J|A|C|S
COMMUNICATIONS

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

Miguel A. Sierra,*,† Israel Fernández,† María J. Mancheño,† Mar Gómez-Gallego,†
M. Rosario Torres,‡ Fernando P. Cossío,*,§ Ana Arrieta,§ Begoña Lecea,|| Ana Poveda,⊥ and
Jesús Jiménez-Barbero#

*Departamento de Química Orgánica and Laboratorio de Difracción de Rayos X, Facultad de Química,
Universidad Complutense, 28040-Madrid, Spain, Kimika Fakultatea, Euskal Herriko Unibertsitatea, P.K. 1072,
28080 San Sebastián-Donostia, Spain, Farmazi Fakultatea, P.K. 450, 01080 Vitoria-Gasteiz, Spain,
SIDI-Universidad Autónoma, Cantoblanco, 28053-Madrid, Spain, and Centro de Investigaciones Biológicas (CSIC),
Velázquez 144, 28006-Madrid, Spain*

Received April 14, 2003; E-mail: sierraor@quim.ucm.es; qopcomof@sq.ehu.es

Photochemistry of chromium(0)carbene complexes[1] is one of the fundamental pillars on which the synthetic versatility[2] 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).

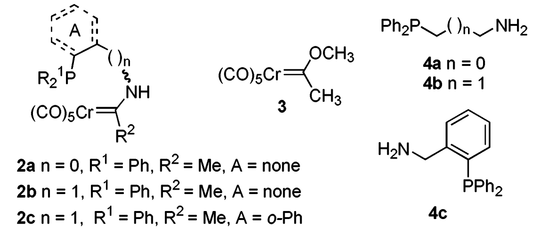
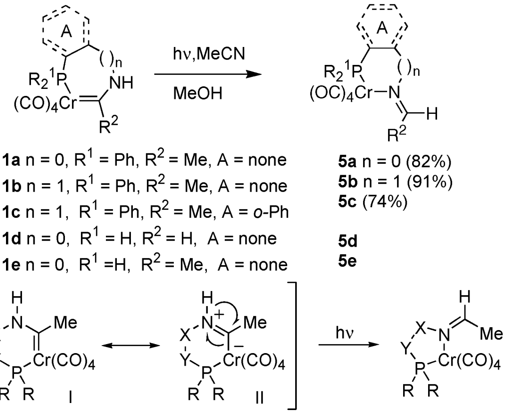


Figure 1.

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 (^{1}H−^{13}C HSQC, ^{1}H−^{13}C HMBC, ^{1}H−^{31}P HMBC, and ^{1}H−^{15}N HSQC) experiments was performed to assign most of the ^{1}H, ^{13}C, and ^{31}P signals of compounds **5b** and **5c**. The structure of the reaction products was finally resolved by X-ray diffraction analysis[9] 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 complex) 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 S$_0$. Because in the experimentally studied imines **5a**−**c** the methyl group is always syn to the chromium atom (R^2 = 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



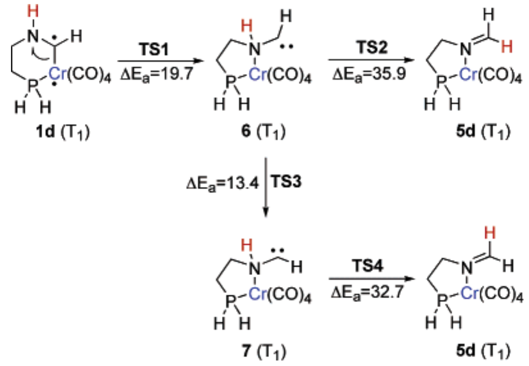
We have found[14] that the lowest energy excited state of **1d** is a triplet, with a vertical excitation energy of 2.66 eV (465.5 nm). The first excited singlet state S$_1$ lays 0.80 eV above the triplet. It can be assumed that the dyotropic reaction starts with a short-lived triplet state T$_1$, formed after initial photoexcitation of the singlet ground state S$_o$ to the excited singlet state S$_1$.[15,16] The triplet state of **1d** has a C−Cr distance ca. 0.2 Å larger than that found at the S$_o$ 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.

---

† Universidad Complutense.
‡ Difracción de Rayos X, Universidad Complutense.
§ Kimika Fakultatea, Euskal Herriko Unibertsitatea.
|| Farmazi Fakultatea, Euskal Herriko Unibertsitatea.
⊥ Universidad Autónoma.
CSIC.

10.1021/ja035614t CCC: $25.00

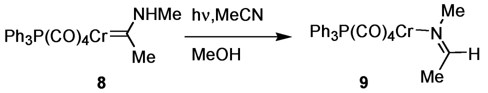
Scheme 2



We have not been able so far to locate and characterize a concerted transition structure that connects **1d** and **5d** in either the S_o 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_o 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**-**6**-**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 rearrangement[18] 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.

