to yield β-lactams began the synthetically useful photochemistry of group 6 (Fischer) carbene complexes.^[2,3] Both alkoxyand aminocarbene complexes of chromium(**0**) are active in these reactions.^[4] The reversible formation of chromiumbound ketenes by irradiation of chromium(**0**) carbene complexes with visible light was further postulated based on indirect evidence.^[5] In contrast, tungsten(**0**) alkoxycarbene complexes do not carbonylate, and all the previous experimental data collected about the photochemical behavior of these compounds have led them to be considered as photoinert.^[6] Recently, we reported^[7] a new photochemical dyotropic rearrangement from aminocarbenes **1** to imines **2** (Scheme 1), which unambiguously demonstrates the possibil-



Scheme 1. Dyotropic rearrangement from aminocarbene complexes 1 to imine complexes 2.

ity of other reaction pathways in these organometallic complexes that do not necessarily involve a photocarbonylation step. According to our calculations, the first triplet state (T_1) in these compounds has a biradical character rather than the metallacyclopropanone structure proposed for the T_1 of alkoxycarbene complexes.^[5,8] This short-lived species evolves stepwise to products **2** on the T_1 hypersurface.

The discovery of these new photochemical reactions in chromium(0) aminocarbene complexes led us to propose that tungsten(0) aminocarbene complexes may, in fact, experience reactions analogous to their chromium counterparts. Should this hypothesis be correct, the photo-inert tungsten(0) carbene complexes could be made photo-active by adequately modifying their structures. Herein we present the experimental confirmation of this hypothesis and show not only that tungsten(0) carbene complexes can be photo-active, but also that they undergo photocarbonylation processes.

The tungsten($\mathbf{0}$) carbene complexes **3a–c** were prepared following our previously reported procedure.^[7] Thus, complexes **4a–c**, obtained by aminolysis of pentacarbonyl[ethoxy-(methyl)carbene]tungsten($\mathbf{0}$) with the corresponding aminophosphanes, were heated in toluene to afford the desired products **3** in good yield (Scheme 2).

Irradiation of complexes 3a-c in MeCN/MeOH yielded the *syn*-metalated imine complexes 5a-c in acceptable yields (Scheme 3). The structures of the *syn*-metalated cyclic imines 5 were assigned by comparison of their spectroscopic data with those of their chromium analogues.^[7] To the best of our knowledge, the 1,2-dyotropic rearrangement represented in Scheme 3 is the first photoreaction reported to date of the presumed photochemically unreactive tungsten(**0**) carbene complexes.^[6]

It may be possible that the dyotropic reaction represented in Scheme 3 is a particular process restricted to complexes **3**.

Carbene Complex Chemistry

DOI: 10.1002/anie.200501590

The Photochemical Reactivity of the "Photo-Inert" Tungsten (Fischer) Carbene Complexes**

Israel Fernández, Miguel A. Sierra,* Mar Gómez-Gallego, María J. Mancheño, and Fernando P. Cossío*

The seminal discovery in 1982^[1] of the sunlight-promoted reaction between chromium(**0**) carbene complexes and imines

[*]	I. Fernández, Prof. M. A. Sierra, Prof. M. Gómez-Gallego,
	Dr. M. J. Mancheño
	Departamento de Química Orgánica
	Facultad de Química
	Universidad Complutense
	28040 Madrid (Spain)
	Fax: (+34) 91-394-4310
	E-mail: sierraor@quim.ucm.es
	Prof. F. P. Cossío
	Kimika Fakultatea
	Euskal Herriko Unibertsitatea, P.K. 1072
	20080 San Sebastián–Donostia (Spain)
	Fax: (+34) 943015270
	E-mail: fp.cossio@ehu.es
	· · · · · · · · · · · · · · · · · · ·

[**] Support for this work under grants CTQ2004-06250-C02-01/BQU (Madrid group) and CTQ2004-0681/BQU (San Sebastián–Donostia group) from the Ministerio de Ciencia y Tecnología (Spain), and the Euskal Herriko Unibertsitatea (9/UPV 00040.215-13548/2001) (San Sebastian–Donostia group) is gratefully acknowledged. I.F. thanks the Ministerio de Educación y Cultura (Spain) for a predoctoral (FPU) grant.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

Angew. Chem. Int. Ed. 2006, 45, 125–128

© 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



125

Communications



Scheme 2. Synthesis of cyclic tungsten(0) carbene complexes **3**. For details, see Experimental Section.



