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The first synthesis of cyclopropanone acetals from the reaction of Fischer carbene complexes with ketene acetals

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Abstract

The reaction of *iso*-propoxy stabilized Fischer carbene complexes with ketene acetals gives moderate to excellent yields of cyclopropanone acetals when carried out under a carbon monoxide atmosphere. This is in contrast to the known reaction of methoxy substituted complexes which give cyclic *ortho* esters under the same conditions. A mechanism is proposed which involves a branch point between the two products as the zwitterionic intermediate resulting from nucleophilic addition of the ketene acetal to the carbene carbon. A 1,3-migration of the methoxyl group to the cationic center leads to the *ortho* ester and a ring closure by backside attack leads to the cyclopropanone acetal. A double-labeling experiment shows that the 1,3-migration occurs by an intramolecular process that is proposed to involve a bridging oxonium ion. The effect of the isopropoxy group is thus interpreted to be to sterically hinder the formation of a bridged oxonium ion.

Keywords: Cyclopropanone acetals; Fischer carbene complexes; Cross-over experiment; Ketene acetals; Zwitterionic intermediate

1. Introduction

The formal transfer of a carbene to an alkene represents one of the key methods for the synthesis of cyclopropanes [1,2]. The first method involving an isolated transition metal carbene complex was reported by Fischer for a chromium pentacarbonyl complex [3–5]. Cyclopropanation with Fischer carbene complexes has been extensively investigated mechanistically and synthetically. However, ketene acetals have never been reported as substrates [2]. These would be valuable substrates for this reaction since the products, cyclopropanone acetals, are useful synthetic intermediates for a variety of reactions [6]. In earlier investigations, we found that the reactions of Fischer carbene complexes with ketene acetals unexpectedly gave butyrolactones, thwarting our efforts to prepare cyclopropanone acetals by this reaction [7]. We herein wish to report a solution to this problem and the first synthesis of cyclopropanone acetals from the reaction of Fischer carbene complexes with ketene acetals (see Scheme 1).

The first step in the mechanism that was proposed to account for the formation of butyrolactones is the attack of the ketene acetal on the carbene carbon to give the zwitterionic intermediate **5** in Scheme 2 [7]. A 1,3-migration of the methoxyl group would give the unstablized carbene complex **7**, which upon C–H insertion would produce the cyclic *ortho* ester **8** that after hydrolysis would provide a butyrolactone [7,8]. The 1,3-migration of the methoxyl group may occur via a bridged oxonium ion as indicated in Scheme 2, via an intermolecular transfer or via dissociation of methoxyl to form an ion pair. The dissociation into ion pairs may be facilitated by the replacement of the methoxyl substituent with a bulkier alkoxide, but if an oxonium ion is involved, a bulkier alkoxide may slow down the 1,3-migration. This would then be expected to favor cyclopropane

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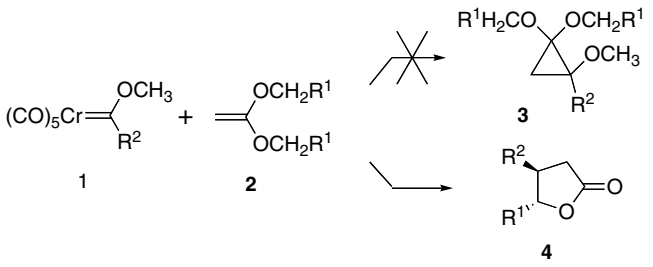
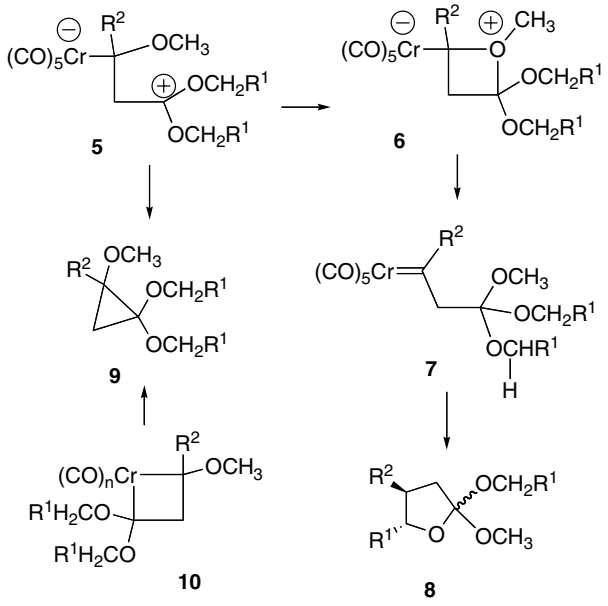


Scheme 1.



