

## Friedel–Crafts Acylation of Chromium-Carbene-Complex-Derived Ketenes

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Photolysis of chromium alkoxy-carbene complexes containing electron-rich aromatic systems on either the oxygen or carbon group of the carbene carbon resulted in intramolecular Friedel–Crafts acylation of the arene.

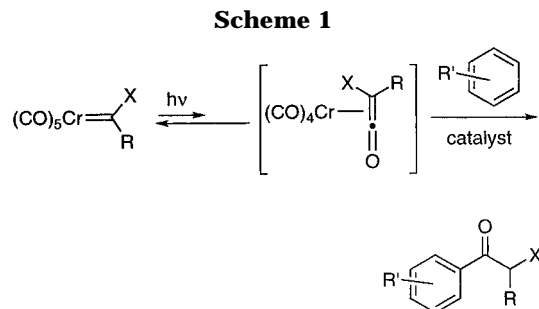
The Friedel–Crafts acylation represents one of the most common methods for the synthesis of aromatic ketones.<sup>1</sup> The reaction consists of the electrophilic substitution of an aromatic ring by an acyl or acyl equivalent group. A catalyst is usually required to generate a species which is sufficiently electrophilic to be attacked by an aromatic ring. The most common acylating reagents are acyl halides, carboxylic acids, and acid anhydrides. However, methods in which other electrophiles such as nitriles,<sup>2</sup> isocyanates,<sup>3</sup> and isothiocyanates<sup>4</sup> serve as acylating groups have been developed as well.

Studies involving ketenes have appeared only scarcely in the literature, because the yields are generally low.<sup>5</sup> In activated aromatic systems where ortho- and para-substitution could compete, mixtures of both regioisomers were observed.<sup>6</sup> Photolysis of chromium carbene complexes generates species which have ketene-like reactivity.<sup>7</sup> On the basis of the synthetic importance of the Friedel–Crafts acylation, the use of chromium-stabilized ketenes as electrophiles for the reaction with activated aromatic ring systems was examined (Scheme 1).

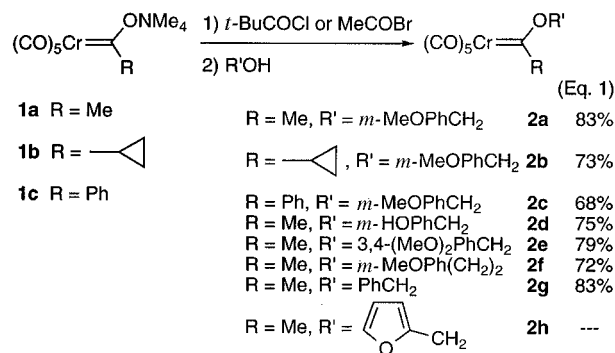
### Results and Discussion

Initial studies centered on intramolecular Friedel–Crafts acylation. The favorable entropy effects of intramolecular reactions provide the most facile reaction conditions for the exploration of scope and limitations, while obviating the need to utilize the aromatic substrate in large excess or as the solvent. Furthermore, the aromatic system could be attached to the heteroatom of the chromium carbene complex or to the R group, providing differently substituted aromatic ketones.

**a. Synthesis of the Carbene Complexes.** Carbene complexes in which the aromatic system was tethered



by the heteroatom were generated by the exchange reaction of aromatic ring-containing alcohols (commercially available or obtained by reduction of the corresponding aldehydes) with (acyloxy)carbene complexes generated in situ from tetramethylammonium ate complexes.<sup>8</sup> The results are shown in eq 1.



This method provided fair to good yields of substituted alkoxy-carbene complexes in most cases. The yield of the furan-substituted carbene **2h** could not be determined due to its instability. Once it was synthesized, it had to be directly used in the photoreaction without purification. The addition of the 3-(hydroxymethyl)indole to the (acyloxy)carbene complex led to decomposition of both reagents.

Alternatively, carbene complexes containing the aromatic ring on the alkyl portion were synthesized by alkylation of a preformed carbene<sup>9</sup> or by utilizing chromium pentacarbonyl dianion and the requisite acid

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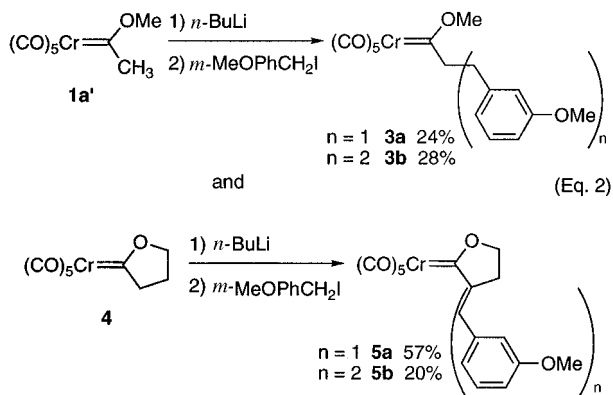
(5) (a) Hurd, C. *J. Am. Chem. Soc.* **1925**, *47*, 2777. (b) Spring, F. S.; Vickerstaff, T. *J. Chem. Soc. (London)* **1935**, 1873. (c) Williams, J. W.; Osborn, J. M. *J. Am. Chem. Soc.* **1939**, *61*, 3438.

