

The Noncarbonylative Photochemistry of Group 6 Fischer Carbene Complexes

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The different photochemical reaction mechanisms of group 6 Fischer carbene complexes have been studied by a joint experimental and density functional theory (DFT) computational study. This study unifies the photochemical behavior of group 6 metal carbene complexes ($M = \text{Cr}$ or W), which may occur by three different photoreactions, namely photocarbonylation, stepwise 1,2-dyotropic rearrangement, and α -fragmentation. The metal atom and the substituent on the nitrogen atom attached to the carbene carbon atom influence the topography of the potential energy surface, which leads to two different activated species, diradicals or metallacyclopentanones. Complexes having a hydrogen substituent at the nitrogen atom experience a stepwise dyotropic migration with no significant differences between the chromium- and

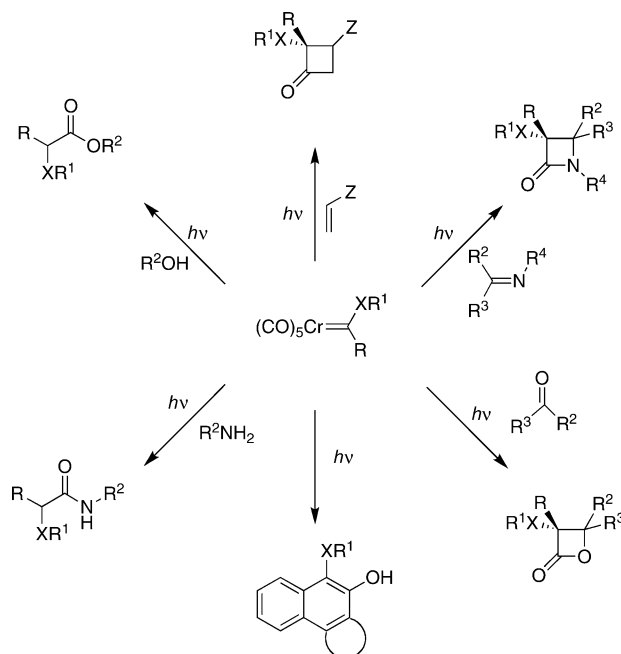
tungsten-carbene complexes. The excitation of complexes having substituents other than hydrogen at the nitrogen atom leads to two different T1 species, and hence to the formation of mixtures of products arising from α -fragmentation (noncarbonylation) and amino esters (photocarbonylation). The two triplet states are isoenergetic in the Cr derivatives, but the T1 species that leads to α -fragmentation is strongly favored for the W derivatives. Finally, both the chromium- and tungsten-carbene complexes are photoreactive in spite of the longstanding claim that tungsten-carbene complexes were photochemically inert.

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Introduction

The irradiation of group 6 (Fischer) metal carbene complexes with visible light in the presence of nucleophiles leads to the formation of β -lactams,^[1] cyclobutanones,^[2] amino acids and peptides,^[3] polynuclear hydrocarbons,^[4] and β -lactones (Scheme 1).^[5] This rich and synthetically powerful photoreactivity^[6] has no parallel in the photochemistry of any other class of organometallic compounds. In fact, it is only comparable with the amazingly diverse thermal chemistry of these metal-carbene complexes.^[7]

Nevertheless, the synthetically useful photochemistry of chromium(0)- and molybdenum(0)-carbene complexes [but not tungsten(0)-carbene complexes] relies exclusively on the reversible insertion of a CO ligand into the $M=C$ bond to yield ketene-like species.^[8,9] This mechanistic insight was reported by Hegedus in 1988,^[10] who systematized the photochemistry of group 6 carbene complexes in the presence of nucleophiles. Despite the close parallelism of the ketenes derived from the irradiation of group 6 metal carbene complexes and free ketenes, the different efforts directed toward



Scheme 1.

the detection of these elusive intermediates were fruitless.^[11]

We have recently shown^[8] that the combination of computational and experimental tools is appropriate to study the mechanism of the photocarbonylation of group 6 metal carbene complexes. The irradiation of alkoxychromium(0)-

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carbene complexes, either in the region of the LF band followed by relaxation to the MLCT band or directly in the region of the MLCT band, results in the excitation of these complexes to the S_1 state. The S_1 decays to T_1 by intersystem crossing (ISC) because of spin-orbit coupling to form metallacyclopropanone species **I** (Figure 1). These coordinatively unsaturated species change their multiplicity to S_0 by filling the free coordination site with a molecule of a coordinating solvent in the apical position to form acylchromate complexes **II**. These complexes evolve to ketene-derived products on the S_0 hypersurface. The absence of nucleophiles does not lead to other forms of reactivity and species **I** reverts to the starting carbene complex in a strongly exothermic process (Figure 1).

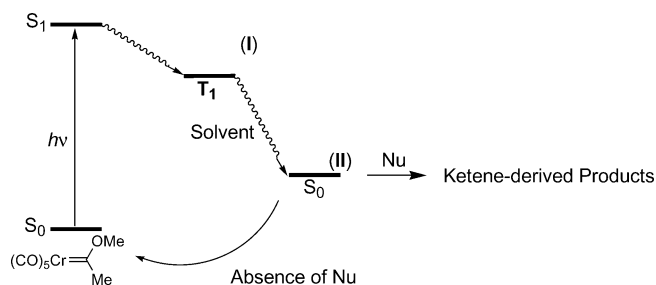
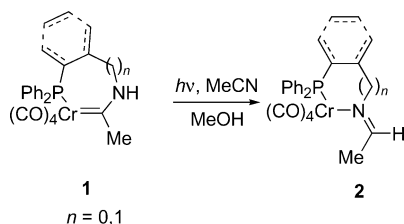


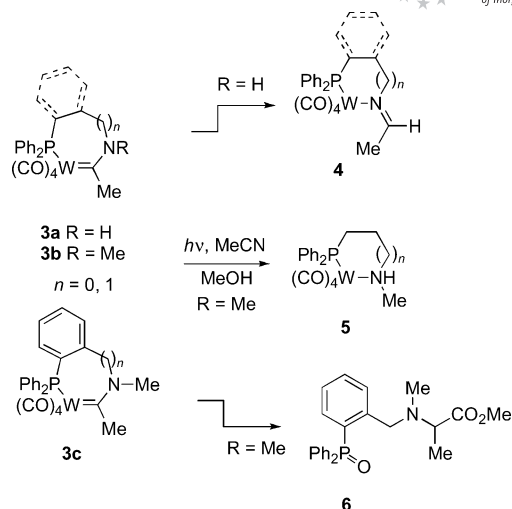
Figure 1. The carbonylation step in chromium(0)carbene photochemistry.

