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Synthesis of β-keto Fischer carbene complexes

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Abstract

The synthesis of β-keto Fischer carbene complexes is reported. Deprotonation of alkyl Fischer carbene complexes followed by acylation of the resulting metal enolates with acid chlorides yielded β-keto carbene complexes in yields up to 50%. The complexes were relatively stable and could be characterized spectroscopically. Upon treatment with bases such as pyridine, these complexes produced β-methoxy unsaturated ketones. © 1998 Elsevier Science S.A.

Keywords: Carbene; Chromium; Carbonyl; Acylation

1. Introduction

Since the first synthesis of a stable transition metal carbene complex by Fischer and Massböl [1], Fischer carbene complexes have generated much interest among chemists and have found increasing applications in organic synthesis due to their rich chemistry [2–8]. Being heteroatom-stabilized metal carbene species, they undergo several unique organometallic reactions such as cyclopropanation reactions with electrophilic olefins [9,10], metathesis reactions with electron rich olefins [11,12], addition reactions with isonitriles generating ketenimines [13] and photochemically induced carbon monoxide insertion forming ketenes [14,15]. Unsaturated alkoxycarbene complexes undergo the well known Dötz reaction with alkynes to produce *p*-hydroquinone derivatives [2–8,16–21]. The metal–carbon bond of group six Fischer carbene complexes is highly polarized due to the strongly electron withdrawing $M(CO)_5$ moiety such that the carbene carbon is quite electrophilic. Thus, Fischer carbene complexes resemble the corresponding esters, but are much more activated toward reaction with nucleophiles. Much of their chemistry can be interpreted by this resemblance, in contrast with the unique organometallic transformations just presented. For example, Fischer carbene complexes are subject to nucleophilic attack by a wide range of nucleophiles such as amines [22–28] and alkoxides [29–31], much like the corresponding transesterification and aminolysis reactions of organic esters. Protons alpha to the carbene carbon are also very acidic due to the strongly electron withdrawing metal moiety [32,33]. Deprotonation is easily effected and the resulting metal enolate can react with different electrophiles such as aldehydes in formal aldol reactions [34] and α, β-unsaturated carbonyl compounds in formal Michael addition reactions [35–37]. α-Alkylation can be accomplished, but it is often difficult due to the intrinsic lack of reactivity of the metal enolate (pK_a of the α-proton is in the range of 8 to 12 [32,33]) and the steric hindrance from the metal pentacarbonyl moiety [38].

β-Keto esters form an important class of compounds in organic chemistry and are widely used in reactions such as the classical acetoacetic ester synthesis [39,40] and Knoevenagel reactions [41]. β-Hydroxy esters obtained from stereoselective reduction of β-keto esters are important intermediates in many natural product syntheses [42–48]. Surprisingly, there are few reports of the analogous β-keto carbene complexes in the literature. Casey reported the reaction of several carbene enolates with acetyl chloride in attempts to form β-keto carbene complexes and obtained mixed results [49–51]. When the expected carbene product contained an enolizable proton, an enol ester was isolated