Scheme 2.

formation since it is thought to occur either via a direct ring closure by backside attack in the zwitterionic intermediate **5** or via reductive elimination from the metallacycle **10**. This metallacycle could be formed by closure from zwitterion **5** or by direct [2+2] cycloaddition with the carbene complex.

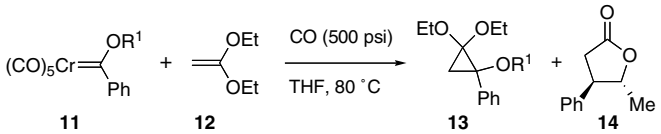
In either event, the mechanism in Scheme 2 would predict that cyclopropane formation from ketene acetals would be favored with carbene complexes with sterically larger oxygen stabilizing groups on the carbene carbon.

Cyclopropanone acetals could indeed be obtained from the reaction of ketene acetals with Fischer carbene complexes derived from secondary alcohols as shown by the data in Tables 1 and 2. Complexes **11**, **15** and **16** were prepared in good yields by the procedure of Connor [9] utilizing isopropanol or menthol and complexes **17** and **18** were prepared by Fischer original synthesis [10] employing isopropyl triflate [11] as alkylating agent. The data in Table 1 reveal that there is a correlation between the size of the alkoxy group and the partition between the cyclopropanone acetal and butyrolactone products.

Chromium carbene complex **11** provides a much more efficient transfer of phenyl(isopropoxy)methylene to diethyl ketene acetal than does either of the corresponding molybdenum or tungsten complexes **15** and **16** (Table 2). The electron rich 2-furyl carbene complex **17** is unreactive and is recovered in high yield after 96 h at 75 °C, but a slow reaction was observed at 100 °C. The *n*-butyl carbene complex is also slower than the aryl complex although moderate yields of the cyclopropanone acetal could be obtained. The secondary alkyl complex **32c** does not give a cyclopropanone acetal but rather suffers an internal proton transfer to give the enol ether **33** (Scheme 3). The more hindered carbene complex **11f** derived from L-menthol gave excellent yield with dimethyl ketene acetal, but disappointingly only a 2:1 stereoselectivity was observed and the relative stereochemistry of the major product was not determined. A higher selectivity (4:1) is seen with the *o*-xylyl ketene acetal **20** but the yield is reduced. No further increase in asymmetric induction is observed with the 9-phenylmentholoxy carbene complex **11g**.

It proved possible to probe the mechanism of the reaction with the finding that small amounts of the cyclopropanone acetal **35** could be obtained from the reaction of the methoxy carbene complex **11a** with the acetal **20** if the

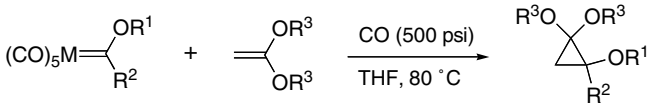
Table 1
Cyclopropanone acetals from Fischer carbene complexes[a]



Carbene complex	R^1	Time (h)	**13**	Yield of **13** (%)[b]	Yield of **14** (%)[b]
11a	Methyl	22	**13a**	0	76
11b	Ethyl	20	**13b**	26	60
11c	Isopropyl	24	**13c**	75	0
11d	Cyclopentyl	72	**13d**	47	0
11e	Cyclopentyl	48	**13e**	71	0

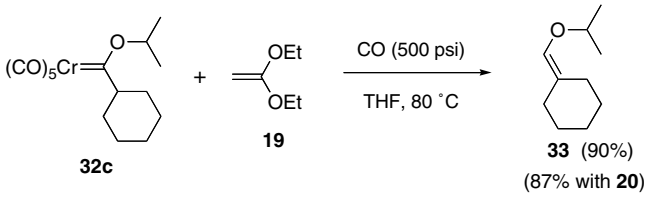
[a] Unless otherwise specified all reactions were carried out at 0.1 M in carbene complex in THF with 1.2 equiv of ketene acetal at 80 °C under 500 psi of CO in a Paar bomb. The reaction mixture was deoxygented before transfer to bomb.
[b] Isolated yields.