Scheme 3. Photochemical metalladyotropic type I rearrangement of complexes **3**. For details, see Experimental Section.

Therefore, to extend our knowledge of this reaction and to check the generality of tungsten($\mathbf{0}$)-carbene photochemistry, complexes **6** were prepared in almost quantitative yields by alkylation of complexes **3** with MeI/Cs₂CO₃, and irradiated in MeCN/MeOH (10:1; complexes **6a** and **6b**) or MeCN/THF/MeOH (5:5:1; complex **6c**; Scheme 4). Complexes **6** did not lead to the expected products analogous to **5** derived from a type I 1,2-dyotropic rearrangement.



Scheme 4. Photochemical α -fragmentation and carbonylation reactions of *N*-methylated complexes **6**. For details, see Experimental Section.

126 www.angewandte.org

© 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

In fact, two different classes of compounds were obtained, either as mixtures (for complex 6c) or as single products (for complexes 6a and 6b). The structure of a cyclic tetracarbonyl(phosphanylamino)tungsten complex was assigned to compounds 7a and 7b (derived from complexes 6a and 6b) on the basis of their spectroscopic data. Thus, complex 7a shows a set of four ¹³C NMR signals in the range $\delta = 202.9$ – 210.8 ppm as doublets (due to P-C coupling) corresponding to the $[W(CO)_4]$ fragment, while the signal for the N-Me moiety appears at $\delta = 56.1$ ppm. It should be pointed out that complexes 7 lack the Me group and the carbon earbon atom of the starting complexes 6. The product isolated from 6c lacks the metal moiety and has an amino ester structure.^[9] The ¹³C NMR spectrum of this compound contains a signal at $\delta =$ 174.0 ppm attributable to the ester carbonyl group. This feature shows unambiguously that carbonylation has occurred. The oxidation of the phosphorus atom was confirmed from the ³¹P NMR spectrum ($\delta \approx 34$ ppm) and additionally by ESI mass spectrometry (m/z 407), thus confirming the presence of the phosphane oxide moiety (Scheme 4).

The UV-visible photochemistry of tungsten($\mathbf{0}$) aminocarbene complexes is therefore quite sensitive to the substitution at the nitrogen atom and can lead to up to three different photochemical reactions. This is remarkable for a class of compounds that had previously been considered as photo-inert. To confirm that this reactivity could also be observed in chromium($\mathbf{0}$) aminocarbene complexes, compound **6d** was prepared and irradiated under similar conditions. Now, in a very efficient process, both the *N*methylamino ester **9** and the (aminophosphanyl)tetracarbonylchromium complex **10** were obtained (Scheme 5).



Scheme 5. Competitive α -fragmentation and carbonylation reactions of chromium(0) carbene 6d.

To rationalize the results obtained above we propose that the irradiation of complex **11** produces the biradical species **11*** (Scheme 6). This excited species evolves into the final *N*-metalated imine **13** via carbene **12**. This reaction pathway is analogous to that observed for chromium(**0**) carbene complexes.^[7] In contrast, the biradical **14*** derived from the irradiation of **14**, which has a methyl substituent at nitrogen, evolves by fragmentation of the α -N–C=[W] bond to form a new biradical **15**. This process is similar to the α fragmentation of amides,^[10] which are the isolobal analogues of aminocarbene complexes.^[11] Capture of two hydrogen atoms from the solvent forms the species **16**. The evolution of this kind of complex into a metalated amine product like **17** has been previously observed by us and others.^[12,13]



Scheme 6. Proposed reaction pathways for the photoreaction of tungsten(**0**) aminocarbene complexes to yield *syn*-metalated imines **13** (path a) or α -fragmentation products **17** (path b).

