Carbene Complex Chemistry

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

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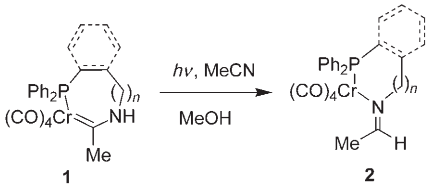
The seminal discovery in 1982[1] of the sunlight-promoted reaction between chromium(0) carbene complexes and imines to yield β-lactams began the synthetically useful photochemistry of group 6 (Fischer) carbene complexes.[2,3] Both alkoxy- and aminocarbene complexes of chromium(0) are active in these reactions.[4] The reversible formation of chromium-bound 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 photo-inert.[6] Recently, we reported[7] a new photochemical dyotropic rearrangement from aminocarbenes **1** to imines **2** (Scheme 1), which unambiguously demonstrates the possibility 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.



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

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(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(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**.

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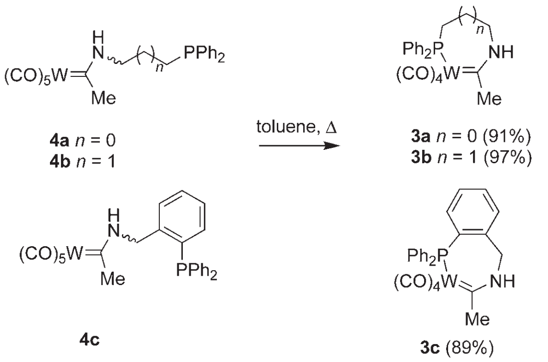
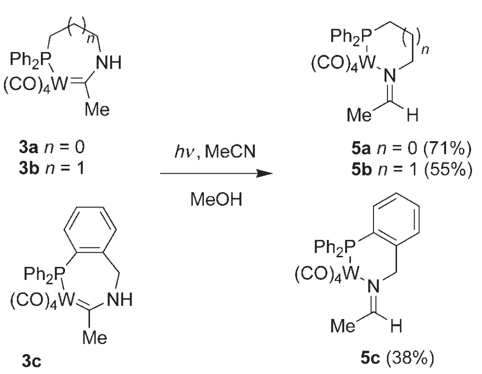
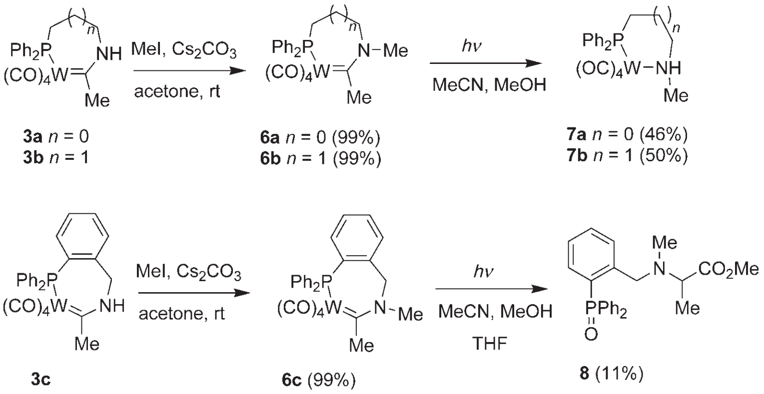


Scheme 2. Synthesis of cyclic tungsten(0) carbene complexes **3**. For details, see Experimental Section.



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

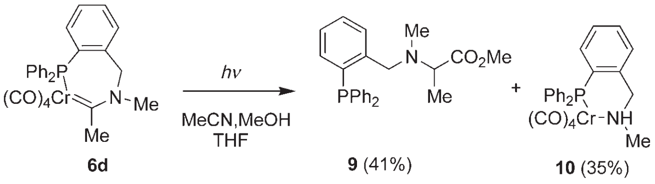
Therefore, to extend our knowledge of this reaction and to check the generality of tungsten(0)–carbene photochemistry, complexes **6** were prepared in almost quantitative yields by alkylation of complexes **3** with MeI/Cs_2CO_3, and irradiated in MeCN/MeOH (10:1; complexes **6a** and **6b**) or MeCN/THF/MeOH (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.