Table 2
Cyclopropanone acetals from Fischer carbene complexes[a]



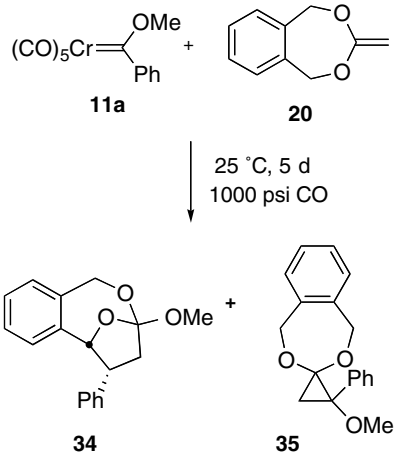
Carbene complex	M	R^1	R^2	Acetal	R^3	Time (h)	Product	Product yield	Rec (%)
11c	Cr	*i*-Pr	Ph	**19**	Et	24	**22**	75	0
11c	Cr	*i*-Pr	Ph		Et	24		69[b]	0
15c	Mo	*i*-Pr	Ph		Et	24		39	30
16c	W	*i*-Pr	Ph		Et	22		19	49
17c	Cr	*i*-Pr	2-Fu		Et	96	**23**	0	97
17c	Cr	*i*-Pr	2-Fu	**20**	*o*-Xylyl	48	**24**	13[c]	0
11c	Cr	*i*-Pr	Ph		*o*-Xylyl	69	**25**	76	–
11e	Cr	Cy	Ph		*o*-Xylyl	24	**26**	77	–
18c	Cr	*i*-Pr	*n*-Bu		*o*-Xylyl	92	**27**	48	–
11f	Cr	L-Menthol	Ph	**21**	Me	22	**28**	98[d]	–
11f	Cr	L-Menthol	Ph	**19**	Et	72	**29**	75[e]	–
11f	Cr	L-Menthol	Ph	**20**	*o*-Xylyl	72	**30**	40[f]	–
11g	Cr	Phenmen[h]	[1]Ph		*o*-Xylyl	72	**31**	24[g]	–

[a] Unless otherwise specified all reactions were carried out at 0.1 M in carbene complex in THF with 1.2 equiv of ketene acetal at 75–80 °C under 500 psi of CO in a Paar bomb. The reaction mixture was deoxygented before transfer to bomb.
[b] Reaction performed in the presence of 10 equiv of *i*-Propanol.
[c] Reaction at 100 °C, 22% of *iso*-propyl-2-furoate also obtained.
[d] 2.0:1 mixture of diastereomers.
[e] 2.2:1 mixture of diastereomers.
[f] 4.0:1 mixture of diastereomers.
[g] 4.4:1 mixture of diastereomers.
[h] 9-Phenylmentholoxy carbene complex.



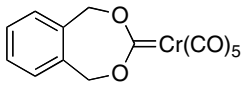
Scheme 3.

reaction is run at room temperature rather than at 70 °C (Scheme 4) [7]. Small amounts of **35** were found in the reactions in THF and acetonitrile but not in hexane, which is not consistent with a mechanism in which the *ortho* ester **34** is formed from the zwitterion **5** and the cyclopropanone acetal formed by the direct [2+2] cycloaddition of **11a** with **20** to give **10** (Scheme 2). The metallacycle **10** can be an intermediate in the reaction, however, as indicated by the isolation of the metathesis product **36** in the absence of carbon monoxide [12]. In this case, the metallacycle **10** must be unsaturated ($n = 4$) since under 1000 psi of CO the formation of carbene complex **36** is completely suppressed [2]. The reaction of **11a** with **20** was also carried out in THF in the presence of 10 equivalents of methanol-d_4 in an effort to trap the oxonium cation in the zwitterion **5**. However, both the *ortho* ester **34** and the cyclopropanone acetal **35** showed no detectable amount of deuterium incorporation in the methoxyl group. Thus, if the 1,3-migration of the methoxyl group in **5** involves

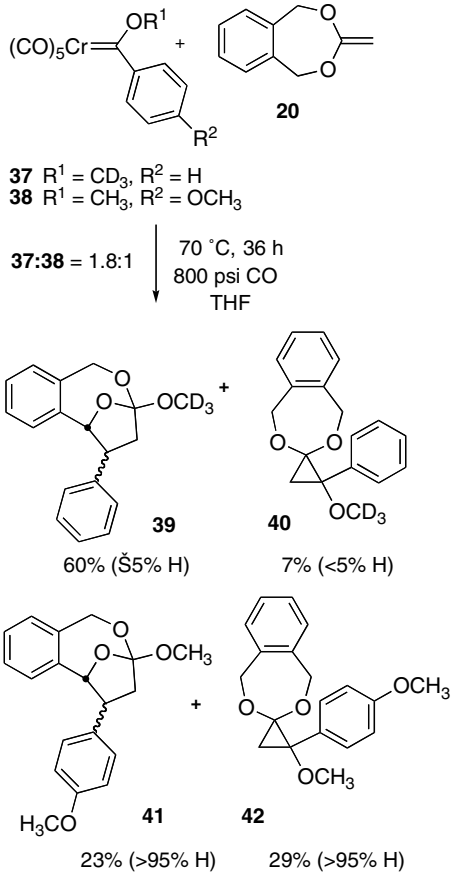


Solvent	Yield **34** (cis:trans)	Yield **35**
hexanes	60 (7 : 1)	Š 1
THF	78 (6 : 1)	17
CH_3CN	56 (8 : 1)	6
THF[a]	26 (5 : 1)[b]	62[b]

[a] (10 equiv CD_3OD) [b] Š 5% CD_3 incorporation



Scheme 4.