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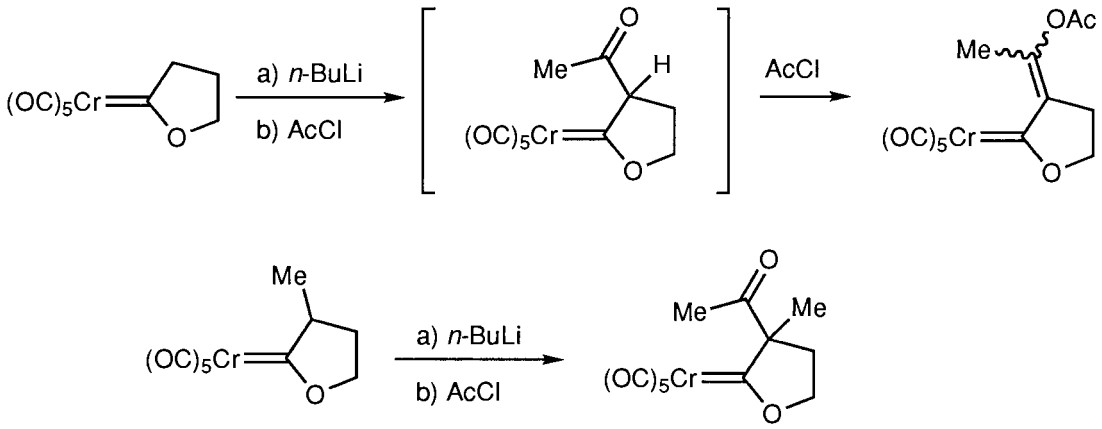
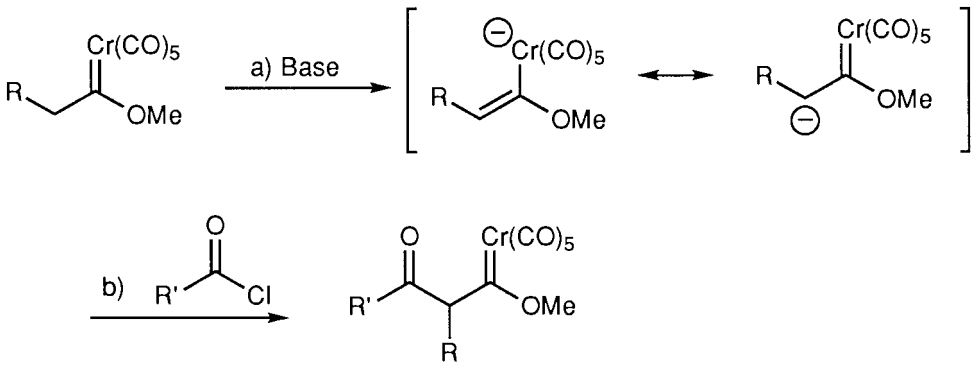


Scheme 1.

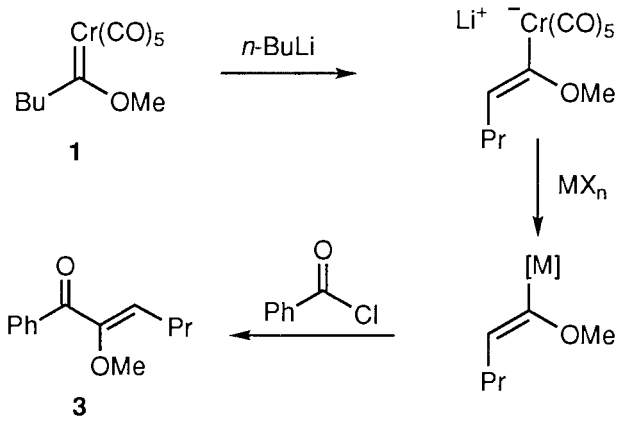
instead of a β-keto carbene complex (Scheme 1). Without the enolizable proton, a β-keto carbene complex was formed in 65% yield. Given the paucity of chemistry reported on β-keto carbene complexes and the importance and versatility of the analogous β-keto esters in synthesis, we embarked on a study to examine this chemistry further. Herein, we report our results on the synthesis and reactivity of β-keto carbene complexes which provides contrasts with the results reported by Casey.

2. Synthesis of a benzoyl carbene complex

Our synthetic plan (Scheme 2) was analogous to Casey's treatment of an alkyl carbene complex with a base to deprotonate at the α-position and then reaction of the resulting metal enolate anion with an acid chloride to form a β-keto carbene complex. In the event, butyl chromium carbene **1** reacted with *n*-butyllithium at −78°C to produce a yellow solution of the anion which was then cannulated into a solution of excess benzoyl chloride in THF at 0°C. After stirring at 0°C for 30 min, the solution was filtered through a pad of silica gel, concentrated and the crude product was purified by column chromatography to provide benzoyl carbene complex **2** in yields ranging from 31 to 39%. The product was identified by its ^{1}H NMR spectrum; in particular, the methine proton signal as a triplet at 6.04 ppm. In contrast with expectations from Casey's work, no enol ester was detected. Significant quantities (about 10–30%) of starting butyl carbene complex were also recovered. When the reaction temperature was lowered to −20°C, a yield of 50% could be achieved. It should be noted that since the product has a very acidic proton, once formed, it could react with the starting carbene enolate anion, thus consuming the metal enolate that would have reacted with benzoyl chloride. Therefore, the maximum theoretical yield may only be 50% when one equivalent of *n*-butyllithium is used. By analogy, the Claisen condensation of esters generally requires excess base since the β-keto ester products are more acidic than the initial esters. When a second equivalent of base such as potassium *t*-butoxide was added to deprotonate the product, thus preventing it from reacting with the starting metal enolate, the yield was slightly improved vs. that when only one equivalent of *n*-butyllithium was used at 0°C. However, it was still lower