Concomitant to these studies, we discovered that group 6 aminocarbene complexes having phosphane ligands can evolve by different noncarbonylative pathways.^[12,13] Far from being limited to the carbonylation reaction, group 6 Fischer carbene complexes have a rich and very complex photochemistry, which strongly depends on the nature of the ligands. For example, the stepwise type I 1,2-dyotropic rearrangement^[12] converts chromium(0)–phosphinoaminocarbene **1** to *syn-N*-metalated imine **2** (Scheme 2).



Scheme 2.

Subsequently, we found that the “photoinert” tungsten(0)–carbene complexes were indeed photoreactive, provided that their structures would be adequately designed.^[13] Up to three new photoprocesses were discovered for tungsten(0)–carbene complexes **3**: 1,2-dyotropic rearrangement leading to imino complexes **4**, α -fragmentation to form **5**, and more strikingly, photocarbonylation to form the *N*-methylamino ester **6** (Scheme 3). These processes are remarkable since tungsten(0)–carbenes were considered as photoinert until we reported these findings.



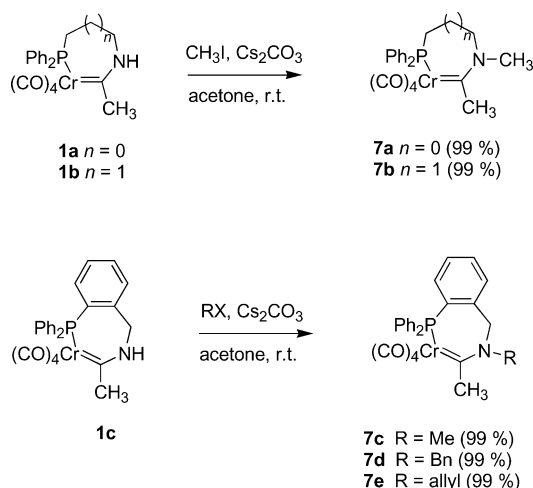
Scheme 3.

The different reaction pathways observed for these compounds provides a good opportunity for applying the combination of experimental and computational methods previously developed by us while studying the photocarbonylation reaction.^[8,12] We herein report an extensive computational and experimental study on the mechanisms of the different reaction pathways for the processes shown in Scheme 2 and Scheme 3. Similarities and differences of the photoreactivity of chromium- and tungsten Fischer carbene complexes are also explored and discussed.

Results and Discussion

The noncarbonylative photochemistry of group 6 metal carbene complexes presented above clearly shows a strong dependence of the nature of the reaction products on the substituent on the nitrogen atom bonded to the carbene carbon atom.^[12,13] This fact clearly differentiates these photochemical reactions from the photocarbonylation pathway^[2,3,5] that either leads to ketene-derived products or unreacted starting materials. Complexes **1** and tungsten(0)–carbene complexes **3a** lead to *syn-N*-metalated imine compounds **2** and **4** through 1,2-dyotropic processes. This rearrangement is limited to complexes such as **1** and **3a** that have a hydrogen atom bonded to the nitrogen atom attached to the carbene carbon atom. *N*-methylated complexes **3b** experience two different processes, namely α -fragmentation and photocarbonylation.^[13]

To study the generality of these processes, chromium(0)–carbene complexes having different tethers that join the carbene nitrogen atom and the phosphane ligand and having different alkyl substituents at the nitrogen atom were prepared. Thus, the chromium–carbene complexes **7a–e** were obtained in almost quantitative yields by reaction of complexes **1a–c** with MeI/Cs₂CO₃ (complexes **7a–c**), benzyl bromide/Cs₂CO₃ (complex **7d**), or allyliodide/Cs₂CO₃ (complex **7e**) at room temperature in acetone as a solvent (Scheme 4).



Scheme 4.

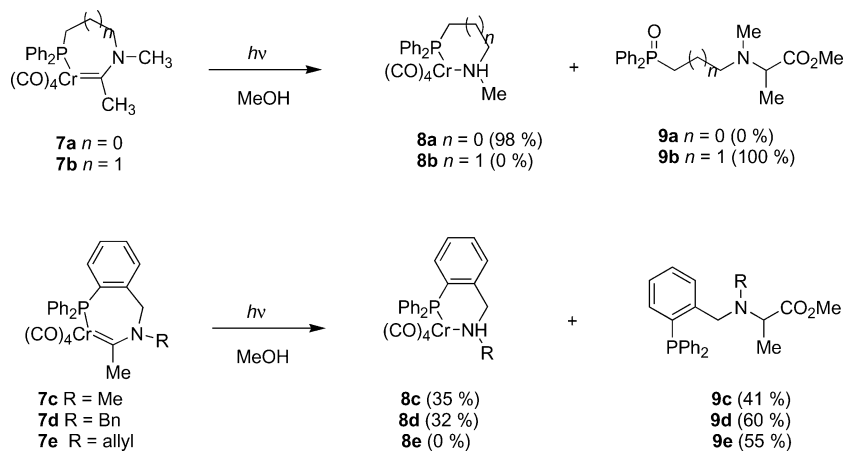
Complexes **7** were irradiated (450 W, medium-pressure Hg lamp, Pyrex filter and Pyrex well) in MeCN/MeOH (10:1) (complexes **7a,b**) or MeCN/thf/MeOH (5:5:1) (complexes **7c–e**). Two different products were obtained in these reactions, either as single reaction products (**7a**, **7b**, and **7e**) or as mixtures of two products (**7c,d**). The reaction products were identified either as cyclic complexes **8** on the basis of their spectroscopic data and by comparison with previously reported tungsten analogues^[13,14] or as amino esters **9** arising from the photocarbonylation reaction (Scheme 5).^[15]

The data above allow for the conclusion that substitution at the nitrogen atom of the aminocarbenes **7** inhibits 1,2-dyotropic transformation, which is the exclusive photoprocess observed for complexes **1** and **3a**. The formation of complexes **8** together with the carbonylation derivatives **9** indicate the co-existence of at least two different activated species that are formed upon irradiation of metal–carbene complexes **7** and **3b**. We have shown that amino esters **9** are formed from the coordinated-ketene pathway followed by