Scheme 5.

the dissociation of methoxide to give an ion pair, the internal return is so efficient that external methanol cannot compete. Perhaps the most interesting aspect of this experiment is the observation that the presence of 10 equivalents of methanol-d_4 increases the ratio of cyclopropanone acetal to *ortho* ester by a factor of 11. While this is not understood, it did not prove to be a general phenomenon. The reaction of **11c** with **19** in the presence of 10 equiv of isopropanol did not lead to an increased yield of **22** (Table 2, entry 2). The use of methanol in this reaction lead to scrambling of the alkoxy group in the carbene complex.

The possibility of a 1,3-migration of methoxyl by an intermolecular exchange was tested with the double-labeling experiment shown in Scheme 5. A 1.8:1 mixture of the complexes **37** and **38** was allowed to react with excess ketene acetal **20** at 70 °C for 36 h. The *para*-methoxyphenyl complex **38** was found to give a much greater proportion of the cyclopropanone acetal than the phenyl complex. However, neither the *ortho* ester **41** or the cyclopropanone acetal **42** contained any detectable amount of deuterium in the methoxyl attached to the sp^3-carbon. Similarly, neither the *ortho* ester **39** or the cyclopropanone acetal **40** were found to contain any detectable loss of deuterium in the methoxyl group. Therefore, the 1,3-migration of the methoxyl group in the zwitterion **5** must occur by an intramolecular process.

Future studies will focus on establishing the scope of this reaction for the preparation of cyclopropanone acetals and its application in synthesis.

2. Experimental

All experiments were performed under an argon atmosphere. Benzene, THF, and Et_2O were distilled from sodium benzophenone ketyl under nitrogen. Methylene chloride was distilled from calcium hydride under nitrogen. *i*-Propanol was distilled from $NaBH_4$ onto 4 Å MS. Other reagents were purified by simple distillation or passing through a pad of activated silica gel. Diethyl ketene acetal was purchased from Fluka, and distilled prior to use. Ketene-[*o*-xylyleneacetal] was prepared as described in the literature [13]. Pentacarbonyl-[(1*R*,2*S*,5*R*)-(−)-menthyloxybenzylidene]-chromium (0) and [(1*R*,2*S*,5*R*)-(−)-phenylmenthyloxybenzylidene]-chromium (0) were prepared as described by Dötz and Stinner [14]. All glassware was washed with aqueous KOH, flame dried under vacuum and cooled under an argon atmosphere prior to use.

^1H and ^{13}C NMR spectra were recorded on a General Electric QE-300 (300 MHz ^1H, 75.5 MHz ^{13}C) or Bruker Avance (400 MHz ^1H, 100 MHz ^{13}C) spectrometer in $CDCl_3$ using residual $CHCl_3$ (7.25 ppm ^1H, 77.25 ppm ^{13}C) as an internal reference unless otherwise stated. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel plates with F-254 indicator. Components were visualized by illumination with long wave ultraviolet light, exposure to iodine vapor, or by staining with one of the following reagents (followed by heating): *p*-anisaldehyde (or vanillin) in ethanol/sulfuric acid; 7% phosphomolybdic acid in ethanol; 0.04 M ammonium molybdate in 10% sulfuric acid. Solvents for extraction and chromatography were reagent grade and used as received. Flash column chromatography was performed by the method of Still [15] using E. Merck silica gel 60 (230–400 mesh).

3. General experimental for synthesis of *iso*-propoxy carbene complexes – illustrated for complex 11c

To a flame dried 250 mL round bottom flask with stir - bar was suspended 10 g (45.5 mmol) of chromium hexacarbonyl in 65 mL of Et_2O. The reaction was cooled to −78 °C, and 28 mL (1.62 M, 45.5 mmol) of phenyllithium was added dropwise. The initially canary yellow suspension was warmed to room temperature, and then became a deep brown-red solution. After 2 h at room temperature, the reaction was concentrated on the roto evaporator and then dried at 5 mm Hg for 0.5 h. After this time, 200 mL of distilled water was added, and the reaction was filtered through Celite directly on to 7.7 g (50 mmol) of tetramethylammonium bromide. The resulting orange suspension was stirred for 15 min, then the solid was collected on a Büchner funnel, and dried overnight to provide 7.1 g

(42%) of the tetramethyl ammonium salt as a bright orange solid.