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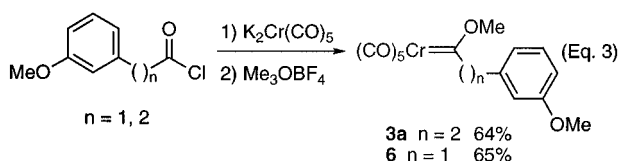
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chloride.<sup>10</sup> Alkylation of chromium carbene complexes **1a'** and **4** with 3-methoxybenzyl iodide provided carbene complexes **3a** and **5a** accompanied by the products of dialkylation **3b** and **5b** (eq 2).

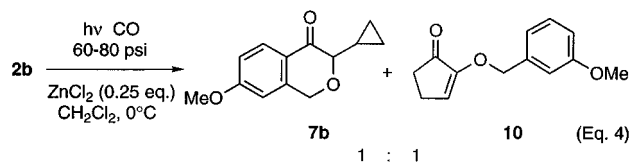


The low yield obtained in the synthesis of **3a** prompted the use of a different route, based on the reaction of an acid chloride with chromium pentacarbonyl dianion. These were also the conditions of choice for the synthesis of carbene complex **6** (eq 3).



**b. Photolytic Reactions.** Photolysis experiments were initiated by adding Lewis acid catalysts to thoroughly degassed solutions of the carbene complex **2a** in various solvents under an argon atmosphere. After being purged with carbon monoxide, the solutions were irradiated at 35 °C under 60–90 psi of carbon monoxide until no more carbene complex was observed by thin-layer chromatography. A thorough screening of reaction conditions (different solvents and catalysts) showed that most of the Lewis acids utilized ( $\text{BF}_3 \cdot \text{Et}_2\text{O}$ ,  $\text{TiCl}_4$ ,  $\text{AlCl}_3$ ,  $\text{AlEt}_2\text{Cl}$ ,  $\text{Ti}(\text{O}^i\text{-Pr})_4$ ,  $\text{LiBF}_4$ ,  $\text{MgBr}_2$ ,  $\text{LiClO}_4$ ) resulted in decomposition of the carbene complex<sup>11</sup> with only traces of the desired product of acylation regardless of solvent used (THF, ether,  $\text{CH}_2\text{Cl}_2$ ). In the absence of a Lewis acid, no acylation occurred, and slow photodecomposition of the carbene complex was observed. Photolysis of **2a** in the presence of 1 equiv of  $\text{ZnCl}_2$  in  $\text{CH}_2\text{Cl}_2$  provided the product of Friedel–Crafts acylation in only 8% yield, accompanied by the free benzyl alcohol. When the reaction was carried out at 0 °C, the formation of the alcohol was suppressed. These were the conditions of choice for the photolysis of the other carbenes. The results are collected in Table 1.

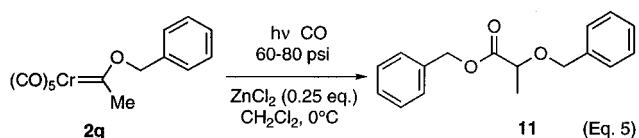
The use of 0.25 or 1 equiv of  $\text{ZnCl}_2$  did not seem to affect the yield of the acylation of **2a** although a much larger effect was observed when other carbenes were photolyzed. The photolysis of **2b** in the presence of 0.25 equiv of  $\text{ZnCl}_2$  led to a mixture of **7b** and **10** (eq 4). The formation of cyclopentenones from cyclopropylcarbene complexes had been previously observed when they were



photolyzed in the absence of the Lewis acid.<sup>12</sup> The formation of the side product was eliminated when 1 equiv of  $\text{ZnCl}_2$  was used. The low yield in the formation of **7c** was probably due to the long reaction times required for completion (7 days).

A free hydroxy group in the aromatic system (**2d**) was as activating as a methoxy group for the acylation. The presence of a second activating group in the ring (**2e**) did not increase the yield of the Friedel–Crafts reaction: carbene **2e** was unstable to the presence of  $\text{ZnCl}_2$ , and some decomposition was observed upon addition of the Lewis acid to the reaction. Decreasing the amount of  $\text{ZnCl}_2$  to 0.1 equiv increased the yield to 38%. Photolytic studies of **2f** and **6** were undertaken to determine if formation of ring sizes other than six were feasible. The reaction of **2f** took place with a yield comparable to those obtained for the synthesis of the benzopyranones, although only traces of the five-membered cycle were observed when **6** was photolyzed. No traces of the Friedel–Craft product were obtained when furan-containing carbene complex (**2h**) was photolyzed. Instead, extensive decomposition was observed. Carbenes **3a** and **3b**, with the aromatic system attached to the alkyl portion of the complex, also underwent reaction in moderate yield, but the cyclic carbene complexes **5a** and **5b** failed to produce any Friedel–Crafts products.

The acylation of a nonactivated aromatic system was briefly studied. Thus, when the known chromium carbene complex **2g** was photolyzed in the presence of the Lewis acid, ester **11** was the major product of the reaction (eq 5). This compound presumably comes from the



reaction of benzyl alcohol (product of decomposition of the carbene) with the photogenerated ketene. Similar decomposition products were obtained when the benzyl alcohol group in complex **2g** was replaced by *N*-benzyl-*N*-*m*-methoxybenzylamine.<sup>13</sup> In this case the resulting aminoketene complex was too electron rich to undergo attack by arenes.<sup>14</sup> The intermolecular version of this reaction was also attempted. Photolysis of carbene chromium complex **1a'** with a slight excess of anisol gave recovery of the starting materials after 48 h of exposure to visible light. Loss of a slight amount of carbene was observed under these conditions.