The formation of α -amino ester **8** from tungsten(0) complex **6c** and the mixture of *N*-metalated amine **10** and the carbonylation product α -amino ester **9** from chromium(0) carbene **6d** indicate the co-existence of different activated species that are formed upon irradiation of these complexes (Scheme 7). It is reasonable to assume that compound **10**



Scheme 7. Proposed reaction pathways for the competitive processes observed in the irradiation of complexes **6c** and **6d**.

would arise from biradical intermediate **18**, while compounds **8** and **9** are formed from coordinated-ketene intermediates **19**.^[13]

In conclusion, tungsten(**0**) carbene complexes, which were previously considered to be photo-inert, show a rich and complex photoreactivity when they are properly substituted, which may be of future interest both theoretically and synthetically. Thus, we have demonstrated experimentally that the excitation of tetracarbonyltungsten(0) (phosphanylamino)carbene complexes produces species having either a biradical structure or a tungstacyclopropanone structure. These species coexist and produce three different classes of products depending mainly on the substitution pattern on the nitrogen atom: *N*-unsubstituted complexes produce cyclic *syn*-metalated imine complexes through a type I metalladyo-tropic process, while *N*-methylated complexes produce pentacarbonyl(phosphanylamino)tungsten(0) complexes and α -amino esters. Further work in this emerging area of tungsten photochemistry as well as the study of other related processes in chromium(0) and molybdenum(0) carbene complexes is currently in progress.

Experimental Section

General procedure for the synthesis of complexes 4: A solution of stoichiometric amounts of pentacarbonyl[ethoxy(methyl)carbene]-tungsten($\mathbf{0}$) and the corresponding aminophosphane, in dry CH₂Cl₂, was stirred at room temperature until the disappearance of the starting material (checked by TLC). Then, the solvent was removed and the product was purified by flash column chromatography to yield pure compounds.

4a: yellow oil (58%). ¹H NMR (300 MHz, CDCl₃): $\delta = 1.75$ (m, 2H; CH₂P), 2.56 (s, 3H; CH₃), 3.95 (m, 2H; CH₂N), 7.32–7.72 (m, 10H; H_{Ar}), 8.46 ppm (br.s, 1H; NH). ¹³C NMR (50 MHz, CDCl₃): $\delta = 28.1$ (d, $J_{CP} = 15.3$ Hz; CH₂P), 47.1 (CH₃), 52.7 (d, $J_{CP} = 16.5$ Hz; CH₂N), 128.9 (d, $J_{CP} = 6.4$ Hz; C_{Ar}), 129.4 (C_{Ar}), 132.7 (d, $J_{CP} = 19.1$ Hz; C_{Ar}), 136.5 (d, $J_{CP} = 11.4$ Hz; C_{Ar}), 198.2 (CO), 203.2 (CO), 255.6 ppm (W=C). IR (CCl₄): $\tilde{\nu} = 2062$, 1965, 1927 cm⁻¹. C₂₁H₁₈NO₅PW: calcd. C 43.55, H 3.13, N 2.42; found C 43.69, H 3.00, N 2.28.

General Procedure for the synthesis of complexes **3**: A solution of the (phosphanylamino)carbene complex was heated at reflux in toluene until the disappearance of the starting material (checked by TLC). The solvent was then removed under reduced pressure to yield pure compounds (unless otherwise specified).