To a flame dried 250 mL three-neck flask with constant addition funnel and stir bar, was charged 6.1 g (16.4 mmol) of the tetramethylammonium salt and 31 mL of CH_2Cl_2. The suspension was cooled to −65 °C, and 2.2 g (18.1 mmol) of acetyl bromide in 31 mL of CH_2Cl_2 was added dropwise. The resulting blood red suspension was stirred for an additional 15 min, and then 1.1 g (18.1 mmol) of *i*-propanol was added dropwise, and the reaction was warmed to −20 °C. After 24 h, the crude reaction was filtered through 1:1/Celite:SiO_2 with 100 mL hexanes, and concentrated to approximately 1/3 the original volume then chromatographed directly (50 mm column, 6″ SiO_2, 100% hexanes) by collecting the resulting red band which was concentrated in vacuo to provide a red solid. Recrystallization with 95:5/pentane:CH_2Cl_2 provided 2.5 g (45%) of the title compound as a bright orange solid; m.p. 45–46 °C (sharp): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.7 (d, 6H, CH(CH_3)$_2$, $J = 6.4$ Hz), 5.7 (m, CH(CH_3)$_2$, 1H), 7.2–7.5 (m, 5H, Ar–CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.6 (CH(CH_3)$_2$), 85.7 (CH(CH_3)$_2$), 122.4 (Ar–C), 128.1 (Ar–C), 129.7 (Ar–C), 153.8 (C_{ipso}), 216.3 (CO), 224.4 (CO), 345.8 (C_{carb}); mass spectrum *m*/*z* (% rel. int.) 312 ($M^+ - CO$, 3), 284 (11), 256 (3), 230 (1), 228 (18), 200 (90), 178 (20), 158 (41), 157 (30), 129 (75), 118 (22), 105 (30), 86 (62), 84 (100); IR (thin film, cm^{-1}) 2061s, 1924s, 1246w, 1079w, 653m. Anal. Calc. for $C_{15}H_{12}CrO_6$: C, 52.82; H, 3.55. Found: C, 52.71; H, 3.65%.

3.1. Pentacarbonyl-[cyclopentyloxybenzylidene]-chromium (0) (**11d**)

This compound was obtained according to the procedure for **11c** and was isolated in 83% yield from the tetramethyl ammonium salt as a yellow crystal. Spectral data for **11d**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.70–1.90 (m, 2H), 1.90–2.05 (m, 2H), 2.05–2.20 (m, 4H), 5.85 (m, 1H), 7.10–7.30 (m, 2H), 7.30–7.55 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.2, 34.2, 94.5, 122.4, 128.1, 129.6, 153.7, 216.3, 224.6, 345.6; IR (film) 455, 621, 654, 692, 702, 762, 897, 1148, 1240, 1273, 1325, 1441, 1917, 1950, 2082, 2878, 2969 cm^{-1}. Anal. Calc. for $C_{17}H_{14}CrO_6$: C, 55.74; H, 3.85. Found: C, 55.49; H, 4.10%.

3.2. Pentacarbonyl-[cyclohexyloxybenzylidene]-chromium (0) (**11e**)

This compound was obtained according to the procedure for **11c** and was isolated in 48% yield from the tetramethyl ammonium salt as a yellow crystal. Spectral data for **11e**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.70–2.20 (m, 10H), 5.85 (m, 1H), 7.10–7.32 (m, 2H), 7.32–7.55 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.4, 24.9, 32.4, 90.4, 122.7, 128.1, 129.9, 153.7, 216.3, 224.4, 345.6; IR (film) 410, 619, 655, 760, 864, 903, 937, 951, 1150, 1173, 1181, 1208, 1232, 1248, 1277, 1443, 1451, 1917, 2080, 2865, 2942 cm^{-1}. Anal. Calc. for $C_{18}H_{16}CrO_6$: C, 56.85; H, 4.24. Found: C, 56.79; H, 4.34%.