In conclusion, photochemically activated chromium carbene complexes are active electrophiles for the intramolecular Friedel–Crafts acylation in the presence of catalytic or equivalent amounts of  $\text{ZnCl}_2$  provided that at least one activating group is present in the aromatic

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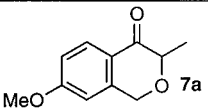
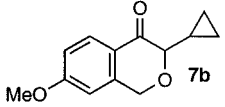
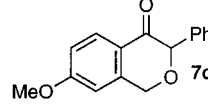
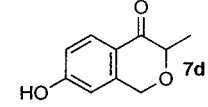
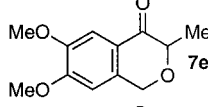
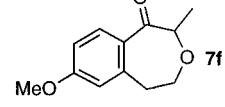
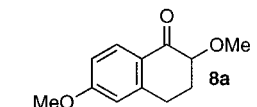
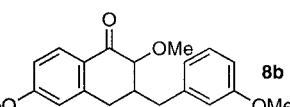
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**Table 1. Friedel–Crafts Acylation of Chromium Carbene Complexes**

Carbene Complex	Product	ZnCl <sub>2</sub> equivalents		
		0.1	0.25	1
		yield (%)		
2a		53	65	69
2b			25	43
2c			---	15
2d			59	16
2e		38	32	
2f			44	54
2g	---			
2h	---			
3a		17		60
3b				62

system. The reaction affords benzopyranones and  $\alpha$ -alkoxytetralones in moderate yields. The acylation is very regioselective, since in no case were the products of electrophilic attack at the ortho position with respect to the activating group observed.

### Experimental Section

**General Procedures.** The 300 MHz <sup>1</sup>H NMR and 75.5 MHz <sup>13</sup>C NMR spectra were obtained on a Bruker ACE-300 spectrometer. Chemical shifts are reported in ppm relative to (CH<sub>3</sub>)<sub>4</sub>Si (0 ppm, <sup>1</sup>H) or CDCl<sub>3</sub> (77.0 ppm, <sup>13</sup>C). Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ. All reactions were performed under an atmosphere of argon except as specified. The crude reaction mixtures were purified by flash column chromatography with silica gel (ICN Biomedicals Silitech 32–63  $\mu$ m).

**Materials.** The benzyl alcohols used to produce carbene complexes **2a–g** were commercially available. Carbene complexes **1a**<sup>15</sup> and **4**<sup>16</sup> were synthesized as described in the literature. Carbene complex **2g**<sup>17</sup> showed identical spectral data to that described in the literature.

**General Procedure for the Synthesis of (Benzyloxy)-carbene Complexes.** The appropriate tetramethylammonium ate complex (3.60 mmol) was taken up in freshly distilled CH<sub>2</sub>Cl<sub>2</sub> (30 mL) and cooled to –40 °C under an argon atmosphere. Pivaloyl chloride (3.60 mmol) was added via syringe, and the resultant solution was allowed to stir at –20 °C for 1 h, during which time it became deep red. A solution of the aryl alcohol (3.44 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (4 mL) was added via cannula, and the resultant solution was allowed to slowly warm to room temperature while stirring over 5 h. The solution was then sequentially washed with saturated aqueous NaHCO<sub>3</sub> (30 mL) and brine (30 mL) and dried over MgSO<sub>4</sub>. Filtration and removal of solvents under reduced pressure afforded the crude carbene complex, which was purified by flash chromatography on silica gel.

**Carbene Complex 2a.** (Methyl)tetramethylammonium ate complex (1.10 g, 3.60 mmol), pivaloyl chloride (0.45 mL, 3.60 mmol), and 3-methoxybenzyl alcohol (0.50 g) were allowed to react following the general procedure. Purification via flash chromatography (hexanes/EtOAc 10:1) gave 1.07 g (83% yield) of carbene complex **2a**: mp 65–66 °C; <sup>1</sup>H NMR  $\delta$  7.36 (t, *J* = 7.8 Hz, 1H), 7.04–6.94 (m, 3H), 5.88 (bs, 2H), 3.83 (s, 3H), 3.00 (s, 3H); <sup>13</sup>C NMR (50 °C)  $\delta$  359.0, 223.3, 216.5, 160.3, 135.6, 130.0, 120.3, 114.9, 113.8, 82.0, 55.3, 48.7; IR (neat)  $\nu$  2063, 1915 cm<sup>-1</sup>; MS 356 (M<sup>+</sup>). Anal. Calcd for C<sub>15</sub>H<sub>12</sub>CrO<sub>2</sub>: C, 50.57; H, 3.40. Found: 50.37; H, 3.67.

**Carbene Complex 2b.** (Cyclopropyl)tetramethylammonium ate complex<sup>18</sup> (0.72 g, 2.11 mmol), pivaloyl chloride (0.26 mL, 2.11 mmol), and 3-methoxybenzyl alcohol (0.25 mL, 2.01 mmol) were allowed to react following the general procedure. Purification (hexanes/EtOAc 20:1) gave 0.56 g (73% yield) of carbene **2b** as a yellow solid: mp 44–45 °C; <sup>1</sup>H NMR  $\delta$  7.34 (t, *J* = 7.6 Hz, 1H), 7.0–6.86 (m, 3H), 5.89 (s, 2H), 3.82 (s, 3H), 3.51 (m, 1H), 1.40 (m, 2H), 1.19 (m, 2H); <sup>13</sup>C NMR  $\delta$  351.8, 223.4, 216.7, 159.9, 135.7, 130.0, 120.3, 114.4, 113.7, 82.1, 55.2, 41.6, 18.1; IR (neat)  $\nu$  2055, 1941 cm<sup>-1</sup>. Anal. Calcd for C<sub>17</sub>H<sub>14</sub>CrO<sub>2</sub>: C, 53.41; H, 3.69. Found: C, 53.30; H, 3.60.