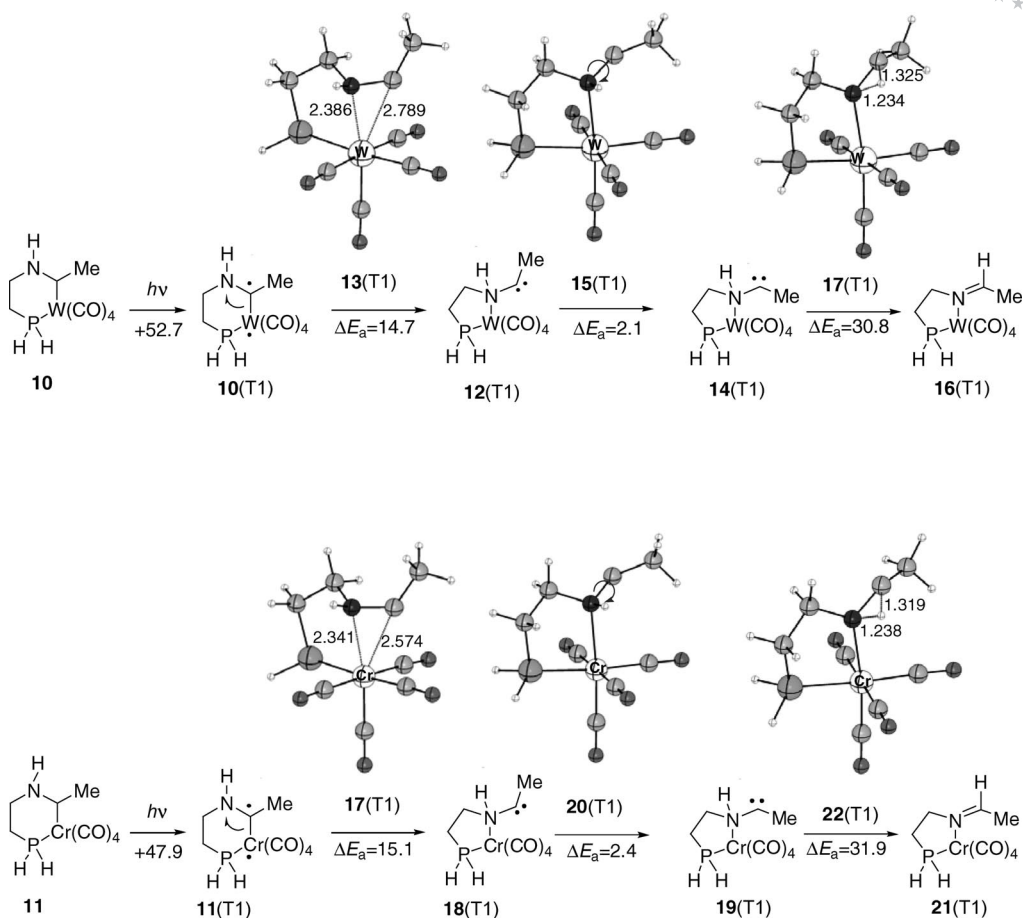
nucleophilic attack by MeOH.^[8b] However, complexes **8** cannot be generated from ketene-like species. Thus, we propose that *N*-substituted aminocarbene complexes **3b** and **7** experience an α -fragmentation process, which is analogous to the α -photofragmentation of amides.^[16,17] In principle, the α -fragmentation process should occur in a triplet species isostructural to those proposed for the 1,2-dyotropic process and formed by the initial capture of the photon by the carbene complex in the S_0 state.

We initiate our attempt to generalize the noncarbon-yative photochemistry of group 6 metal carbenes by comparing the computational results of model tungsten–carbene **10** with the results obtained for the analogous chromium(0)–carbene **11**. The reaction profile of complex **10** was calculated at the uB3LYP/6-31+G(d)&LANL2DZ level (Scheme 6). We propose that the type I dyotropic reaction^[18] of complex **10** starts with a short-lived triplet state **10(T1)**, formed after initial photoexcitation of the singlet ground state S_0 to the excited singlet state S_1 and subsequent ISC. The triplet state **10(T1)** evolves to the carbene species **12(T1)** in the triplet hypersurface via transition state **13**, which is associated with the 1,2-migration of the pentacarbonyltungsten moiety from the carbene carbon atom to the nitrogen atom. Carbene **12(T1)** isomerizes to **14(T1)** by rotation about the N–C(Me) bond via the saddle point **15(T1)** transition structure. Finally, the species **14(T1)** yields the final product **16(T1)** through transition state **17**, a saddle point associated with the migration of the hydrogen atom from the nitrogen atom to the carbene moiety.

It is very significant that the activation barriers of the transformation involving tungsten–carbene complexes are only slightly lower than the activation energies for chromium–carbene complexes. The experimental and computational data demonstrate that group 6 aminocarbene complexes having phosphane ligands and an unsubstituted nitrogen atom attached to the carbene carbon atom react through a 1,2-dyotropic stepwise rearrangement.^[19] With the exception of the relative energies of the starting diradical species with respect to the ground state complexes



Scheme 5.



Scheme 6. Calculated profiles [uB3LYP/6-31+G(d)&LANL2DZ+ΔZPVE level of theory] for the stepwise 1,2-dyotropic process of model structures **10** and **11**. Numbers below the arrows are the relative energies and, when stated, the activation energies in kcal/mol. Bond lengths are in Å.