3.3. Pentacarbonyl-[isopropoxybenzylidene]-molybdenum (0) (**15c**)

This complex was isolated in 28% yield from the tetramethylammonium salt following the procedure for the chromium analog. Orange-rust crystals, mp 62–64 °C (sharp). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.67 (d, 6H, CH(CH_3)$_2$, $J = 6.2$ Hz), 6.15 (m, 1H, CH(CH_3)$_2$), 7.49 (m, Ar–CH, 3H), 7.56 (m, Ar–CH, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.3 (CH(CH_3)$_2$), 88.3 (CH(CH_3)$_2$), 125.8 (Ar–C), 128.0 (Ar–C), 131.5 (Ar–C), 153.9 (C_{ipso}), 205.6 (CO), 213.8 (CO), 332.8 (C_{carb}); IR (thin film, cm^{-1}) 2071m, 1992m, 1965s, 1928s, 1211w; mass spectrum *m*/*z* (% rel. int.) 386 (M^+, ^{98}Mo, 10), 358 ($M^+ - CO$, ^{98}Mo, 35), 330 (^{98}Mo, 19), 302 (^{98}Mo, 40), 154 (84), 136 (46), 105 (100); HRMS calcd for $C_{15}H_{12}MoO_6$ *m*/*z* 385.9692, measd 385.9687. Anal. Calc. for $C_{15}H_{12}MoO_6$: C, 46.79; H, 3.10; Mo, 24.97. Found: C, 45.31; H, 3.10; Mo, 23.84%.

3.4. Pentacarbonyl-[isopropoxybenzylidene]-tungsten (0) (**16c**)

This complex was isolated in 28% yield from the tetramethylammoniium salt following the procedure for the chromium analog. Orange powder, mp 76–77 °C (sharp). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.62 (d, 6H, CH(CH_3)$_2$, $J = 6.4$ Hz), 5.91 (m, 1H, CH(CH_3)$_2$), 7.42–7.50 (m, Ar–CH, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.4 (CH(CH_3)$_2$), 88.8 (CH(CH_3)$_2$), 125.9 (Ar–C), 128.0 (Ar–C), 131.4 (Ar–C), 155.4 (C_{ipso}), 197.2 (t, CO, $J_{CW} = 127$ Hz), 203.7 (CO), 316.1 (C_{carb}); IR (thin film, cm^{-1}) 2069m, 1989m, 1959s, 1922s, 1256w; mass spectrum *m*/*z* (% rel. int.) 472 (M^+, ^{184}W, 2), 444 (4, ^{184}W), 373 (35, ^{184}W), 309 (36), 279 (25), 195 (21), 155 (84), 135 (66), 119 (100); HRMS calcd for $C_{15}H_{12}{}^{184}WO_6$ *m*/*z* 472.0140, measd 472.0143. Anal. Calc. for $C_{15}H_{12}WO_6$: C, 38.09; H, 2.56. Found: C, 37.88; H, 2.49%.

3.5. Pentacarbonyl-[isopropoxy-2-furanyl-methylidene]-chromium (0) (**17c**)

This complex was isolated in 90% yield from 620 mg (9.1 mmol) of furan, 2 g (9.1 mmol) of chromium hexacarbonyl and 3.5 g (18.2 mmol) of isopropyl triflate. The crurde product was chromatorgraphed directly (50 mm column, 6″ SiO_2, 95:5/hexanes:CH_2Cl_2) and collection of the resulting red-purple band as described above gave a purple solid. Recrystallization from pentane provides purple needles, mp 88–90 °C (sharp). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.57 (d, 6 H, CH(CH_3)$_2$, $J = 6.0$ Hz), 6.00 (sept, 1H, CH(CH_3)$_2$), 6.59 (bs, 1H, CH-2), 7.04 (d, 1H, CH-3, $J = 2.7$ Hz), 7.89 (s, 1H, CH-1); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 22.7 (CH(CH_3)$_2$), 85.1 (CH(CH_3)$_2$), 112.8 (C-1), 113.2, 150.3, 164.5 (C-4), 217.2 (CO), 224.6 (CO),

307.9 ($C_{carbene}$); IR (thin film, cm^{-1}) 2060w, 1992w, 1925s, 1889m, 1545w, 1223m, 643m; mass spectrum *m/z* (% rel. int.) 330 M^+ (28), 307 (34), 302 (32), 274 (16), 246 (35), 218 (55), 190 (24), 154 (100), 136 (85), HRMS calcd for $C_{13}H_{10}CrO_7$ *m/z* 329.9831, measd 329.9831.