**Carbene Complex 2c.** (Phenyl)tetramethylammonium ate complex<sup>19</sup> (0.71 g, 1.90 mmol), pivaloyl chloride (0.23 mL, 1.90 mmol), and 3-methoxybenzyl alcohol (0.23 mL, 1.81 mmol) were allowed to react following the general procedure. Purification (hexanes/EtOAc 8:1) gave 0.52 g (68% yield) of carbene **2c** as a red solid: mp 42–44 °C; <sup>1</sup>H NMR  $\delta$  7.45–7.12 (m, 6H), 7.0–6.80 (m, 3H), 5.74 (s, 2H), 3.77 (s, 3H); <sup>13</sup>C NMR  $\delta$  349.6, 224.1, 216.0, 159.8, 153.1, 135.6, 130.0, 129.8, 128.0, 122.5, 120.0, 114.5, 113.3, 81.8, 55.1; IR (neat)  $\nu$  2059, 1935 cm<sup>-1</sup>; MS 418 (M<sup>+</sup>).

**Carbene Complex 2d.** (Methyl)tetramethylammonium ate complex (1.31 g, 4.23 mmol), pivaloyl chloride (0.52 mL, 4.23 mmol), and 3-hydroxybenzyl alcohol (0.30 g, 4.03 mmol) were allowed to react following the general procedure. Chromatographic column (hexanes/EtOAc 3:1) gave 0.62 g (75% yield) of carbene **2d** as a yellow oil: <sup>1</sup>H NMR  $\delta$  7.32 (t, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 7.6 Hz, 1H), 6.94 (bs, 1H), 6.88 (dd, *J* = 2.5, 8.3 Hz, 1H), 5.88 (bs, 2H), 5.18 (bs, 1H), 3.00 (s, 3H); <sup>13</sup>C NMR  $\delta$  358.6, 223.3, 216.3, 155.6, 135.8, 130.3, 120.6, 116.1, 115.0, 53.4; IR (neat)  $\nu$  3347, 2059, 1942 cm<sup>-1</sup>; MS 342 (M<sup>+</sup>).

**Carbene Complex 2e.** (Methyl)tetramethylammonium ate complex (1.12 g, 3.60 mmol), pivaloyl chloride (0.45 mL, 3.60 mmol), and 3,4-dimethoxybenzyl alcohol (0.58 g, 3.44 mmol) were allowed to react following the general procedure. Chromatographic column (hexanes/EtOAc 20:1) gave 1.10 g (79% yield) of carbene **2e** as an orange oil: <sup>1</sup>H NMR  $\delta$  6.99 (d, *J* = 8.2 Hz, 1H), 6.96 (s, 1H), 6.87 (d, *J* = 8.2 Hz, 1H), 5.79 (bs, 2H), 3.86 (s, 3H), 3.85 (s, 3H), 2.95 (s, 3H); <sup>13</sup>C NMR (50 °C)  $\delta$  357.8, 223.4, 216.5, 149.9, 149.4, 126.3, 121.6, 111.7, 111.2, 82.4, 55.9, 48.5; IR (neat)  $\nu$  2062, 1916 cm<sup>-1</sup>; MS 386 (M<sup>+</sup>).

**Carbene Complex 2f.** (Methyl)tetramethylammonium ate complex (2.26 g, 7.29 mmol), pivaloyl chloride (0.90 mL, 7.30 mmol), and 3-methoxyphenethyl alcohol (1.03 mL, 7.29 mmol) were allowed to react according to the general procedure.

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Chromatographic column (hexanes/EtOAc 19:1) afforded 1.94 g (72%) of **2f** as an orange oil:  $^1\text{H NMR}$   $\delta$  7.29 (dd,  $J = 7.5$ , 7.8 Hz, 1H), 6.91 (d,  $J = 7.5$  Hz, 1H), 6.87 (s, 1H), 6.85 (d,  $J = 7.8$  Hz, 1H), 5.13 (bs, 2H), 3.82 (s, 3H), 3.29 (t,  $J = 6.8$  Hz, 2H), 2.94 (s, 3H);  $^{13}\text{C NMR}$  (50 °C)  $\delta$  358.6, 223.3, 216.5, 160.2, 138.1, 129.8, 121.2, 114.8, 112.6, 80.7, 55.1, 48.4, 35.8; IR (neat)  $\nu$  2062, 1919  $\text{cm}^{-1}$ ; MS 370 ( $\text{M}^+$ ).

**Carbene Complex 2h.** (Methyl)tetramethylammonium ate complex (0.40 g, 1.28 mmol) was taken up in freshly distilled  $\text{CH}_2\text{Cl}_2$  (10 mL) and cooled at  $-78$  °C under argon atmosphere. Acetyl bromide (0.10 mL, 1.35 mmol) was added via syringe, and the resultant solution was allowed to stir at  $-78$  °C for 30 min, during which time it became deep brown in color. A solution of the furyl alcohol (0.132 g, 1.35 mmol) in  $\text{CH}_2\text{Cl}_2$  (2 mL) was added via cannula, and the resultant solution was allowed to warm to  $-35 \pm 5$  °C and stirred for 2 h. It was allowed to warm to rt slowly. After the addition of the alcohol (5 h) the crude reaction was filtered through a plug of silica gel under argon and the filtrate was concentrated under high vacuum and photolyzed without further purification:  $^1\text{H NMR}$  (from the crude reaction)  $\delta$  7.52 (bs, 1H), 6.62 (bs, 1H), 6.46 (bs, 1H), 5.90 (s, 2H), 2.98 (s, 3H).