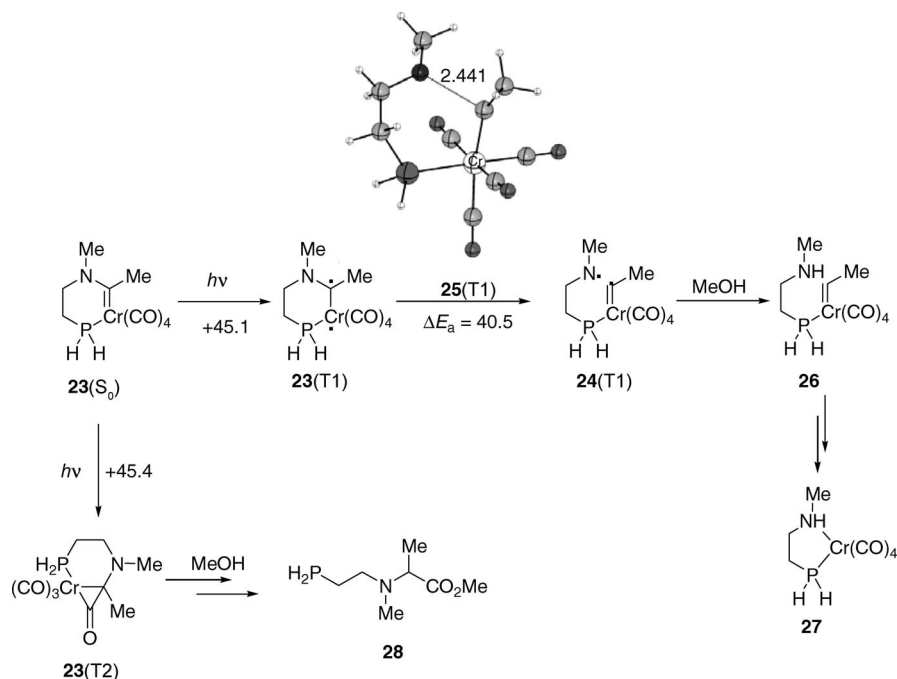
(4.8 kcal/mol higher in tungsten complexes than in their chromium analogues), no significant differences were observed between both metal complexes, which is a very remarkable and unusual result.

The second noncarbonylative pathway, namely the α -fragmentation, was studied for both the Cr and W model compounds **23** and **29**, respectively. The excited states of complex **23** were computed at the uB3LYP/6-31+G(d)&LanL2DZ level (Scheme 7). We located two coexistent triplet species, namely the diradical **23(T1)** and the metallacyclop propane complex **23(T2)**. This second species (see Figure S1 in Supporting Information) is formed through the standard carbonylation process reported by us.^[8a] Both activated species, **23(T1)** and **23(T2)**, are close in energy ($\Delta E_{T1-T2} = 0.3$ kcal/mol), and therefore, mixtures of ketene-derived (amino esters) and α -fragmentation compounds would be expected. This is in full agreement with the experimentally observed mixture of complexed aminophosphanes **8** and carbonylation products **9**.

Species **23(T1)** evolves to the species **24(T1)** in the triplet hypersurface via transition state **25**, which is associated with the cleavage of the N–C bond. As stated above, this process is the organometallic equivalent of the α -fragmentation of amides. Species **24(T1)** is also a diradical (calculated

spin densities N = 0.92 and C = 0.80 a.u.) and captures two hydrogen atoms from the solvent to form the carbene species **26**. The evolution of this type of complexes to the isolated metalated amine products similar to **27** has been previously reported by us and others.^[20] Alternatively, the metallacyclop propane complex **23(T2)** evolves to the α -amino esters such as **28** by reaction of the ketene-like species formed from **23(T2)** with MeOH.

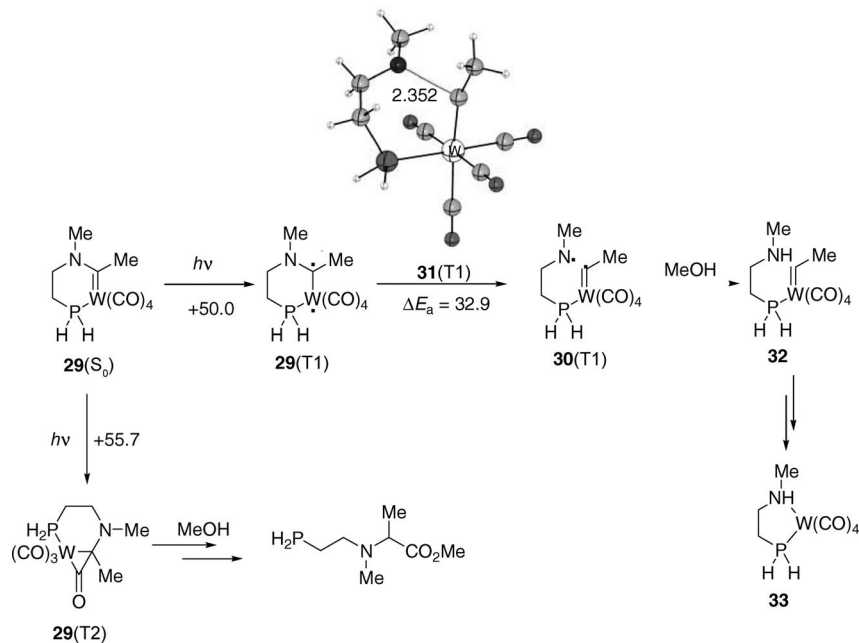
As discussed above,^[13] irradiation of the *N*-methyl-substituted complexes **3b** exclusively results in α -fragmentation reactions leading to complexes **5** (Scheme 3); the exception is the tungsten complex **3c**, which leads to **6** in yields lower than 11% (Scheme 3). It is clear that tungsten–carbene complexes **3** have a strong bias toward α -fragmentation, at the expense of the photocarbonylation reaction. The reason for such a difference in behavior relative to their chromium counterparts could be the higher stabilization of the diradical species **29(T1)** than that of the tungsten–cyclopropanone species **29(T2)**, which leads to photocarbonylation products. Both triplets originate from the excitation of the model tungsten compound **29**. The computed energy difference between the activated species **29(T1)** and **29(T2)** is indeed +5.7 kcal/mol (Scheme 8) (relative to 0.4 kcal/mol for the Cr analogues). This higher difference in energy explains



Scheme 7. Calculated profiles [uB3LYP/6-31+G(d)&LANL2DZ+ΔZPVE level of theory] for transformations of model structure **23**. Numbers below the arrows are the relative energies and, when stated, the activation energies in kcal/mol. Bond lengths are in Å.

the strong preference or even the exclusive formation of complexes **5** instead of the corresponding amino esters for tungsten complexes **3**. Similarly to chromium complex **23(T1)**, triplet **29(T1)** (calculated spin densities W = 0.56 and C = 0.74 a.u.) evolves to diradical **30(T1)** (calculated spin densities N = 0.92 and C = 0.92 a.u.) via the transition state **31**, which is again associated with the breaking of the N–C bond. Interestingly, the activation energy of this pro-

cess is 7.9 kcal/mol lower than the corresponding barrier for the analogous chromium species **23(T1)**, which makes this step easier for tungsten than for chromium. The stronger N–C bond in **23(T1)** than that in the tungsten species **29(T1)** accounts for this observation. In fact, the N–C NBO Wiberg bond order is higher in **23(T1)** (1.40 a.u.) than in **29(T1)** (1.31 a.u.), and the N–C bond length is therefore longer in **29(T1)** (1.398 Å) than in **23(T1)** (1.382 Å). As a



Scheme 8. Calculated profiles [uB3LYP/6-31+G(d)&LANL2DZ+ΔZPVE level of theory] for transformations of model structure **29**. Numbers below the arrows are the relative energies and, when stated, the activation energies in kcal/mol. Bond lengths are in Å.

consequence, the α -fragmentation reaction is kinetically favored in tungsten–carbene complexes in view of the lower activation barrier than that of their chromium analogues.