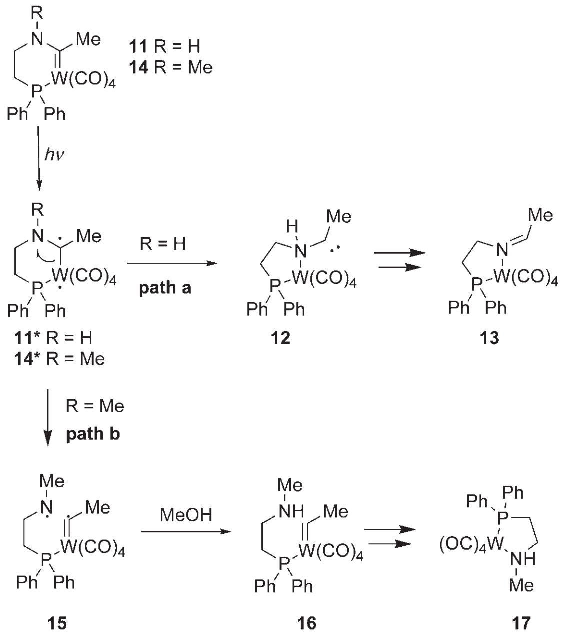
In fact, two different classes of compounds were obtained, either as mixtures (for complex **6c**) or as single products (for complexes **6a** and **6b**). The structure of a cyclic tetracarbonyl(phosphanylamino)tungsten complex was assigned to compounds **7a** and **7b** (derived from complexes **6a** and **6b**) on the basis of their spectroscopic data. Thus, complex **7a** shows a set of four ^{13}C 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 carbene carbon atom of the starting complexes **6**. The product isolated from **6c** lacks the metal moiety and has an amino ester structure.[9] The ^{13}C 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 ^{31}P 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(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(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).



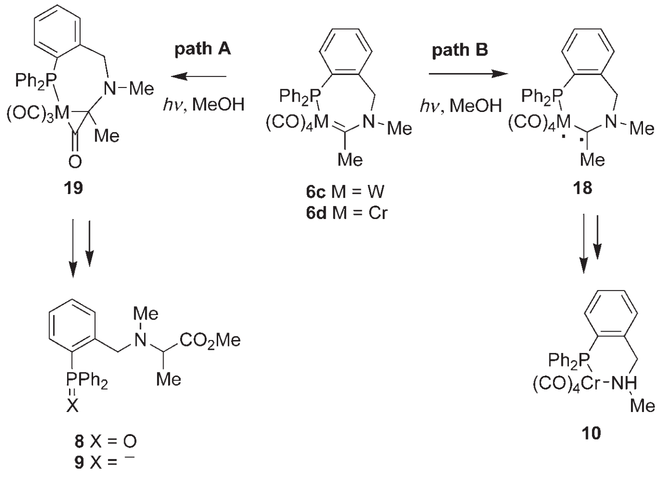
Scheme 5. Competitive α-fragmentation and carbonylation reactions of chromium(0) carbene **6d**.

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



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

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 metalladyotropic 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(0) and the corresponding aminophosphane, in dry CH_2Cl_2, 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 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.75$ (m, 2 H; CH_2P), 2.56 (s, 3 H; CH_3), 3.95 (m, 2 H; CH_2N), 7.32–7.72 (m, 10 H; H_{Ar}), 8.46 ppm (br. s, 1 H; NH). ^{13}C NMR (50 MHz, $CDCl_3$): $\delta =$ 28.1 (d, $J_{C,P} = 15.3$ Hz; CH_2P), 47.1 (CH_3), 52.7 (d, $J_{C,P} = 16.5$ Hz; CH_2N), 128.9 (d, $J_{C,P} = 6.4$ Hz; C_{Ar}), 129.4 (C_{Ar}), 132.7 (d, $J_{C,P} =$ 19.1 Hz; C_{Ar}), 136.5 (d, $J_{C,P} = 11.4$ Hz; C_{Ar}), 198.2 (*C*O), 203.2 (*C*O), 255.6 ppm (W=C). IR (CCl_4): $\tilde{\nu} = 2062$, 1965, 1927 cm^{-1}. $C_{21}H_{18}NO_5PW$: 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 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.36$ (m, 2 H; CH_2P), 2.77 (s, 3 H; CH_3), 3.85 (m, 1 H; CH_2N), 3.92 (m, 1 H; CH_2N), 7.30–7.52 (m, 10 H; H_{Ar}), 8.92 ppm (s, 1 H; NH). ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 25.2$ (d, $J_{C,P} = 23.6$ Hz; CH_2P), 46.6 (d, $J_{C,P} =$ 4.1 Hz; CH_3), 48.9 (d, $J_{C,P} = 6.1$ Hz; CH_2N), 128.5 (d, $J_{C,P} = 9.3$ Hz; C_{Ar}), 129.8 (d, $J_{C,P} = 1.4$ Hz; C_{Ar}), 131.9 (d, $J_{C,P} = 12.0$ Hz; C_{Ar}), 137.0 (d, $J_{C,P} = 38.3$ Hz; C_{Ar}), 203.2 (d, $J_{C,P} = 7.0$ Hz; CO), 209.2 (d, $J_{C,P} =$ 26.8 Hz; CO), 213.4 (d, $J_{C,P} = 7.3$ Hz; CO), 261.4 ppm (d, $J_{C,P} =$ 9.6 Hz; W=C). IR (KBr): $\tilde{\nu} = 3304$, 2002, 1875, 1838 cm^{-1}. $C_{20}H_{18}NO_4PW$: 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 Cs_2CO_3, 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 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.31$ (m, 2 H; CH_2P), 2.67 (s, 3 H; CH_3C), 3.26 (s, 3 H; CH_3N); 4.05 (m, 1 H; CH_2N), 4.14 (m, 1 H; CH_2N), 7.26–7.46 ppm (m, 10 H; H_{Ar}). ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 24.8$ (d, $J_{C,P} = 23.6$ Hz; CH_2P), 42.0 (d, $J_{C,P} =$ 37.2 Hz; CH_2N), 53.4 (CH_3C), 62.5 (d, $J_{C,P} = 7.1$ Hz; CH_3N), 128.5 (d, $J_{C,P} = 9.3$ Hz; C_{Ar}), 129.7 (d, $J_{C,P} = 1.6$ Hz; C_{Ar}), 131.9 (d, $J_{C,P} =$ 12.0 Hz; C_{Ar}), 137.3 (d, $J_{C,P} = 38.2$ Hz; C_{Ar}), 203.9 (d, $J_{C,P} = 6.9$ Hz; CO), 210.1 (d, $J_{C,P} = 28.1$ Hz; CO), 213.0 (d, $J_{C,P} = 6.7$ Hz; CO), 259.7 ppm (d, $J_{C,P} = 10.1$ Hz; W=C). IR (KBr): $\tilde{\nu} = 2000$, 1902, 1857, 1842 cm^{-1}. $C_{21}H_{20}NO_4PW$: 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 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.28$ (d, $J = 5.2$ Hz, 3 H; CH_3), 2.46 (m, 2 H; CH_2P), 3.85 (m, 1 H; CH_2N), 3.93 (m, 1 H; CH_2N), 7.34–7.59 (m, 10 H; H_{Ar}), 7.86 ppm (q, $J = 5.2$ Hz, 1 H; CH). ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 26.0$ (CH_3), 30.7 (d, $J_{C,P} = 21.2$ Hz; CH_2P), 69.6 (d, $J_{C,P} = 10.1$ Hz; CH_2N), 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}. $C_{20}H_{18}NO_4PW$: calcd. C 43.58, H 3.29, N 2.54; found C 43.39, H 3.33, N 2.41.