**Carbene Complexes 3a and 3b.** Chromium carbene complex **1a'** (0.30 g, 1.20 mmol) was dissolved in 10 mL of freshly distilled THF and cooled at  $-78$  °C under an argon atmosphere. *n*-BuLi (1.63M in hexanes, 0.77 mL, 1.26 mmol) was added dropwise and allowed to react for 20 min. 3-Methoxybenzyl iodide (0.48 g, 1.80 mmol) dissolved in 2 mL of THF was added. The reaction was stirred at 0 °C for 5 h. Aqueous  $\text{NH}_4\text{Cl}$  was added, layers were separated, and the aqueous layer was extracted with ether (2  $\times$  20 mL). The combined organic layers were dried over  $\text{MgSO}_4$ , filtered, and concentrated. Purification (hexanes/ $\text{CH}_2\text{Cl}_2$ /ether 16:1:1) gave 0.11 g (24% yield) of carbene **3a** as an orange oil and 0.16 g (29% yield) of carbene **3b**. Spectroscopic data for **3b**:  $^1\text{H NMR}$   $\delta$  7.19 (t,  $J = 7.1$  Hz, 2H), 6.74–6.64 (m, 6H), 4.88 (s, 3H), 4.53 (quin,  $J = 7.0$  Hz, 1H), 3.76 (s, 6H), 2.89 (dd,  $J = 6.7$ , 13.5 Hz, 2H), 2.38 (dd,  $J = 7.0$ , 13.1 Hz, 2H);  $^{13}\text{C NMR}$   $\delta$  368.4, 222.9, 215.7, 159.7, 140.3, 129.3, 121.5, 115.0, 111.6, 74.2, 67.5, 55.0, 37.8; IR (neat)  $\nu$  2057, 1941  $\text{cm}^{-1}$ ; MS 490 ( $\text{M}^+$ ). Carbene complex **3a** was more efficiently prepared by the following route. An airless flask containing  $\text{K}_2\text{Cr}(\text{CO})_5$  (1.33 mmol) in THF (15 mL) was cooled to  $-78$  °C. A solution of acid chloride (eq 3,  $n = 2$ ) (265 mg, 1.33 mmol) in THF (5 mL) was added via syringe under an argon atmosphere, and the resultant solution was allowed to stir at  $-78$  °C for 20 min, at 0 °C for 1 h, and at rt for 1 h. The solvent was removed under reduced pressure, and the residue was taken up in chilled, degassed  $\text{H}_2\text{O}$  (20 mL). Trimethyloxonium tetrafluoroborate (197 mg, 1.33 mmol) was added directly. The solution was then filtered through Celite and extracted with hexanes (3  $\times$  10 mL). The combined organic layers were dried over  $\text{MgSO}_4$ , filtered, and concentrated to an orange oil. Purification via flash chromatography (hexanes) afforded 302 mg (64%) of **3a** as an orange oil:  $^1\text{H NMR}$   $\delta$  7.21 (dd,  $J = 7.9$  Hz, 1H), 6.77–6.72 (m, 3H), 4.80 (s, 3H), 3.79 (s, 3H), 3.61 (t,  $J = 8.0$  Hz, 2H), 2.75 (t,  $J = 8.0$  Hz, 2H);  $^{13}\text{C NMR}$   $\delta$  361.6, 223.0, 216.2, 159.8, 141.7, 129.6, 120.6, 114.1, 111.6, 67.7, 64.3, 55.1, 32.3; IR (neat)  $\nu$  2063, 1916  $\text{cm}^{-1}$ ; MS 370 ( $\text{M}^+$ ).

**Carbene Complexes 5a and 5b.** Chromium carbene complex **4** (0.23 g, 0.86 mmol) was dissolved in 7 mL of freshly distilled THF and cooled at  $-78$  °C under an argon atmosphere. *n*-BuLi (1.63M in hexanes, 0.56 mL, 0.91 mmol) was added dropwise, and it was allowed to react for 20 min. 3-Methoxybenzyl iodide (0.23 g, 0.91 mmol) was added dissolved in 2 mL of THF. The reaction was stirred at 0 °C for 2 h and at rt for 2 h. Aqueous  $\text{NH}_4\text{Cl}$  was added, layers were separated, and the aqueous layer was extracted with ether (2  $\times$  20 mL). Combined organic layers were dried over  $\text{MgSO}_4$ , filtered, and concentrated. Purification (hexanes/ $\text{CH}_2\text{Cl}_2$ /ether 30:1:1) gave 23 mg of recovered **4**, 0.18 g (55% yield, 63% yield based on 87% conversion) of carbene **5a** as an orange oil, and 0.09 g (20% yield) of carbene **5b**. Spectroscopic data for **5a**:  $^1\text{H NMR}$   $\delta$  7.25 (dt,  $J = 1.2$ , 7.6 Hz, 1H), 6.83–6.80 (m, 3H), 4.91–4.73 (m, 2H), 3.92 (m, 1H), 3.81 (s, 3H), 3.72 (dd,  $J =$