In conclusion, the experimental and computational study reported in this paper unifies the noncarbonylative photochemical behavior of group 6 metal carbene complexes ($M = Cr$ or W). These complexes can undergo three different photoreactions, namely: photocarbonylation, stepwise 1,2-dyotropic rearrangement, and α -fragmentation. Both the metal atom and the substitution on the nitrogen atom influence the topography of the potential energy surface, which leads to two different activated species, and hence to the carbonylative or noncarbonylative reaction pathways. Generation of a diradical species instead of metallacyclopropanone leads to two different reaction pathways. Complexes having a spherical hydrogen substituent at the nitrogen atom experience a stepwise dyotropic migration with no significant differences between the chromium- and tungsten–carbene complexes. The excitation of complexes having substituents other than hydrogen at the nitrogen atom gives rise to two different triplet species and hence to the formation of mixtures of products arising from α -fragmentation (non-carbonylation) and amino esters (photocarbonylation). The two triplet states are practically isoenergetic in the Cr derivatives, but the T1 intermediate that leads to α -fragmentation is strongly favored for the W derivatives. Additionally, the α -fragmentation reaction is kinetically facilitated in tungsten–carbene complexes because of a weaker N–C bond relative to that in the chromium complexes, which results in lower barriers for this process in these complexes relative to their chromium counterparts. The experimental consequence of these models is the formation of metalloimines for NH complexes, irrespective of the metal, or of mixtures of α -fragmentation products or of amino esters for the NR complexes. Finally, both chromium- and tungsten–carbene complexes are equally photoreactive in spite of the longstanding claim that tungsten–carbene complexes were photochemically inert.

Experimental Section

General Procedures: 1H NMR, ^{13}C NMR, and ^{31}P NMR spectra were recorded at 22 °C with Bruker Avance 500 (500.1 and 125.7 MHz), 300 (300.1 and 75.4 MHz), or Bruker 200-AC (200.1 and 50 MHz) spectrometers. Chemical shifts are given in ppm relative to TMS (1H , 0.0 ppm), $CDCl_3$ (^{13}C , 77.0 ppm), and H_3PO_4 (^{31}P , 0.0 ppm). IR spectra were recorded on a Perkin–Elmer 781 spectrometer. CH_3CN was distilled from calcium hydride and thf from sodium benzophenone. Flame-dried glassware and standard Schlenk techniques were used for moisture sensitive reactions. Merck silica-gel (230–400 mesh) was used as the stationary phase for purification of crude reaction mixtures by flash column chromatography. Identification of products was made by TLC (Kieselgel 60F-254). UV light ($\lambda = 254$ nm) and 5% phosphomolybdic acid solution in 95% EtOH were used to develop the plates. All commercially available compounds were used without further purification. Aminocarbene complexes **1** were prepared following the previous reported method.^[12]

Computational Details: All the calculations reported in this paper were obtained with the GAUSSIAN 03 suite of programs.^[21] Electron correlation has been partially taken into account by using the hybrid functional usually denoted as B3LYP^[22] and the standard 6-31+G(d) basis sets^[23] for hydrogen, carbon, oxygen, nitrogen, and phosphorus, and the Hay–Wadt small-core effective core potential (ECP) including a double- ξ valence basis set^[24] for chromium and tungsten (LANL2DZ keyword). We denote this basis set as LANL2DZ&6-31+G(d). Zero-point vibrational energy (ZPVE) corrections were computed at the same level, and have not been corrected. Excited states were located at the configuration interaction single (CIS) level,^[25] and triplets were optimized at the uB3-LYP level. Stationary points were characterized by frequency calculations^[26] and have positive, defined 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 using the intrinsic reaction coordinate (IRC) method.^[27] Wiberg bond orders were computed by using the natural bond order (NBO)^[28] method.

General Procedure for the Synthesis of Complexes 7: A solution of complex **1** in degassed acetone (0.025 M) was treated with 2 equiv. of the corresponding alkyl halide and 3 equiv. Cs_2CO_3 and water (drops) at room temperature and left overnight. The crude product was filtered through a short pad of Celite, and the solvent was removed under reduced pressure to yield pure compounds (unless otherwise specified).

7a: 214 mg (99%), yellow solid. 1H NMR (300 MHz, $CDCl_3$): $\delta = 2.26$ (m, 2 H), 2.67 (s, 3 H), 3.31 (d, $J = 1.0$ Hz, 3 H), 4.04 (m, 1 H), 4.13 (m, 1 H), 7.26–7.47 (m, 10 H, ArH) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 25.3$ (d, $J_{C,P} = 18.9$ Hz), 29.2, 40.3 (d, $J_{C,P} = 3.5$ Hz), 57.8 (d, $J_{C,P} = 6.2$ Hz), 128.4 (d, $J_{C,P} = 8.5$ Hz), 129.4 (d, $J_{C,P} = 1.5$ Hz), 131.5 (d, $J_{C,P} = 11.0$ Hz), 138.1 (d, $J_{C,P} = 33.3$ Hz), 222.9 (d, $J_{C,P} = 13.0$ Hz), 228.8 (d, $J_{C,P} = 1.7$ Hz), 231.1 (d, $J_{C,P} = 14.6$ Hz), 281.1 (d, $J_{C,P} = 16.1$ Hz) ppm. IR (KBr): $\tilde{\nu} = 1992, 1900, 1863, 1844$ cm^{-1} . $C_{21}H_{20}CrNO_4P$ (433.36): calcd. C 58.20, H 4.65, N 3.23; found C 58.45, H 4.78.