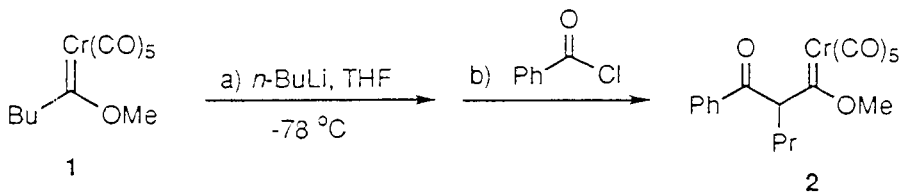


Scheme 2. Synthetic plan for β-keto carbene complexes



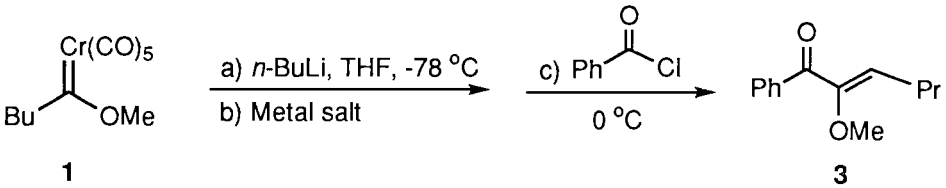
Scheme 3. Mechanism for the formation of compound **3**.

than 50%. Various other conditions were tested in attempts to improve the yield of the product, but none yielded a satisfactory improvement.



(1)

Coutrot and Savignac reported that for the reaction of phosphonate enolates with acid halides, addition of copper (I) iodide minimizes reaction of the resulting β-keto phosphonate with the starting enolate, thus significantly improving reaction yields [52]. However, when CuI or several other metal salts were used in the corresponding chromium carbene reactions, the α-methoxy-α,β-unsaturated ketone **3** was unexpectedly formed in low yields instead of the anticipated β-keto carbene complex **2** (Table 1). Ketone **3** was readily identified by its ^{1}H NMR spectrum with signals at 5.82 and 2.30 ppm corresponding to the vinyl and allylic protons, respectively. Only a single isomer was obtained and the stereochemistry was assumed to be *Z* based on mechanistic considerations as shown in Scheme 3. The initially formed lithium chromium enolate is expected to adopt *Z*-configuration, thus positioning the bulky chromium pentacarbonyl moiety next to the small hydrogen atom minimizing steric interactions. The enolate then undergoes transmetallation (lithium to copper or even chromium to copper) with the metal salt forming a new vinyl metal species which reacts with benzoyl chloride. Acylation at carbon, or acylation at the metal followed by reductive elimination, yields compound **3** with a *Z* double bond. Similar proposals have been advanced for related carbene elimination reactions [53,54]. Interestingly, analogous compounds were prepared from chromium Fischer carbene complexes by Hegedus via an entirely different route employing oxidative coupling of an anionic acyl vinyl complex [55].



(2)

Table 1
Formation of compound **3**

Entry	Metal salt	Temperature (°C)	Yield (%)
1	CuI	−78 to −30	12
2	CuI	−78 to 0	15
3	CuCN	−78 to −30	13
4	$MgBr_2 \cdot Et_2O$	−78 to −30	13

3. Synthesis of other β-keto carbene complexes

β-Keto carbene complexes other than compound **2** were also synthesized in a similar manner and the results are summarized in Table 2. When acetyl chloride was used with the butyl carbene, acetyl chromium carbene complex **4** was isolated in up to 37% yield (entry 2). Acetyl bromide, as a more reactive acylating reagent, on the other hand, only reacted with the THF solvent under the reaction conditions to form **4**-bromobutyl acetate. Amino carbene complex **6** was obtained in a comparable yield starting from the dimethylamino chromium carbene complex **5** (entry 3). The tungsten analogue **7** also provided similar results (entry 4).

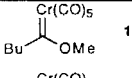
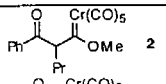
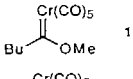
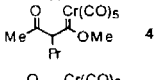
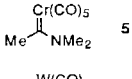
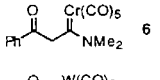
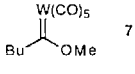
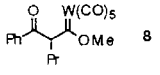
Again, it is of interest to note contrasts with the results expected from Casey's study. The acylated compounds **4**, **6** and **8** were obtained in modest yields while enol ester compounds, which would result from further reaction with the acid chlorides, were not observed, even though more acid chloride was used in our study (5 equivalents vs. less than 2 equivalents) [49–51]. Different experimental conditions may account for the difference, such as the lower temperature employed in our study (-20°C and 0°C) and the order of addition which may prevent further reaction of the product with starting anion and more acid chloride.