3.7, 13.7 Hz, 1H), 2.34 (dd,  $J = 11.6$ , 13.7 Hz, 1H), 1.94–1.65 (m, 2H);  $^{13}\text{C NMR}$   $\delta$  346.0, 223.0, 216.4, 159.9, 139.9, 129.8, 121.0, 114.5, 112.0, 84.0, 72.2, 55.1, 36.9, 25.6; IR (neat)  $\nu$  2063, 1947  $\text{cm}^{-1}$ ; MS 382 ( $\text{M}^+ + 1$ ). Spectroscopic data for **5b**:  $^1\text{H NMR}$   $\delta$  7.20 (t,  $J = 8.0$  Hz, 2H), 6.80 (dd,  $J = 2.1$ , 7.9 Hz, 2H), 6.70 (d,  $J = 7.7$  Hz, 2H), 6.64 (s, 2H), 4.08 (t,  $J = 7.7$  Hz, 2H), 3.77 (s, 6H), 3.36 and 3.16 (AB system,  $J = 13.7$  Hz, 4H), 1.86 (t,  $J = 7.6$  Hz, 2H);  $^{13}\text{C NMR}$   $\delta$  352.7, 222.4, 216.9, 159.6, 137.9, 129.4, 122.7, 116.2, 112.2, 86.4, 76.2, 55.2, 43.8, 30.3; IR (neat) 2060, 1945  $\text{cm}^{-1}$ ; MS 502 ( $\text{M}^+$ ).

**Carbene Complex 6.** An airless flask containing  $\text{K}_2\text{Cr}(\text{CO})_5$  (2.71 mmol) in THF (20 mL) was cooled to  $-78$  °C. A solution of 3-methoxyphenylacetyl chloride (0.42 mL, 2.70 mmol) in THF (5 mL) was added via syringe under an argon atmosphere, and the resultant solution was allowed to stir at  $-78$  °C for 15 min, at 0 °C for 1 h, and at rt for 20 min. The solvent was removed under reduced pressure, and the residue was taken up in chilled  $\text{H}_2\text{O}$  (20 mL). Trimethyloxonium tetrafluoroborate (401 mg, 2.71 mmol) was added directly. The solution was then filtered through Celite and extracted with hexanes (2  $\times$  10 mL). The combined organic layers were adsorbed onto silica gel, dry loaded onto a flash column, and eluted with 95/5 hexanes/EtOAc to afford 0.62 g (65%) of **6** as an orange solid which was recrystallized from hexanes:  $^1\text{H NMR}$   $\delta$  7.22 (dd,  $J = 7.5$ , 8.1 Hz, 1H), 6.80 (dd,  $J = 2.7$ , 8.4 Hz, 1H), 6.72 (d,  $J = 7.5$  Hz, 1H), 6.68 (d,  $J = 2.1$  Hz, 1H), 4.76 (s, 3H), 4.56 (s, 2H), 3.79 (s, 3H);  $^{13}\text{C NMR}$  (50 °C)  $\delta$  359.0, 223.0, 216.3, 160.0, 136.4, 129.5, 121.9, 115.5, 112.5, 68.0, 67.8, 55.2; IR (neat)  $\nu$  2062, 1922  $\text{cm}^{-1}$ ; MS 356 ( $\text{M}^+$ ).

**General Procedure for the Photolysis of Carbene Complexes.** The carbene complex was taken up in freshly distilled  $\text{CH}_2\text{Cl}_2$  (solution 0.1 M) in an Airless Ace tube, provided with a septum.  $\text{ZnCl}_2$  (1.0 M solution in ether) was added via syringe. The septum was substituted by a pressure head, and the solution was freeze–pump–thaw degassed (liquid  $\text{N}_2$ ) for several cycles. The reaction mixture was purged with CO several times and then irradiated under 60–80 psi CO until consumption of the carbene was complete by TLC. The solution was then filtered through a plug of Florisil eluting with hexanes/EtOAc 2:1. Removal of the solvent under reduced pressure afforded the product, which was purified via flash chromatography.

**Compound 7a.** Carbene complex **2a** (0.19 g, 0.52 mmol) and  $\text{ZnCl}_2$  (0.66 mL, 0.52 mmol) were photolyzed according to the general procedure (40 h). Purification via flash chromatography (hexanes/EtOAc 4:1) afforded 69 mg (69%) of **7a** as a white sticky solid:  $^1\text{H NMR}$   $\delta$  7.98 (d,  $J = 8.7$  Hz, 1H), 6.87 (dd,  $J_1 = 8.7$  Hz,  $J_2 = 2.4$  Hz, 1H), 6.61 (s, 1H), 4.86 (s, 2H), 4.21 (q,  $J = 6.7$  Hz, 1H), 3.84 (s, 3H), 1.49 (d,  $J = 6.7$  Hz, 3H);  $^{13}\text{C NMR}$   $\delta$  194.8, 163.9, 144.4, 129.3, 122.8, 114.1, 108.4, 78.3, 67.0, 55.5, 15.8; IR (neat)  $\nu$  1684, 1601  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{11}\text{H}_{12}\text{O}_3$ : C, 68.74; H, 6.29. Found: C, 68.59; H, 6.19.