7b: 221 mg (99%), yellow solid. 1H NMR (300 MHz, $CDCl_3$): $\delta = 1.97$ (m, 2 H), 2.50 (m, 2 H), 2.72 (s, 3 H), 3.78 (s, 3 H), 3.718–7.71 (m, 10 H, ArH) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 22.1, 25.8$ (d, $J_{C,P} = 15.6$ Hz), 39.6, 40.4, 61.1 (d, $J_{C,P} = 10.1$ Hz), 128.3–133.6 (m), 222.7 (d, $J_{C,P} = 9.8$ Hz), 228.5 (d, $J_{C,P} = 1.8$ Hz), 230.6 (d, $J_{C,P} = 15.0$ Hz), 281.9 (d, $J_{C,P} = 9.2$ Hz) ppm. IR (KBr): $\tilde{\nu} = 1990, 1901, 1871, 1832$ cm^{-1} . $C_{22}H_{22}CrNO_4P$ (447.38): calcd. C 59.06, H 4.96, N 3.13; found C 58.87, H 4.84.

7c: 245 mg (99%), yellow solid. 1H NMR (300 MHz, $CDCl_3$): $\delta = 2.70$ (s, 3 H), 3.34 (s, 3 H), 4.23 (m, 1 H), 6.05 (m, 1 H), 6.88 (m, 1 H, ArH), 7.30–7.56 (m, 13 H, ArH) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 40.2$ (d, $J_{C,P} = 3.7$ Hz), 40.9, 65.9 (d, $J_{C,P} = 12.5$ Hz), 128.2 (d, $J_{C,P} = 8.9$ Hz), 129.5, 129.5 (d, $J_{C,P} = 5.3$ Hz), 129.7, 130.2 (d, $J_{C,P} = 1.6$ Hz), 133.0 (d, $J_{C,P} = 10.9$ Hz), 133.6 (d, $J_{C,P} = 18.5$ Hz), 133.7, 136.0 (d, $J_{C,P} = 34.2$ Hz), 140.0 (d, $J_{C,P} = 14.0$ Hz), 222.2 (d, $J_{C,P} = 10.1$ Hz), 228.4, 229.7 (d, $J_{C,P} = 15.6$ Hz), 280.7 (d, $J_{C,P} = 12.0$ Hz) ppm. IR (KBr): $\tilde{\nu} = 1998, 1905, 1877, 1838$ cm^{-1} . $C_{26}H_{22}CrNO_4P$ (495.43): calcd. C 63.03, H 4.48; found C 63.25, H 4.58.

7d: 283 mg (99%), yellow solid. 1H NMR (300 MHz, $CDCl_3$): $\delta = 2.81$ (s, 3 H), 4.21 (br. s, 1 H), 4.62 (br. s, 1 H), 5.20 (br. s, 1 H), 5.91 (br. s, 1 H), 6.89 (m, 1 H, ArH), 7.05–7.35 (m, 18 H, ArH) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 40.2$ (d, $J_{C,P} = 3.8$ Hz), 55.3, 62.5 (d, $J_{C,P} = 12.5$ Hz), 126.3, 128.1, 128.2 (d, $J_{C,P} = 8.3$ Hz), 129.4, 129.6 (d, $J_{C,P} = 4.2$ Hz), 130.1 (d, $J_{C,P} = 6.1$ Hz), 130.3,

133.0 (d, $J_{C,P}$ = 11.2 Hz), 133.5 (d, $J_{C,P}$ = 6.9 Hz), 134.0 (d, $J_{C,P}$ = 18.6 Hz), 136.0 (d, $J_{C,P}$ = 34.5 Hz), 140.0 (d, $J_{C,P}$ = 14.1 Hz), 222.4 (d, $J_{C,P}$ = 7.4 Hz), 228.4 (d, $J_{C,P}$ = 1.8 Hz), 229.9 (d, $J_{C,P}$ = 16.4 Hz), 282.9 (d, $J_{C,P}$ = 12.6 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 1994, 1913, 1871, 1840 cm^{-1} . $\text{C}_{32}\text{H}_{26}\text{CrNO}_4\text{P}$ (571.52): calcd. C 67.25, H 4.59, N 2.45; found C 67.01, H 4.43, N 2.34.

7e: 258 mg (99%), yellow solid. ^1H NMR (300 MHz, CDCl_3): δ = 2.74 (s, 3 H), 4.20 (br. s, 2 H), 5.11 (br. s, 1 H), 5.25 (d, J = 10.2 Hz, 2 H), 5.72 (m, 1 H), 5.94 (br. s, 1 H), 6.90 (m, 1 H, ArH), 7.26–7.54 (m, 13 H, ArH) ppm. ^{13}C NMR (75.5 MHz, CDCl_3): δ = 39.5 (d, $J_{C,P}$ = 4.1 Hz), 54.4, 62.9 (d, $J_{C,P}$ = 12.1 Hz), 117.8, 128.2 (d, $J_{C,P}$ = 9.0 Hz), 129.5, 129.6, 130.1 (d, $J_{C,P}$ = 6.3 Hz), 130.3, 132.9 (m), 133.6, 133.8 (d, $J_{C,P}$ = 18.5 Hz), 136.1 (d, $J_{C,P}$ = 34.2 Hz), 140.1 (d, $J_{C,P}$ = 14.2 Hz), 222.4 (d, $J_{C,P}$ = 10.6 Hz), 228.4 (d, $J_{C,P}$ = 1.7 Hz), 229.8 (d, $J_{C,P}$ = 16.4 Hz), 282.0 (d, $J_{C,P}$ = 12.8 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 1996, 1894, 1875, 1846 cm^{-1} . $\text{C}_{28}\text{H}_{24}\text{CrNO}_4\text{P}$ (521.46): calcd. C 64.49, H 4.64, N 2.69; found C 64.61, H 4.73.

General Procedure for the Photochemical Reactions of Complexes 7: Photochemical reactions were conducted by using a 450 W medium-pressure Hg lamp, through a Pyrex filter in dry degassed CH_3CN or $\text{CH}_3\text{CN}/\text{thf}$ containing CH_3OH in a sealed Pyrex tube filled with argon. In a typical experiment, after irradiation for 30 h, the solution was filtered through a short pad of Celite, the solvent was removed under reduced pressure, and the crude product was submitted to flash chromatography to give pure complexes **8** and **9**.