3.6. Pentacarbonyl-[1-isopropoxy-n-pentylidene]-chromium (0) (18c)

To a flame dried 50 mL round bottom flask equipped with a stir bar and septa was suspended 2.8 g (12.8 mmol) of chromium hexacarbonyl in 50 mL of Et_2O. The reaction was cooled to −78 °C, and 5.8 mL (2.19 M, 12.8 mmol) of butyllithium was added dropwise. The initially canary yellow suspension was warmed to room temperature which then became a deep brown-red solution. After 1.5 h at RT, the reaction was filtered through a pad of Celite, concentrated and then dried at 5 mm Hg for 0.5 h. After this time, the brown solid was suspended in 50 mL of CH_2Cl_2, and the mixture reaction was cooled to 0 °C. To the brown-yellow solution was added 3.7 g (19.3 mmol) of isopropyl triflate [16] in 10 mL of CH_2Cl_2 dropwise. After the addition was complete, the now red reaction mixture was warmed to RT for 1 h. After this time, the reaction was filtered through 1:1/Celite:SiO_2 with 100 mL hexanes, concentrated to approximately 1/3 the original volume, then chromatographed directly (30 mm column, 4″ SiO_2, 100% hexanes) by collecting the resulting yellow-orange band which was concentrated to provide 1.7 g (41%) of the title compound as bright yellow crystals, mp 34–36 °C (sharp). ^1H NMR (300 MHz, $CDCl_3$) δ 0.92 (t, 3H, $J = 7.1$ Hz, Butyl CH_3), 1.38 (m, 2H, CH_2), 1.46 (m, 2H, CH_2), 1.64 (d, 6H, $CH(CH_3)_2$, $J = 5.6$ Hz), 3.27 (t, 2H, $J = 7.2$ Hz, $CH_2C_{carbene}$), 5.84 (brs, 1H, $CH(CH_3)_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1 (CH_3), 22.5 ($CH(CH_3)_2$), 22.8 (CH_2), 28.6 (CH_2), 63.5 ($C_{carbene}CH_2$), 87.8 ($CH(CH_3)_2$), 217.1 (CO), 224.2 (CO), 355.4 (C_{carb}); IR (thin film, cm^{-1}) 2061s, 1978m, 1923s, 1261m; mass spectrum *m/z* (% rel. int.) 320 M^+ (7), 292 (13), 264 (9), 236 (5), 208 (21), 180 (100), 138 (33), HRMS calcd for $C_{13}H_{16}CrO_6$ *m/z* 320.0351, measd 320.0351. Anal. Calc. for $C_{13}H_{16}CrO_6$: C, 48.75; H, 5.03, Cr, 16.24. Found: C, 48.38; H, 5.03; Cr, 16.70%.

3.7. Pentacarbonyl-[isopropoxy-cyclohexyl-methylidene]-chromium (0) (32c)

Yellow crystal. Spectral data for **32c**: ^1H NMR (300 MHz, $CDCl_3$) δ 1.00–1.40 (m, 10H), 1.53 (d, $J = 5.7$ Hz, 3H), 1.78 (d, $J = 5.7$ Hz, 3H), 3.83 (m, 1H), 5.80 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.1, 25.6, 25.9, 28.3, 71.3, 86.8, 216.5, 223.5, 357.3; IR (film) 590, 648, 666, 853, 914, 982, 1062, 1100, 1258, 1325, 1368, 1443, 1916, 2080, 2857, 2934 cm^{-1}. Anal. Calc. for $C_{15}H_{18}CrO_6$: C, 52.03; H, 5.24. Found: C, 51.89; H, 5.37%.

4. General experimental for cyclopropanation reaction with ketene acetals – illustrated for 1,1-diethoxy-2-isopropoxy-2-phenyl-cyclopropane 13c

To a flame dried 25 mL Schlenk flask with a stir bar and septa was charged 430 mg (1.3 mmol) of pentacarbonyl-[isopropoxybenzylidene]-chromium (0) **11c**, 13 mL of THF and 177 mg (1.52 mmol) of diethyl ketene acetal. The clear orange solution was deoxygenated by the freeze–pump–thaw method (three cycles) and then transferred into a Parr high pressure reactor filled with argon, sealed, and pressurized to 500 psi of CO. The reactor was heated at 75 °C for 24 h, cooled to room temperature and then the contents were concentrated in vacuo. The crude green-yellow solution was chromatographed (30 mm column, 4″ SiO_2, 20:1/hexanes:EtOAc) to provide 245 mg (74%) of the title compound as a clear, very light yellow liquid. TLC (SiO_2, 5:1/hexanes:EtOAc, $R_f = 0.45$). ^1H NMR ($CDCl_3$, 300 MHz) δ 0.8 (t, 3H, CH_3, $J = 7.1$ Hz), 1.0 (d, 3H, $CH(CH_3)_2$, $J = 6.2$ Hz), 1.2 (d, 3H, $CH(CH_3)_2$, $J = 6.1$ Hz), 1.3 (t, 3H, CH_2CH_3, $J = 7.1$ Hz), 1.36 (d, 1H, CH_2, $J = 7.2$ Hz), 1.7 (d, 1H, CH_2, $J = 7.2$ Hz), 3.17 (m, 1H, OCH_2), 3.50 (m, 1H, OCH_2), 3.73 (m, 2H, $CH(CH_3)_2 + OCH_2CH_3$), 3.87 (m, 1H, OCH_2), 7.20–7.32 (m, 3H), 7.4 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.0 (OCH_2CH_3), 15.6 (OCH_2CH_3), 21.3 (C-3, $J_{CH} = 158$ Hz), 23.3 (*i*-Pr-CH_3), 23.6 (*i*-Pr-CH_3), 61.6 (OCH_2CH_3), 62.9 (OCH_2CH_3), 69.4 (C-2), 70.6 ($OCH(CH_3)_2$), 92.7 (C-1), 126.8 (C–Ar), 127.7 (C–Ar), 138.4 (C_{ipso}); IR (neat, cm^{-1}) 2974s, 2930s, 2886m, 1448m, 1368m, 1267w, 1209s, 1119s, 1050s, 698s; mass spectrum *m/z* (% rel. int.) 221 ($M - i$-Pr)$^+$ (30), 193 (19), 147 (14), 105 (100). Anal. Calc. for $C_{16}H_{24}O_3$: C, 72.69; H, 9.15. Found: C, 73.03; H, 9.11%.