7a: yellow solid (46 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.21$ (m, 1 H; CH_2P), 2.48 (m, 1 H; CH_2P), 2.76 (m, 1 H; CH_2N), 2.89 (d, $J = 5.9$ Hz, 3 H; CH_3), 3.20 (m, 1 H; CH_2N), 7.32–7.62 ppm (m, 10 H; H_{Ar}). ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 30.0$ (d, $J_{C,P} = 21.6$ Hz; CH_2P), 48.1 (CH_3), 56.1 (d, $J_{C,P} = 10.2$ Hz; CH_2N), 128.7 (d, $J_{C,P} = 3.9$ Hz; C_{Ar}), 128.9 (d, $J_{C,P} = 3.6$ Hz; C_{Ar}), 130.3 (C_{Ar}), 131.7 (d, $J_{C,P} = 12.7$ Hz; C_{Ar}), 132.1 (d, $J_{C,P} = 12.6$ Hz; C_{Ar}), 134.8 (d, $J_{C,P} = 19.9$ Hz; C_{Ar}), 135.3 (d, $J_{C,P} = 22.9$ Hz; C_{Ar}), 202.9 (d, $J_{C,P} = 6.8$ Hz; CO), 204.0 (d, $J_{C,P} = 7.8$ Hz; CO), 210.2 (d, $J_{C,P} = 31.9$ Hz; CO), 210.8 ppm (d, $J_{C,P} = 4.1$ Hz; CO). IR (CCl_4): $\tilde{\nu} = 2012$, 1954, 1888 cm^{-1}. $C_{19}H_{18}NO_4PW$: 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. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.86$ (d, $J = 6.9$ Hz, 3 H; CH_3C), 1.91 (s, 3 H; CH_3N), 3.31 (q, $J = 6.9$ Hz, 1 H; C*H*CH_3), 3.54 (s, 3 H; CH_3O), 3.92 (d, $J = 10.6$ Hz, 2 H; AB system, CH_2), 6.95–7.59 ppm (m, 14 H; H_{Ar}). ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 14.0$ (CH_3C), 36.5 (CH_3N), 51.1 (CH_3O), 56.9 (CH), 60.7 (CH_2), 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; 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). ^{31}P NMR (internal H_3PO_4 reference): $\delta = 34.2$ ppm. IR (CCl_4): $\tilde{\nu} = 1736$, 1437, 1194, 1159, 1119 cm^{-1}. $C_{24}H_{20}NO_3P$: calcd. C 70.75, H 6.43, N 3.44; found C 70.60, H 6.61, N 3.59.

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[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].

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[9] The ^{1}H 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).

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[13] Preliminary DFT calculations carried out at the uB3LYP/6-31 g(d)&LANL2DZ + ΔZPVE level of theory are consistent with these mechanistic proposals.