The β-keto carbene complexes **2**, **4**, **6** and **8** are relatively stable. Once purified, they can be stored in the refrigerator for several days without apparent decomposition. Initial purification by column chromatography, however, was often accompanied by extensive gas evolution, presumably due to decomposition of one or more unstable by-products from the reaction.

4. Elimination reactions of β-keto carbene complexes

Alkyl carbene complexes bearing acidic α-protons are known to undergo elimination reactions yielding vinyl ethers upon thermal treatment with bases such as pyridine [53,54,56–59]. β-Keto carbene complexes have a doubly activated proton at the α position and should thus undergo such reaction more readily. Indeed, when treated with pyridine at room temperature, compound **2** yielded the elimination product **9** in 59% yield (Eq. (3)). The reaction is accelerated significantly when conducted in refluxing hexane and the yield improved to 74% (1 h). Ketone **9**, like ketone **3**, was identified by the vinyl and allylic proton signals at 6.86 and 2.41 ppm in the ^{1}H NMR spectrum. The stereochemistry is assumed to be *E* based on both mechanistic and thermodynamic considerations. Mechanistically, the elimination process most likely involves a six-membered transition state in which the proton is positioned between the chromium atom and the carbonyl oxygen by intramolecular hydrogen bonding (Fig. 1). The hydrogen bonding is thus similar to that in β-dicarbonyl compounds. Reductive elimination then yields the *E*-alkene. Thermodynamically, β-alkoxy enones with an *E* double bond are more stable than those with a *Z* double bond. Both Fedor and Castells observed the isomerization of *Z*-β-alkoxy enones to *E*-enones [60,61]. The corresponding tungsten carbene complex **8** gave similar results (69% yield, Table 3). Other bases such as triethylamine and DABCO also induced elimination but gave lower yields of product (41% and 53%, respectively) than pyridine. Surprisingly, carbene complexes **4** and **6** did not yield detectable amounts of elimination products. There are a variety of other methods to prepare β-alkoxy enones and, interestingly, Hudlicky synthesized trans-β-methoxy enones in excellent yields via rhodium carbene intermedi-

Table 2

Entry	Starting Material		Product		Yield (%)
1		1		2	50
2		1		4	37
3		5		6	41
4		7		8	28

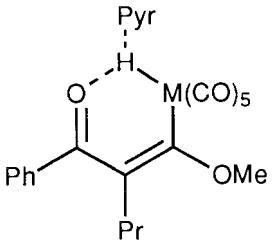
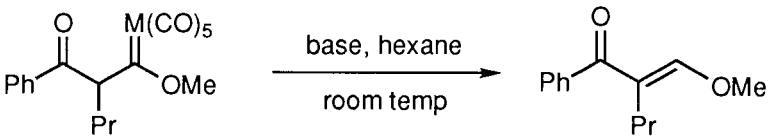


Fig. 1.

ates [62]. β-Alkoxy enones as a class of compounds are of synthetic interests as protected aldehydes [63,64], and as substrates for hetero-Diels–Alder reactions [65–68].



2 M = Cr
8 M = W

9

(3)

In summary, we have accomplished the first syntheses of β-keto Fischer carbene complexes which bear acidic α-protons. These species are stable and can be isolated and fully characterized. Upon reaction with bases, these compounds gave elimination products as expected of alkyl carbene complexes, but under much milder conditions.

5. Experimental

5.1. General

All reactions were performed in flame-dried glassware under a positive pressure of argon or nitrogen. Air- and moisture-sensitive liquids and solutions were transferred via a syringe or cannula into the reaction vessel through rubber septa. Diethyl ether and tetrahydrofuran were distilled from sodium benzophenone ketyl under nitrogen. Hexane was distilled from calcium hydride. Acetyl chloride was refluxed with PCl_5 then distilled at 51–54°C. Benzoyl chloride was dried over $CaCl_2$ and distilled (49.5–50°C, 3–4 mm Hg). Pyridine was refluxed with potassium hydroxide and fractionally distilled at 115–118°C. Triethyl amine was dried over $CaSO_4$ and distilled at 88–91°C. All other reagents were used as received. Flash chromatography was performed on Merck silica gel 60 (230–260 mesh). Thin layer chromatography was performed on Polygram SIL G/UV254 TLC plates. Infrared spectra were recorded on a Nicolet 510P FT-IR spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker ARX 400 spectrometer. Chemical shifts are reported in ppm with Me_4Si or $CDCl_3$ as internal standards. High resolution mass spectra were recorded at 70 eV on an AEI MS902 instrument.