References

(1) For reviews in the photochemistry of group 6 metal−carbene complexes, see: (a) Hegedus, L. S. *Tetrahedron* **1997**, *53*, 4105. (b) Hegedus, L. S. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 12, p 549. (c) Schwindt, M. A.; Miller, J. R.; Hegedus, L. S. *J. Organomet. Chem.* **1991**, *413*, 143.

(2) Selected reviews: (a) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. (b) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 5, p 1065. (c) Wulff, W. D. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 12, p 470. (d) Harvey, D. F.; Sigano, D. M. *Chem. Rev.* **1996**, *96*, 271. (e) Aumann, R.; Nienaber, H. *Adv. Organomet. Chem.* **1997**, *41*, 163. (f) Sierra, M. A. *Chem. Rev.* **2000**, *100*, 3591. (g) de Meijere, A.; Schirmer, H.; Duetsch, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 3964.

(3) Hegedus, L. S.; de Weck, G.; D'Andrea, S. *J. Am. Chem. Soc.* **1988**, *110*, 2122.

(4) Gallager, M. L.; Greene, J. B.; Rooney, A. D. *Organometallics* **1997**, *16*, 5260.

(5) The first ketene to carbene isomerizations have been recently reported by Grötjahn in an Ir nucleus. See: (a) Grötjahn, D. B.; Bikzhanova, G. A.; Collins, L. S. B.; Concolino, T.; Lam, K. C.; Rheingold, A. L. *J. Am. Chem. Soc.* **2000**, *122*, 5222. (b) Urtel, H.; Bikzhanova, G. A.; Grötjahn, D. B.; Hofmann, P. *Organometallics* **2001**, *20*, 3938. (c) Grötjahn, D. B.; Collins, L. S. B.; Wolpert, M.; Bikzhanova, G. A.; Lo, H. C.; Combs, D.; Hubbard, J. L. *J. Am. Chem. Soc.* **2001**, *123*, 8260.

(6) Arrieta, A.; Cossío, F. P.; Fernández, I.; Gómez-Gallego, M.; Lecea, B.; Mancheño, M. J.; Sierra, M. A. *J. Am. Chem. Soc.* **2000**, *122*, 11509.

(7) Sierra, M. A.; del Amo, J. C.; Mancheño, M. J.; Gómez-Gallego, M. *Tetrahedron Lett.* **2001**, *42*, 5345.

(8) The irradiation of group 6 metal−carbene complexes with UV-light produced CO extrusion and syn−anti isomerization of the group tethered to the ligand. See: Doyle, K. O.; Gallagher, M. L.; Pryce, M. T.; Rooney, A. D. *J. Organomet. Chem.* **2001**, *617*, 269.

(9) See the Supporting Information for a full experimental procedure, crystallographic determination of **5c**, and all of the data concerning the calculations reported in this work.

(10) (a) Reetz, M. T. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 129. (b) Reetz, M. T. *Tetrahedron* **1973**, *29*, 2189.

(11) All calculations were carried out using the Gaussian 98 suite of programs. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.5; Gaussian, Inc.: Pittsburgh, PA, 1998.

(12) All calculations were performed at the UB3LYP level of theory. See: (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (c) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.

(13) The LANL2 DZ effective core potential and basis set were used for chromium during the optimizations and harmonic analysis to compute zero-point vibrational energies (not corrected). To obtain more accurate energies, the basis set for the explicit electrons of chromium was augmented with a set of f-polarization functions. See: (a) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299. (b) Ehlers, A. W.; Böhme, M.; Dapprich, S.; Gobbi, A.; Höllwarth, A.; Jonas, V.; Köhler, K. F.; Stegman, R.; Veldkam, A.; Frenking, G. *Chem. Phys. Lett.* **1993**, *208*, 111. The remaining elements were described with the standard 6-31+G* basis set. See: Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986; p 76 and references therein.

(14) These computations were performed at the configuration interaction singles (CIS) level of theory starting from the HF wave function. See: Foresman, J. B.; Head-Gordon, M.; Pople, J. A.; Frisch, M. J. *J. Phys. Chem.* **1992**, *96*, 135.

(15) (a) Zimmermann, H. E.; Sebek, P.; Zhu, Z. *J. Am. Chem. Soc.* **1998**, *120*, 8549. (b) Dauben, W. G.; Hecht, S. *J. Org. Chem.* **1998**, *63*, 6102. (c) Gómez, I.; Olivella, S.; Reguero, M.; Riera, A.; Solé, A. *J. Am. Chem. Soc.* **2002**, *124*, 15375.

(16) It has been reported experimentally that in photochemical reactions of organometallic carbenes such as bis(tricyclohexylphosphine) benzylidene ruthenium dichloride (Grubbs's catalyst) the reactive excited state is a triplet. See: Kunkely, H.; Vogler, A. *Inorg. Chim. Acta* **2001**, *325*, 179.

(17) González, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523

(18) Another very interesting experimental and theoretical study of a stepwise dyotropic rearrangement has been reported while this paper was under revision. See: Zhang, X.; Houk, K. N.; Lin, S.; Danishefsky, S. J. *J. Am. Chem. Soc.* **2003**, *125*, 5111.

JA035614T