8a: 199 mg (98%), yellow solid. ^1H NMR (300 MHz, CDCl_3): δ = 2.03 (m, 1 H), 2.22 (m, 1 H), 2.58 (d, J = 4.1 Hz, 3 H), 2.69 (m, 1 H), 2.69 (m, 1 H), 2.96 (m, 1 H), 7.31–7.60 (m, 10 H, ArH) ppm. ^{13}C NMR (75.5 MHz, CDCl_3): δ = 28.1 (d, $J_{C,P}$ = 16.1 Hz), 46.1, 54.0 (d, $J_{C,P}$ = 11.8 Hz), 128.7 (d, $J_{C,P}$ = 9.3 Hz), 128.8 (d, $J_{C,P}$ = 9.1 Hz), 129.9 (d, $J_{C,P}$ = 1.6 Hz), 130.0 (d, $J_{C,P}$ = 1.7 Hz), 131.1 (d, $J_{C,P}$ = 11.7 Hz), 131.6 (d, $J_{C,P}$ = 11.8 Hz), 135.7 (d, $J_{C,P}$ = 17.6 Hz), 136.2 (d, $J_{C,P}$ = 14.6 Hz), 218.1 (d, $J_{C,P}$ = 13.7 Hz), 218.4 (d, $J_{C,P}$ = 14.1 Hz), 226.6 (d, $J_{C,P}$ = 2.6 Hz), 228.0 (d, $J_{C,P}$ = 12.8 Hz) ppm. IR (CCl_4): $\tilde{\nu}$ = 2012, 1954, 1888 cm^{-1} . $\text{C}_{19}\text{H}_{18}\text{CrNO}_4\text{P}$ (407.32): calcd. C 56.03, H 4.45, N 3.44; found C 56.28, H 4.59.

8c: 82 mg (35%), yellow solid. ^1H NMR (300 MHz, CDCl_3): δ = 2.41 (d, J = 6.3 Hz, 3 H), 2.98 (br. s, 1 H), 3.43 (m, 2 H), 6.74 (m, 1 H, ArH), 7.28–7.42 (m, 13 H, ArH) ppm. ^{13}C NMR (75.5 MHz, CDCl_3): δ = 46.1, 60.7 (d, $J_{C,P}$ = 12.7 Hz), 128.5 (d, $J_{C,P}$ = 1.8 Hz), 128.7 (d, $J_{C,P}$ = 2.0 Hz), 129.9, 130.2 (d, $J_{C,P}$ = 13.6 Hz), 131.1 (d, $J_{C,P}$ = 22.6 Hz), 131.5, 132.0 (d, $J_{C,P}$ = 7.4 Hz), 132.9 (d, $J_{C,P}$ = 11.5 Hz), 134.1 (d, $J_{C,P}$ = 34.8 Hz), 138.7 (d, $J_{C,P}$ = 17.1 Hz), 218.2 (d, $J_{C,P}$ = 13.1 Hz), 218.8 (d, $J_{C,P}$ = 13.1 Hz), 225.1, 226.2 (d, $J_{C,P}$ = 13.6 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 3288, 2004, 1878, 1838 cm^{-1} . $\text{C}_{24}\text{H}_{20}\text{CrNO}_4\text{P}$ (469.39): calcd. C 61.41, H 4.29, N 2.98; found C 61.25, H 4.46.

8d: 87 mg (32%), yellow solid. ^1H NMR (300 MHz, CDCl_3): δ = 3.22–3.45 (m, 4 H), 4.08 (d, J = 13.2 Hz, 1 H), 6.79–6.88 (m, 2 H), 7.11–7.45 (m, 17 H, ArH) ppm. ^{13}C NMR (75.5 MHz, CDCl_3): δ = 54.4 (d, $J_{C,P}$ = 12.0 Hz), 60.8, 128.2, 128.4, 128.5 (d, $J_{C,P}$ = 5.3 Hz), 128.6 (d, $J_{C,P}$ = 5.5 Hz), 129.1, 129.9 (d, $J_{C,P}$ = 2.7 Hz), 129.9, 130.1, 130.1 (d, $J_{C,P}$ = 5.5 Hz), 131.6, 131.7, 131.9, 132.2 (d, $J_{C,P}$ = 7.5 Hz), 132.5, 132.8 (d, $J_{C,P}$ = 11.5 Hz), 133.2, 133.4 (d, $J_{C,P}$ = 36.8 Hz), 133.7 (d, $J_{C,P}$ = 11.6 Hz), 134.2 (d, $J_{C,P}$ = 34.9 Hz), 136.7, 138.5 (d, $J_{C,P}$ = 16.5 Hz), 218.2 (d, $J_{C,P}$ = 12.9 Hz), 219.0 (d, $J_{C,P}$ = 12.9 Hz), 224.8, 226.4 (d, $J_{C,P}$ = 13.4 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 3288, 2004, 1878, 1838 cm^{-1} . $\text{C}_{30}\text{H}_{24}\text{CrNO}_4\text{P}$ (545.48): calcd. C 66.06, H 4.43, N 2.57; found C 65.87, H 4.66.

9b: 180 mg (quantitative yield), pale yellow oil. ^1H NMR (300 MHz, CDCl_3): δ = 1.17 (d, J = 7.0 Hz, 3 H), 1.17 (m, 2 H),

2.16 (s, 3 H), 2.21 (m, 2 H), 2.50 (m, 2 H), 3.28 (q, J = 7.0 Hz, 1 H), 3.60 (s, 3 H), 7.38–7.71 (m, 10 H, ArH) ppm. ^{13}C NMR (75.5 MHz, CDCl_3): δ = 14.4, 19.7 (d, $J_{C,P}$ = 3.3 Hz), 27.0 (d, $J_{C,P}$ = 73.1 Hz), 37.5, 51.1, 54.2 (d, $J_{C,P}$ = 15.4 Hz), 61.1, 128.5 (d, $J_{C,P}$ = 11.5 Hz), 130.7 (d, $J_{C,P}$ = 9.2 Hz), 131.6 (d, $J_{C,P}$ = 2.6 Hz), 133.0 (d, $J_{C,P}$ = 98.3 Hz), 173.6 ppm. ^{31}P NMR (121, MHz, CDCl_3): δ = 34.1 ppm. IR (CCl_4): $\tilde{\nu}$ = 1936, 1732, 1437, 1215 cm^{-1} . ESI-MS: m/z = 359. $\text{C}_{20}\text{H}_{26}\text{NO}_3\text{P}$ (359.40): calcd. C 66.84, H 7.29, N 3.90; found C 66.67, H 7.05.