3a: yellow solid (91 %). ¹H NMR (300 MHz, CDCl₃): $\delta = 2.36$ (m, 2H; CH₂P), 2.77 (s, 3H; CH₃), 3.85 (m, 1H; CH₂N), 3.92 (m, 1H; CH₂N), 7.30–7.52 (m, 10H; H_{Ar}), 8.92 ppm (s, 1H; NH). ¹³C NMR (75.5 MHz, CDCl₃): $\delta = 25.2$ (d, $J_{CP} = 23.6$ Hz; CH₂P), 46.6 (d, $J_{CP} = 4.1$ Hz; CH₃), 48.9 (d, $J_{CP} = 6.1$ Hz; CH₂N), 128.5 (d, $J_{CP} = 9.3$ Hz; C_{Ar}), 129.8 (d, $J_{CP} = 1.4$ Hz; C_{Ar}), 131.9 (d, $J_{CP} = 12.0$ Hz; C_{Ar}), 137.0 (d, $J_{CP} = 38.3$ Hz; C_{Ar}), 203.2 (d, $J_{CP} = 7.0$ Hz; CO), 209.2 (d, $J_{CP} = 26.8$ Hz; CO), 213.4 (d, $J_{CP} = 7.3$ Hz; CO), 261.4 ppm (d, $J_{CP} = 9.6$ Hz; W=C). IR (KBr): $\tilde{\nu} = 3304$, 2002, 1875, 1838 cm⁻¹. C₂₀H₁₈NO₄PW: calcd. C 43.58, H 3.29, N 2.54; found C 43.74, H 3.51, N 2.70.

General Procedure for the synthesis of complexes **6**: A solution of complex **3** in degassed acetone (0.025 M) was treated with two equivalents of MeI, three equivalents of Cs₂CO₃, and water (drops) at room temperature overnight. The crude reaction mixture was filtered through a short pad of celite and the solvent was removed under reduced pressure to yield pure compounds (unless otherwise specified).

6a: yellow solid (99%). ¹H NMR (300 MHz, CDCl₃): $\delta = 2.31$ (m, 2 H; CH₂P), 2.67 (s, 3 H; CH₃C), 3.26 (s, 3 H; CH₃N); 4.05 (m, 1 H; CH₂N), 4.14 (m, 1 H; CH₂N), 7.26–7.46 ppm (m, 10 H; H_{Ar}). ¹³C NMR (75.5 MHz, CDCl₃): $\delta = 24.8$ (d, $J_{CP} = 23.6$ Hz; CH₂P), 42.0 (d, $J_{CP} = 37.2$ Hz; CH₂N), 53.4 (CH₃C), 62.5 (d, $J_{CP} = 7.1$ Hz; CH₃N), 128.5 (d, $J_{CP} = 9.3$ Hz; C_{Ar}), 129.7 (d, $J_{CP} = 1.6$ Hz; C_{Ar}), 131.9 (d, $J_{CP} = 12.0$ Hz; C_{Ar}), 137.3 (d, $J_{CP} = 38.2$ Hz; C_{Ar}), 203.9 (d, $J_{CP} = 6.9$ Hz; CO), 210.1 (d, $J_{CP} = 28.1$ Hz; CO), 213.0 (d, $J_{CP} = 6.7$ Hz; CO),

Communications

259.7 ppm (d, $J_{\rm C,P}\!=\!10.1$ Hz; W=C). IR (KBr): $\tilde{\nu}\!=\!2000,\,1902,\,1857,\,1842~{\rm cm}^{-1}.$ C $_{21}{\rm H}_{20}{\rm NO}_4{\rm PW}:$ calcd. C 44.63, H 3.57, N 2.48; found C 44.44, H 3.40, N 2.55.

General Procedure for the photochemical reactions of complexes **3** and **6**: Photochemical reactions were conducted with a 450-W medium-pressure Hg lamp through a Pyrex filter in dry, degassed MeCN containing MeOH (10:1 ratio) or in MeCN, THF, and MeOH (5:5:1 ratio) in a sealed Pyrex tube filled with argon. In a typical experiment, after irradiation for 10 h the solution (0.015 M) was filtered through a short pad of celite, the solvents were removed under reduced pressure, and the crude product was submitted to flash chromatography to give pure complexes, unless otherwise specified.