5.2. ((1-Benzoylbutyl)methoxymethylene)pentacarbonylchromium (2)

n-Butyllithium in hexane (2.5 M, 0.8 ml, 2 mmol) was slowly injected in a solution of (butylmethoxymethylene)pentacarbonylchromium (584 mg, 2 mmol) in THF (10 ml) at −78°C under argon. The light orange solution turned darker. The solution was stirred at −78°C for 30 min and then was slowly cannulated into a

Table 3
Elimination reactions of β-keto carbene complexes

Entry	Carbene complex	Base	Conditions	Yield of elimination product (%)
1	**2**	pyridine	room temp. overnight	59
2	**2**	pyridine	refluxing hexane, 1–5 h	43–74
3	**2**	TEA	refluxing hexane, 2 h	41
4	**2**	DABCO	refluxing hexane, 3–5 h	47–53
5	**8**	pyridine	room temp. overnight	69
6	**4**	pyridine	refluxing hexane, 5 h	0
7	**6**	pyridine	refluxing hexane, 2.5 h	0

stirred solution of benzoyl chloride (1.18 ml 10 mmol) in THF (5 ml) at −20°C (40:60 isopropanol: water–dry ice). The solution turned dark orange and was stirred at −20°C for 30 min and then warmed to room temperature and filtered through a pad of silica gel and concentrated. The crude product was purified by column chromatography with 100% petroleum ether followed by 20:1 petroleum ether: ether. The product (**2**, 401 mg, 50%) was obtained as an orange solid.

IR ($CDCl_3$ solution, thin film on salt plate): 2961, 2934, 2064, 1977, 1931 (strong), 1686, 1450, 1260, 667, 650 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): 0.93 (3H, t, $J = 7.3$ Hz, Me), 1.37 (2H, m, CH_2), 1.87 (2H, m, CH_2), 4.84 (3H, s, MeO), 6.04 (1H, t, $J = 6.6$ Hz, CH), 7.49 (2H, t, $J = 7.6$ Hz), 7.59 (1H, t, $J = 7.3$ Hz), 7.95 (2H, d, $J = 7.4$ Hz).

^{13}C NMR (100 MHz, $CDCl_3$): 355.72, 222.40, 215.88, 194.57, 136.76, 133.45, 128.86, 128.40, 78.74, 68.48, 33.59, 21.91, 14.22.

MS m/z: 368.0 ($[M–CO]^+$, 41), 340.0 ($[M–2CO]^+$, 51), 312.0 (14), 284.0 (33), 256.0 (34), 213.0 (56), 185.0 (44), 105.0 (100).

HRMS: calculated for $C_{17}H_{16}CrO_6$ [M–CO] 368.0352, found 368.0350; calculated for $C_{16}H_{16}CrO_5$ [M–2(CO)] 340.0403, found 340.0430.

*5.3. 2-Methoxy-1-phenyl-2-hexen-1-one (**3**)*

n-Butyllithium in hexane (2.5 M, 0.40 ml, 1.0 mmol) was slowly injected in a solution of (butylmethoxymethylene)pentacarbonylchromium (292 mg, 1.0 mmol) in THF (10 ml) at −78°C under argon. The solution was stirred at −78°C for 20 min. Copper iodide (209 mg, 1.1 mmol) was added, turning the solution from orange to dark brown. The solution was stirred at −78°C for 10 min, then switched to −30°C (1:1 isopropanol: water–dry ice) and stirred for 1 h. The dark brown solution was slowly cannulated into a solution of benzoyl chloride (0.6 ml, 5.2 mmol) in THF (5 ml) at 0°C. The solution was stirred at 0°C for 1.5 h then at room temperature for 2 h. The brown clear solution was filtered through a pad of silica gel, concentrated and the crude product was purified by column chromatography with 14:1 petroleum ether: ether to provide product (**3**, 25 mg, 12%) as a colorless oil.

