogen atom to the carbene moiety). This step has an activation energy of 35.9 kcal/mol. However, if the **1d** → **5d** transformation should take place along the **TS1**-**TS2** pathway, the stereochemistry of the reaction should be contrary to that experimentally observed.

Triplet carbene **6** can isomerize to intermediate **7** through transition structure **TS3** with an associated activation energy of 13.4 kcal/mol. In addition, **7** is 0.9 kcal/mol more stable than its stereoisomer **6** at the T_1 state. Conversion of **7** into **5d** takes place via **TS4**, with an activation energy 3.2 kcal/mol lower than that computed for conversion of **6** into **5d**, thus indicating that the **7** → **5d** reaction pathway is kinetically favored. Therefore, this pathway is in full agreement with the experimental data. The rigidity imposed by the cyclic structure of complexes **1** is not responsible for this new photochemical reaction because the irradiation of complex **8** produced the unstable iminochromium complex **9** in 86% yield (Scheme 3).

Scheme 3



In conclusion, an unprecedented photochemical pathway alternative to the now classical Hegedus's photocarbonylation has been disclosed. Both theoretical and experimental results are in full agreement with this new dyotropic rearrangement¹⁸ of the carbene ligand to an imine ligand in complexes **1**. Efforts directed to fully understand the general mechanism of the photochemistry of group 6 metal-carbene complexes are now deeply active in our laboratories.

Acknowledgment. Support for this work from grant BQU2001-1283 (Madrid-group), grant BQU2001-0904 (San Sebastián-Donostia group) from the Ministerio de Ciencia y Tecnología (Spain), and the Euskal Herriko Unibertsitatea (9/UPV 00040.215-13548/2001) (San Sebastián-Donostia group) is gratefully acknowledged. I.F. thanks the Ministerio de Educación y Cultura (Spain) for a predoctoral (FPU) grant.

Supporting Information Available: Full experimental details for the preparation of all new compounds, X-ray characterization of compound **5c**, and full computational data for the calculations in this

work (CIF and PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA035614T