5a: yellow solid (71 %). ¹H NMR (300 MHz, CDCl₃): δ = 2.28 (d, J = 5.2 Hz, 3 H; CH₃), 2.46 (m, 2 H; CH₂P), 3.85 (m, 1 H; CH₂N), 3.93 (m, 1 H; CH₂N), 7.34–7.59 (m, 10 H; H_{Ar}), 7.86 ppm (q, J = 5.2 Hz, 1 H; CH). ¹³C NMR (75.5 MHz, CDCl₃): δ = 26.0 (CH₃), 30.7 (d, J_{C,P} = 21.2 Hz; CH₂P), 69.6 (d, J_{C,P} = 10.1 Hz; CH₂N), 128.8 (d, J_{C,P} = 9.9 Hz; C_{Ar}), 130.2 (d, J_{C,P} = 1.7 Hz; C_{Ar}), 131.9 (d, J_{C,P} = 12.2 Hz; C_{Ar}), 135.5 (d, J_{C,P} = 40.4 Hz; C_{Ar}), 172.9 (CH), 203.0 (d, J_{C,P} = 7.0 Hz; CO), 210.1 (d, J_{C,P} = 32.0 Hz; CO), 211.6 ppm (d, J_{C,P} = 5.1 Hz; CO). IR (KBr): $\tilde{\nu}$ = 2008, 1867, 1838 cm⁻¹. C₂₀H₁₈NO₄PW: calcd. C 43.58, H 3.29, N 2.54; found C 43.39, H 3.33, N 2.41.

7a: yellow solid (46%). ¹H NMR (300 MHz, CDCl₃): $\delta = 2.21$ (m, 1 H; CH₂P), 2.48 (m, 1 H; CH₂P), 2.76 (m, 1 H; CH₂N), 2.89 (d, J = 5.9 Hz, 3 H; CH₃), 3.20 (m, 1 H; CH₂N), 7.32–7.62 ppm (m, 10 H; H_{Ar}). ¹³C NMR (75.5 MHz, CDCl₃): $\delta = 30.0$ (d, $J_{CP} = 21.6$ Hz; CH₂P), 48.1 (CH₃), 56.1 (d, $J_{CP} = 10.2$ Hz; CH₂N), 128.7 (d, $J_{CP} = 3.9$ Hz; C_{Ar}), 128.9 (d, $J_{CP} = 3.6$ Hz; C_{Ar}), 130.3 (C_{Ar}), 131.7 (d, $J_{CP} = 12.7$ Hz; C_{Ar}), 132.1 (d, $J_{CP} = 12.6$ Hz; C_{Ar}), 134.8 (d, $J_{CP} = 19.9$ Hz; C_{Ar}), 135.3 (d, $J_{CP} = 22.9$ Hz; C_{Ar}), 202.9 (d, $J_{CP} = 6.8$ Hz; CO), 204.0 (d, $J_{CP} = 7.8$ Hz; CO), 210.2 (d, $J_{CP} = 31.9$ Hz; CO), 210.8 ppm (d, $J_{CP} = 4.1$ Hz; CO). IR (CCl₄): $\tilde{\nu} = 2012$, 1954, 1888 cm⁻¹. C₁₉H₁₈NO₄PW: calcd. C 42.33, H 3.37, N 2.60; found C 42.28, H 3.50, N 2.74.