IR ($CDCl_3$ solution, thin film on salt plate): 3061, 2961, 2934, 2872, 1655, 1631, 1449, 1275, 1109, 914, 714, 694, cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): 0.96 (3H, t, $J = 7.4$ Hz, Me), 1.47 (2H, s, $J = 7.4$ Hz, CH2), 2.30 (2H, q, $J = 7.4$ Hz, CH2), 3.64 (3H, s, MeO), 5.82 (1H, t, $J = 7.5$ Hz, CH), 7.43 (2H, t, $J = 7.9$ Hz), 7.54 (1H, t, $J = 7.8$ Hz), 7.79 (2H, d, $J = 7.4$ Hz).

^{13}C NMR (100 MHz, $CDCl_3$): 192.69, 153.75, 137.96, 132.27, 130.88, 129.29, 128.22, 59.12, 27.69, 22.10, 13.97.

MS m/z: 204.1 (M^+, 17), 175.1 (6), 157.2 (17), 143.0 (18), 115.1 (10), 105.0 (100).

HRMS: calculated for $C_{13}H_{16}O_2$ 204.1150, found 204.1153.

*5.4. ((1-Acetylbutyl)methoxymethylene)pentacabonylchromium (**4**)*

n-Butyllithium in hexane (2.5 M, 0.96 ml, 2.4 mmol) was slowly injected in a solution of (butylmethoxymethylene)pentacarbonylchromium (584 mg, 2 mmol) in THF (20 ml) at −78°C (dry ice–acetone) under argon. The solution was stirred at −78°C for 30 min then was slowly cannulated to a stirred solution of acetyl chloride (1.42 ml, 20 mmol) in 5 ml of THF at 0°C. Solution turned dark orange and was stirred at 0°C for 30 min. The solution was warmed to room temperature and filtered through a pad of silica gel and concentrated. The crude product was purified by column chromatography with 20:1 petroleum ether: ether to provide product (**4**, 249 mg, 37%) as an orange to red oil along with recovery of 13% of starting carbene complex.

IR ($CDCl_3$ solution, thin film on salt plate): 2932, 2064, 1927, 1725, 1455, 1209, 666, 646 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): 0.91 (3H, t, $J = 7.3$ Hz, Me), 1.32 (2H, m, CH_2), 1.53 (1H, m), 1.70 (1H, m), 2.15 (3H, Me), 4.81 (3H, s, MeO), 5.16 (dd, 1H, CH).

^{13}C NMR (100 MHz, $CDCl_3$): 356.24, 222.50, 215.81, 201.21, 84.75, 68.22, 31.97, 31.00, 21.66, 14.17.

MS m/z: 305.9 ($[M–CO]^+$, 95), 277.9 (28), 234.9 (20), 194.0 (25), 157.1 (25), 143.1 (100), 127.1 (35).

HRMS: calculated for $C_{12}H_{14}CrO_6$ [M–CO] 306.0195, found 306.0197.

*5.5. ((Benzoylmethyl)dimethylaminomethylene)pentacabonylchromium (**6**)*

n-Butyllithium in hexane (2.32 M, 0.43 ml of 1.0 mmol) was slowly injected in a pale yellow solution of (butyl(dimethylamino)methylene)pentacarbonylchromium(263 mg, 1.0 mmol) in THF (10 ml) at −78 under argon. The dark orange solution was stirred at −78°C for 45 min then was slowly cannulated to a stirred solution of benzoyl

chloride (0.58 ml 5 mmol) in THF (5 ml) at 0°C. The solution was stirred at 0°C for 30 min, warmed to room temperature and filtered through a pad of silica gel and concentrated. The crude product was purified by column chromatography with 3:1 hexane: ethyl acetate to provide compound **6** (149 mg, 41%) as a yellow solid.

IR ($CDCl_3$ solution, thin film on salt plate): 2054, 1970, 1908 (strong), 1684, 1541, 1296, 1206, 675, 656 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): 3.27 (3H, s), 4.02 (3H, s), 4.98 (2H, s), 7.51 (2H, t, $J = 7.5$ Hz), 7.63 (1H, t, $J = 7.4$ Hz), 7.97 (2H, d, $J = 7.3$ Hz).

^{13}C NMR (100 MHz, $CDCl_3$): 269.34, 223.15, 217.39, 192.44, 136.08, 133.89, 128.94, 128.12, 60.19, 53.42, 43.63.