9c: 80 mg (41%), yellow solid. ^1H NMR (300 MHz, CDCl_3): δ = 0.84 (d, J = 7.1 Hz, 3 H), 2.00 (s, 3 H), 3.32 (q, J = 7.1 Hz, 1 H), 3.59 (s, 3 H), 3.83 (qd, J_1 = 6.0, J_2 = 1.7 Hz, 2 H), 6.86 (m, 1 H, ArH), 7.10–7.37 (m, 13 H, ArH) ppm. ^{13}C NMR (75.5 MHz, CDCl_3): δ = 14.4, 35.5, 51.0, 58.2 (d, $J_{C,P}$ = 18.2 Hz), 59.7, 127.2, 128.1, 128.3 (d, $J_{C,P}$ = 10.3 Hz), 128.3 (d, $J_{C,P}$ = 6.9 Hz), 128.6, 129.3 (d, $J_{C,P}$ = 5.7 Hz), 133.4 (d, $J_{C,P}$ = 19.3 Hz), 133.7 (d, $J_{C,P}$ = 22.3 Hz), 134.4, 136.7 (d, $J_{C,P}$ = 15.5 Hz), 137.8 (d, $J_{C,P}$ = 10.3 Hz), 137.9 (d, $J_{C,P}$ = 10.0 Hz), 144.2 (d, $J_{C,P}$ = 23.6 Hz), 173.9 ppm. ^{31}P NMR (121, MHz, CDCl_3): δ = –12.6 ppm. IR (CCl_4): $\tilde{\nu}$ = 1942, 1736, 1433 cm^{-1} . $\text{C}_{24}\text{H}_{26}\text{NO}_2\text{P}$ (391.44): calcd. C 73.64, H 6.69, N 3.58; found C 73.89, H 6.48.

9d: 140 mg (60%), pale yellow oil. ^1H NMR (300 MHz, CDCl_3): δ = 1.14 (d, J = 7.1 Hz, 3 H), 3.38 (q, J = 7.1 Hz, 1 H), 3.56 (s, 3 H), 3.58 (q, J = 14.1 Hz, 2 H), 3.87 (qd, J_1 = 17.8, J_2 = 3.3 Hz, 2 H), 6.73 (m, 1 H, ArH), 7.04–7.29 (m, 17 H, ArH), 7.68 (m, 1 H, ArH) ppm. ^{13}C NMR (75.5 MHz, CDCl_3): δ = 14.3, 51.2, 52.1 (d, $J_{C,P}$ = 24.6 Hz), 54.4, 56.5, 126.8 (d, $J_{C,P}$ = 9.2 Hz), 128.1, 128.4, 128.5 (d, $J_{C,P}$ = 3.5 Hz), 128.6 (d, $J_{C,P}$ = 6.6 Hz), 128.7, 128.8 (d, $J_{C,P}$ = 11.5 Hz), 133.1, 133.7 (d, $J_{C,P}$ = 3.5 Hz), 134.0 (d, $J_{C,P}$ = 3.2 Hz), 136.0 (d, $J_{C,P}$ = 14.5 Hz), 136.5 (d, $J_{C,P}$ = 10.6 Hz), 136.8 (d, $J_{C,P}$ = 10.5 Hz), 139.7, 144.0 (d, $J_{C,P}$ = 22.2 Hz), 174.2 ppm. ^{31}P NMR (121, MHz, CDCl_3): δ = –14.8 ppm. IR (CCl_4): $\tilde{\nu}$ = 1942, 1736, 1433 cm^{-1} . $\text{C}_{30}\text{H}_{30}\text{NO}_2\text{P}$ (467.54): calcd. C 77.07, H 6.47, N 3.00; found C 76.89, H 6.66.

9e: 115 mg (55%), pale yellow oil. ^1H NMR (300 MHz, CDCl_3): δ = 1.02 (d, J = 7.1 Hz, 3 H), 3.03 (qd, J_1 = 13.6, J_2 = 5.6 Hz, 2 H), 3.38 (q, J = 7.1 Hz, 1 H), 3.54 (s, 3 H), 3.88 (qd, J_1 = 15.9, J_2 = 2.2 Hz, 2 H), 4.93 (d, J = 10.1 Hz, 1 H), 5.02 (dd, J_1 = 17.2, J_2 = 1.5 Hz, 1 H), 5.60 (m, 1 H), 6.78 (m, 1 H, ArH), 7.06–7.27 (m, 12 H, ArH), 7.55 (m, 1 H, ArH) ppm. ^{13}C NMR (75.5 MHz, CDCl_3): δ = 14.5, 51.1, 52.8 (d, $J_{C,P}$ = 22.4 Hz), 53.4, 57.0, 116.8, 126.9, 128.3, 128.4, 128.5 (d, $J_{C,P}$ = 3.2 Hz), 128.9 (d, $J_{C,P}$ = 5.4 Hz), 133.6, 133.7 (d, $J_{C,P}$ = 10.9 Hz), 133.9 (d, $J_{C,P}$ = 9.8 Hz), 136.0 (d, $J_{C,P}$ = 14.7 Hz), 136.6, 136.9 (d, $J_{C,P}$ = 10.2 Hz), 137.3 (d, $J_{C,P}$ = 10.9 Hz), 144.3 (d, $J_{C,P}$ = 22.8 Hz), 174.3 ppm. ^{31}P NMR (121, MHz, CDCl_3): δ = –13.4 ppm. IR (CCl_4): $\tilde{\nu}$ = 1942, 1736, 1433 cm^{-1} . $\text{C}_{26}\text{H}_{28}\text{NO}_2\text{P}$ (417.48): calcd. C 78.40, H 6.76, N 3.36; found C 78.55, H 6.58, N 3.55.

Supporting Information (see footnote on the first page of this article): 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.

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- [15] Compounds **9** also lack the pentacarbonylchromium(0) moiety and show the typical amino ester structure derived from a phototocarbonylation process. The ¹³C NMR spectrum of these compounds show a signal in the range δ = 173.6–174.30 ppm attributable to the ester carbonyl group. ³¹P NMR spectroscopy ascertained the oxidation of the phosphorus in the latter compounds. While ester **9b** presents a ³¹P signal at δ = 34.1 ppm, compounds **9c–e** present a ³¹P signal in the range –12.6 to 14.8 ppm (referenced to internal H₃PO₄). These data indicate that oxidation of the phosphane moiety occurs in compound **9b**. Additional ESI-MS confirms the presence of the phosphane oxide moiety in compound **9b** (*m/z* = 359).
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