8: pale-yellow oil (11%). The solvent was removed in vacuo and the residue was dissolved in a mixture of hexane and EtOAc (1:1) and exposed to direct sunlight until a clear solution was obtained. The solution was then filtered through a short pad of celite, the solvent eliminated, and the residue was purified by flash column chromatography to yield pure compound. ¹H NMR (300 MHz, CDCl₃): $\delta = 0.86$ (d, J=6.9 Hz, 3H; CH₃C), 1.91 (s, 3H; CH₃N), 3.31 (q, J=6.9 Hz, 1H; CHCH₃), 3.54 (s, 3H; CH₃O), 3.92 (d, J=10.6 Hz, 2H; AB system, CH₂), 6.95–7.59 ppm (m, 14H; H_{Ar}). ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 14.0 (CH_3C)$, 36.5 (CH₃N), 51.1 (CH₃O), 56.9 (CH), 60.7 (CH₂), 126.1 (d, $J_{C,P} = 13.2$ Hz; C_{Ar}), 128.4 (d, $J_{C,P} = 9.1$ Hz; C_{Ar}), 130.1, 131.2 (d, $J_{C,P} = 9.4$ Hz; C_{Ar}), 131.6 (C_{Ar}), 131.8 (d, $J_{C,P} = 8.6$ Hz; $\begin{array}{l} C_{Ar}),\,132.0\,\,(C_{Ar}),\,133.2\,\,(C_{Ar}),\,133.6\,\,(d,\,J_{C,P}\,{=}\,12.0\,\,Hz;\,C_{Ar}),\,145.5\,\,(d,\,J_{C,P}\,{=}\,9.4\,\,Hz;\,C_{Ar}),\,174.0\,\,ppm~(CO). \end{array} \right.^{31} P\,\,NMR~(internal~\,H_3PO_4)$ reference): $\delta = 34.2$ ppm. IR (CCl₄): $\tilde{\nu} = 1736$, 1437, 1194, 1159, 1119 cm⁻¹. C₂₄H₂₀NO₃P: calcd. C 70.75, H 6.43, N 3.44; found C 70.60, H 6.61, N 3.59.

Received: May 10, 2005 Revised: September 23, 2005 Published online: November 22, 2005

Keywords: carbene ligands · carbonylation · photochemistry · rearrangement · tungsten

- a) M. A. McGuire, L. S. Hegedus, J. Am. Chem. Soc. 1982, 104, 5538; b) L. S. Hegedus, M. A. McGuire, L. M. Schultze, C. Yijun, O. P. Anderson, J. Am. Chem. Soc. 1984, 106, 2680.
- [2] For reviews on the photochemistry of Group 6 metal-carbene complexes, see: a) L. S. Hegedus, *Tetrahedron* 1997, 53, 4105;
 b) L. S. Hegedus in *Comprehensive Organometallic Chemistry II, Vol.* 12 (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson),

Pergamon, Oxford, **1995**, p. 549; c) M. A. Schwindt, J. R. Miller, L. S. Hegedus, *J. Organomet. Chem.* **1991**, *413*, 143.