**Compound 7b.** Carbene complex **2b** (0.19 g, 0.50 mmol) and  $\text{ZnCl}_2$  (0.62 mL, 0.50 mmol) were photolyzed according to the general procedure (36 h). Purification via flash chromatography (hexanes/ $\text{CH}_2\text{Cl}_2$ /ether 10:1:1) afforded 47 mg (43%) of **7b** as a white solid: mp 89–91 °C;  $^1\text{H NMR}$   $\delta$  8.01 (d,  $J = 8.8$  Hz, 1H), 6.89 (dd,  $J = 2.4$ , 8.8 Hz, 1H), 6.62 (d,  $J = 2.4$  Hz, 1H), 4.98 and 4.80 (AB system,  $J = 15.3$  Hz, 2H), 3.86 (s, 3H), 3.61 (d,  $J = 7.7$  Hz, 1H), 1.40–1.25 (m, 1H), 0.80–0.45 (m, 4H);  $^{13}\text{C NMR}$   $\delta$  193.8, 163.9, 144.2, 129.3, 123.1, 114.1, 108.2, 84.4, 66.2, 55.5, 11.1, 3.0, 1.4; IR ( $\text{CHCl}_3$ )  $\nu$  1681, 1595  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{13}\text{H}_{14}\text{O}_3$ : C, 71.54; H, 6.47. Found: 71.70; H, 6.62. When carbene complex **2b** (0.15 g, 0.39 mmol) and  $\text{ZnCl}_2$  (0.10 mL, 0.1 mmol) were photolyzed according to the general procedure, purification via flash chromatography (hexanes/EtOAc 4:1) afforded 23 mg (27% yield) of **7b** and 30 mg (35% yield) of **10** as a colorless oil. Spectroscopic data for **10**:  $^1\text{H NMR}$   $\delta$  7.26 (t,  $J = 7.7$  Hz, 1H), 6.95–6.88 (m, 2H), 6.85 (dd,  $J = 2.7$ , 8.2 Hz, 1H), 6.39 (t,  $J = 3.1$  Hz, 1H), 4.95 (s, 2H), 3.80 (s, 3H), 2.48–2.41 (m, 4H);  $^{13}\text{C NMR}$   $\delta$  202.4, 159.7, 156.1, 137.3, 129.5, 128.7, 119.5, 113.7, 112.6, 71.5, 55.1, 32.9, 21.8; IR ( $\text{CHCl}_3$ ) 1709, 1633  $\text{cm}^{-1}$ .

**Compound 7c.** Carbene complex **2c** (0.13 g, 0.32 mmol) and  $\text{ZnCl}_2$  (0.40 mL, 0.32 mmol) were photolyzed according to

the general procedure (168 h). Purification via flash chromatography (hexanes/CH<sub>2</sub>Cl<sub>2</sub>/ether 10:1:1) afforded 12 mg (15%) of **7c** as an unstable white solid: <sup>1</sup>H NMR δ 8.06 (d, *J* = 8.5 Hz, 1H), 7.40–7.28 (m, 5H), 6.92 (dd, *J* = 2.4, 8.5 Hz, 1H), 6.65 (d, *J* = 2.5 Hz, 1H), 5.22 (s, 1H), 4.91 (s, 1H), 3.88 (s, 1H); <sup>13</sup>C NMR δ 192.6, 164.2, 144.3, 135.5, 133.1, 129.6, 128.4, 127.9, 123.4, 114.2, 108.4, 83.3, 65.8, 55.6.

**Compound 7d.** Carbene complex **2d** (0.12 g, 0.35 mmol) and ZnCl<sub>2</sub> (0.09 mL, 0.09 mmol) were photolyzed according to the general procedure (36 h). Purification via flash chromatography (hexanes/EtOAc 2:1) afforded 33 mg (59%) of **7d** as a white solid: mp 141–144 °C; <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>) δ 7.85 (d, *J* = 8.4 Hz, 1H), 6.88 (dd, *J* = 2.2, 8.4 Hz, 1H), 6.72 (d, *J* = 2.6 Hz, 1H), 4.22 (q, *J* = 6.6 Hz, 1H), 3.00 (bs, 1H), 1.38 (d, *J* = 6.7 Hz, 3H); <sup>13</sup>C NMR (acetone-*d*<sub>6</sub>) δ 194.8, 163.2, 146.2, 129.7, 122.9, 116.0, 111.0, 78.7, 67.4, 16.1; IR (KBr) ν 3170, 1658, 1586 cm<sup>-1</sup>. Anal. Calcd for C<sub>10</sub>H<sub>10</sub>O<sub>3</sub>: C, 67.41; H, 5.66. Found: C, 67.48; H, 5.47.

**Compound 7e.** Carbene complex **2e** (0.14 g, 0.35 mmol) and ZnCl<sub>2</sub> (0.04 mL, 0.04 mmol) were photolyzed according to the general procedure (36 h). Purification via flash chromatography (hexanes/EtOAc 2:1) afforded 30 mg (38%) of **7e** as a white solid: mp 116–119 °C; <sup>1</sup>H NMR δ 7.42 (s, 1H), 6.55 (s, 1H), 4.83 and 4.77 (AB system, *J* = 15.0 Hz, 2H), 4.16 (q, *J* = 6.6 Hz, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 1.45 (d, *J* = 6.6 Hz, 3H); <sup>13</sup>C NMR δ 195.0, 154.2, 148.9, 137.1, 122.6, 108.1, 106.1, 78.1, 66.7, 56.4, 56.3, 16.0; IR (neat) ν 1671, 1602 cm<sup>-1</sup>. Anal. Calcd for C<sub>12</sub>H<sub>14</sub>O<sub>4</sub>: C, 64.85; H, 6.35. Found: C, 64.61; H, 6.29.