MS m/z: 272 (14), 227 (36, M–5CO), 220 (27), 176 (85), 175 (70, M–$Cr(CO)_5$), 158 (99), 105 (34), 98 (100).

5.6. ((1-Benzoylbutyl)methoxymethylene)pentacabonyltungsten (8)

n-Butyllithium in hexane (2.32 M, 0.545 ml, 1.26 mmol) was slowly injected in a solution of (butylmethoxymethylene)pentacarbonyltungsten (424 mg, 1.26 mmol) in THF (10 ml) at −78°C under argon. The solution was stirred at −78°C for 40 min then was slowly cannulated to a stirred solution of benzoyl chloride (0.734 ml, 6.32 mmol) in THF (5 ml) at 0°C. The solution turned dark orange and was stirred at 0°C for 1 h and then warmed to room temperature, filtered through a pad of silica gel, and concentrated. The crude product was purified by column chromatography with 20:1 petroleum ether: ether to provide compound 8 (193 mg 29%) as an orange solid.

IR ($CDCl_3$ solution, thin film on salt plate): 2963, 2934, 2072, 1923 (strong), 1688, 1451, 1264, 986, 689 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): 0.94 (3H, t, $J = 7.3$ Hz, Me), 1.41 (2H, m, CH_2), 1.90 (2H, m, CH_2), 4.60 (3H, s, MeO), 5.84 (1H, dd, $J = 7.1$, 5.6 Hz, CH), 7.49 (2H, t, $J = 7.6$ Hz), 7.59 (1H, t, $J = 7.4$ Hz), 7.95 (2H, d, $J = 7.1$ Hz).

^{13}C NMR (100 MHz, $CDCl_3$): 328.79, 202.13, 196.85, 194.54, 136.97, 133.50, 128.87, 128.48, 80.33, 71.00, 33.17, 21.86, 14.19.

MS m/z (70 eV): 499.9 ($[M–CO]^+$, 85), 409.1 (10), 369.0 (18), 309.1(21), 204.0 (57), 175.1 (15), 105.0 (100).

HRMS: calculated for $C_{17}H_{16}O_6W$ [M–CO] 500.0483, found 500.0472.

5.7. 3-Methoxy-1-phenyl-2-propyl-2-propen-1-one (9)

5.7.1. Method A

A solution of ((1-benzoylbutyl)methoxymethylene)pentacabonylchromium (2, 160 mg, 0.25 mmol) and pyridine (242 ml, 3 mmol) in hexane (10 ml) was degased three times (freeze, pump, thaw) and then stirred at room temperature overnight under argon. The solution turned from orange to red with the formation of red precipitate. The solution was filtered through a pad of silica gel and concentrated. The crude product was purified by column chromatography with 85:15 hexane: ethyl acetate to provide product (**9**, 30 mg, 59%) as a colorless to light yellow oil.

5.7.2. Method B

A solution of ((1-benzoylbutyl)methoxymethylene)pentacabonylchromium (**2**, 280 mg, 0.71 mmol) and pyridine (687 ml, 8.5 mmol) in hexane (10 ml) was degased three times (freeze and thaw). The solution was then gently refluxed for 1 h under argon. Workup as described above produced the product (**9**, 108 mg, 74%).

IR ($CDCl_3$ solution, thin film on salt plate): 2959, 2932, 1624, 1447, 1321, 1142, 989, 721, 700, 656 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): 0.94 (3H, t, $J = 7.4$ Hz, Me), 1.48 (2H, sextet, $J = 7.4$ Hz, CH_2), 2.41 (2H, t, $J = 7.6$ Hz, CH_2), 3.77 (3H, s, MeO), 6.86 (1H, s), 7.40 (2H, t, $J = 7.9$ Hz), 7.47 (1H, t, $J = 7.3$ Hz), 7.54 (2H, d, $J = 8.3$ Hz).

^{13}C NMR (100 MHz, $CDCl_3$): 196.81, 164.16, 140.22, 130.62, 128.67, 128.07, 122.17, 61.36, 25.54, 21.63, 14.08.

MS m/z (70 eV): 205.1 ($[M + H]^+$, 100), 204.1 (Mu^+, 81), 203.1 ($[M–H]^+$, 65), 175.1 (16), 127.1 (19), 105.1 (93).

HRMS: calculated for $C_{13}H_{16}O_2$ 204.1150, found 204.1149.

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