- [3] For reviews on different aspects of metal-carbene chemistry, see: a) K. H. Dötz, H. Fischer, P. Hofmann, R. Kreissel, U. Schubert, K. Weiss, Transition Metal Carbene Complexes, Verlag Chemie, Deerfield Beach, FL, 1983; b) K. H. Dötz, Angew. Chem. 1984, 96, 573; Angew. Chem. Int. Ed. Engl. 1984, 23, 587; c) W. D. Wulff in Comprehensive Organic Synthesis, Vol. 5 (Eds.: B. M. Trost, I. Fleming), Pergamon, Oxford, 1991, p. 1065; d) H. Rudler, M. Audouin, E. Chelain, B. Denise, R. Goumont, A. Massoud, A. Parlier, A. Pacreau, M. Rudler, R. Yefsah, C. Alvarez, F. Delgado-Reyes, Chem. Soc. Rev. 1991, 20, 503; e) D. B. Grötjahn, K. H. Dötz, Synlett 1991, 381; f) W. D. Wulff in Comprehensive Organometallic Chemistry II, Vol. 12 (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon, Oxford, 1995, p. 470; g) D. F. Harvey, D. M. Sigano, Chem. Rev. 1996, 96, 271; h) R. Aumann, H. Nienaber, Adv. Organomet. Chem. 1997, 41, 163; i) B. Alcaide, L. Casarrubios, G. Domínguez, M. A. Sierra, Curr. Org. Chem. 1998, 2, 551; j) M. A. Sierra, Chem. Rev. 2000, 100, 3591; k) A. de Meijere, H. Schirmer, M. Duetsch, Angew. Chem. 2000, 112, 4124; Angew. Chem. Int. Ed. 2000, 39, 3964; l) J. Barluenga, J. Flórez, F. J. Fañanás, J. Organomet. Chem. 2001, 624, 5.
- [4] A. Hafner, L. S. Hegedus, G. de Weck, B. Hawkins, K. H. Dötz, J. Am. Chem. Soc. 1988, 110, 8413.
- [5] L. S. Hegedus, G. de Weck, S. D'Andrea, J. Am. Chem. Soc. 1988, 110, 2122.
- [6] Strictly speaking tungsten(0) Fischer carbene complexes may experience loss of CO ligands as well as syn-anti isomerization upon irradiation. Nevertheless, to the best of our knowledge these complexes are photo-inert toward nucleophiles. The irradiation of chromium(0) carbene complexes with UV light also produces CO extrusion and syn-anti isomerization of the group tethered to the ligand. See: K. O. Doyle, M. L. Gallagher, M. T. Pryce, A. D. Rooney, J. Organomet. Chem. 2001, 617, 269. For the purposes of this work we will always refer to visible light photochemistry, using medium-pressure Hg lamps, a Pyrex filter, and a Pyrex well. Under these conditions medium-pressure Hg lamps radiate predominantly at 365-366 nm as well as significant amounts in the visible region at 404-408, 436, 546, and 577-579 nm. Under these experimental conditions, to the best of our knowledge, only photocarbonylation and carbene-transfer processes have been reported for chromium(0) and molybdenum(**0**) carbene complexes. See references [1] and [2]
- [7] M. A. Sierra, I. Fernández, M. J. Mancheño, M. Gómez-Gallego, M. R. Torres, F. P. Cossío, A. Arrieta, B. Lecea, A. Poveda, J. Jiménez-Barbero, J. Am. Chem. Soc. 2003, 125, 9572.
- [8] I. Fernández, M. A. Sierra, M. Gómez-Gallego, M. J. Mancheño, F. P. Cossío, *Chem. Eur. J.* 2005, 20, 5988.
- [9] The ¹H NMR spectrum of the reaction mixture shows the presence of the cyclic phosphane–amine analogue to **7** (signals at $\delta = 2.73$ (d) and 3.62 ppm (m)) as the main reaction product. However, all attempts to isolate this compound were fruitless. The crude reaction mixture was oxidized and chromatographed to isolate compound **8** (see Scheme 4).
- [10] a) J. D. Coyle, Chem. Rev. 1978, 78, 97; b) A. G. Gilbert, J. Baggott, Essentials of Molecular Photochemistry, Blackwell Science, Oxford, 1991, pp. 328–329.
- [11] a) R. Hoffmann, Science 1981, 211, 995; b) R. Hoffmann, Angew. Chem. 1982, 94, 711; Angew. Chem. Int. Ed. Engl. 1982, 21, 711.
- [12] a) C. K. Murray, B. P. Warner, V. Dragisich, W. D. Wulff, R. D. Rogers, *Organometallics* **1990**, *9*, 3142; b) I. Fernández, M. J. Mancheño, M. Gómez-Gallego, M. A. Sierra, T. Lejon, L. K. Hansen, *Organometallics* **2004**, *23*, 1851.
- [13] Preliminary DFT calculations carried out at the uB3LYP/6-31 g(d)&LANL2DZ + Δ ZPVE level of theory are consistent with these mechanistic proposals.