**Compound 7f.** Carbene complex **2f** (0.19 g, 0.52 mmol) and ZnCl<sub>2</sub> (0.64 mL, 0.52 mmol) were photolyzed according to the general procedure (60 h). Purification via flash chromatography (hexanes/EtOAc 3:1) afforded 58 mg (54%) of **7f** as a white solid: mp 85–87 °C; <sup>1</sup>H NMR δ 7.72 (d, *J* = 8.7 Hz, 1H), 6.84 (dd, *J* = 2.4, 8.7 Hz, 1H), 6.69 (d, *J* = 2.4 Hz, 1H), 4.21 (q, *J* = 6.6 Hz, 1H), 4.04 (ddd, *J* = 1.8, 7.5, 10.8 Hz, 1H), 3.91 (dt, *J* = 5.1, 10.8 Hz, 1H), 3.84 (s, 3H), 3.27 (ddd, *J* = 7.5, 10.8, 14.7 Hz, 1H), 2.80 (ddd, *J* = 1.8, 5.1, 14.7 Hz, 1H), 1.44 (d, *J* = 6.6 Hz, 3H); <sup>13</sup>C NMR δ 207.0, 163.1, 140.0, 131.2, 131.0, 114.5, 112.2, 78.3, 66.4, 55.4, 34.7, 17.7; IR (neat) ν 1668, 1597 cm<sup>-1</sup>. Anal. Calcd for C<sub>12</sub>H<sub>14</sub>O<sub>3</sub>: C, 69.89; H, 6.84. Found: C, 69.42; H, 6.62.

**Compound 8a.** Carbene **3a** (0.11 g, 0.28 mmol) and ZnCl<sub>2</sub> (0.35 mL, 0.28 mmol) were photolyzed according to the general procedure (36 h). Purification via flash chromatography (hexanes/EtOAc 3:1) afforded 32 mg (60%) of **8a** as a colorless

oil: <sup>1</sup>H NMR δ 7.97 (d, *J* = 8.7 Hz, 1H), 6.80 (dd, *J* = 2.4, 8.7 Hz, 1H), 6.65 (d, *J* = 2.4 Hz, 1H), 3.86 (dd, *J* = 4.2, 10.5 Hz, 1H), 3.81 (s, 3H), 3.53 (s, 3H), 3.07 (dt, *J* = 5.1, 17.1 Hz, 1H), 2.93 (ddd, *J* = 4.8, 9.6, 16.5 Hz, 1H), 2.37–2.27 (m, 1H), 2.21–2.08 (m, 1H); <sup>13</sup>C NMR δ 195.1, 163.7, 145.9, 130.1, 125.3, 113.4, 112.3, 81.3, 58.1, 55.4, 29.4, 27.4; IR (neat) ν 1685, 1600 cm<sup>-1</sup>. Anal. Calcd for C<sub>12</sub>H<sub>14</sub>O<sub>3</sub>: C, 68.89; H, 6.84. Found: C, 68.89; H, 6.67.

**Compound 8b.** Carbene **3b** (0.09 g, 0.19 mmol) and ZnCl<sub>2</sub> (0.19 mL, 0.19 mmol) were photolyzed according to the general procedure (24 h). Purification via flash chromatography (hexanes/EtOAc 4:1) afforded 39 mg (62%) of **8b** as a colorless oil formed by a 10:1 mixture of diastereoisomers: <sup>1</sup>H NMR (for the major diastereoisomer) δ 7.99 (d, *J* = 8.5 Hz, 1H), 7.21 (t, *J* = 7.9 Hz, 1H), 6.84–6.63 (m, 5H), 3.83 (s, 3H), 3.78 (s, 3H), 3.68 (d, *J* = 2.8 Hz, 1H), 3.47 (s, 3H), 3.06–2.40 (m, 5H); <sup>13</sup>C NMR δ 194.2, 163.7, 159.7, 145.3, 141.2, 130.0, 129.4, 124.7, 121.5, 114.9, 113.4, 112.6, 111.4, 82.4, 57.9, 55.4, 55.1, 41.6, 36.0, 31.3; IR (neat) ν 1679, 1603 cm<sup>-1</sup>.

**Compound 11.** Carbene complex **2g** (0.1 g, 0.30 mmol) and ZnCl<sub>2</sub> (0.08 mL, 0.08 mmol) were photolyzed according to the general procedure (12 h). Purification via flash chromatography (hexanes/EtOAc 12:1) gave 9 mg (22% yield) of **11** as a colorless oil: <sup>1</sup>H NMR δ 7.38–7.26 (m, 10H), 5.22 and 5.17 (AB system, *J* = 12.2 Hz, 2H), 4.69 and 4.44 (AB system, *J* = 11.5 Hz, 2H), 4.10 (q, *J* = 6.8 Hz, 1H), 1.45 (d, *J* = 6.8 Hz, 3H); <sup>13</sup>C NMR δ 173.1, 137.4–127.8 (12C), 74.0, 72.0, 66.5, 18.7; IR (CHCl<sub>3</sub>) ν 1741 cm<sup>-1</sup>.

**Supporting Information Available:** <sup>1</sup>H NMR spectra for compounds **2c**, **2d**, **2e**, **2f**, **2h**, **3a**, **3b**, **5a**, **5b**, **6**, **7c**, **8b**, **10**, and **11** and <sup>13</sup>C NMR spectra for compounds **2c**, **2d**, **2e**, **2f**, **3a**, **3b**, **5a**, **5b**, **6**, **7c**, **8b**, **10**, and **11** (27 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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