4.1. c1,1-Diethoxy-2-isopropoxy-2-phenyl-cyclopropane (13d)

Colorless oil, 47% yield. Spectral data for **13d**: ^1H NMR (300 MHz, $CDCl_3$) δ 0.84 (t, $J = 7.1$ Hz, 3H), 1.26–1.46 (m, 4H), 1.31 (t, $J = 7.1$ Hz, 3H), 1.43 (d, $J = 7.1$ Hz, 1H), 1.54–1.80 (m, 4H), 1.68 (d, $J = 7.1$ Hz, 1H), 3.12–3.24 (m, 1H), 3.46–3.60 (m, 1H), 3.72–3.82 (m, 1H), 3.84–3.92 (m, 1H), 3.93–4.04 (m, 1H), 7.20–7.45 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.9, 15.5, 21.5, 23.0, 23.3, 33.0, 61.5, 62.8, 69.9, 80.3, 92.8, 126.6, 127.4, 127.6, 138.3 (1 aliphatic C not located). Anal. Calc. for $C_{18}H_{26}O_3$: C, 74.45; H, 9.02. Found: C, 74.48; H, 9.21%.

4.2. 1-o-Xyleneacetal-2-isopropoxy-2-furanyl-cyclopropane (24)

This compound was isolated in 13% yield as a light yellow liquid using the procedure described above with 200 mg (0.61 mmol) of pentacarbonyl-[isopropoxyfuranyl]-chromium (0) **17c**, 8 mL of THF and 197 mg (1.21 mmol) of ketene acetal. The reaction was performed at 100 °C under 500 psi CO for 48 h. ^1H NMR ($CDCl_3$,

300 MHz) δ 1.08 (d, 3H, CH(CH_3)$_2$,$J = 6.2$ Hz), 1.15 (d, 3H, CH(CH_3)$_2$,$J = 6.2$ Hz), 1.55 (d, 1H, CH_2, $J = 7.1$ Hz), 1.73 (d, 1H, CH_2, $J = 7.1$ Hz), 3.84 (hept, 1H, $CH(CH_3)_2$, $J = 6.1$ Hz), 4.53 (2, 1H, CH_2, $J = 14.1$ Hz), 4.93 (2, 1H, CH_2, $J = 14.1$ Hz), 5.00 (2, 1H, CH_2, $J = 14.0$ Hz), 5.20 (2, 1H, CH_2, $J = 14.1$ Hz), 6.32 (m, 1H, furyl), 6.38 (m, 1H, furyl), 7.09 (m, 1H, Ar–CH), 7.19 (m, 3H, Ar–CH), 7.40 (bs, 1H, furyl); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.9 (CH_3), 24.6 (C-3, $J_{CH} = 160$ Hz), 71.1, 71.5, 72.1, 77.5, 95.8, 109.3 (C-furyl), 110.7 (C-furyl), 127.5 (2xC–Ar), 127.6 (C–Ar), 127.6 (C–Ar), 138.7 (C_{ipso}), 139.0 (C_{ipso}), 142.3 (C-furyl), 152.2 (C_{ipso}-furyl); IR (thin film, cm^{-1}) 2964m, 1372w, 1266w, 1132m, 1062w, 1027w; mass spectrum *m*/*z* (% rel. int.) 300 (88), 257 (24), 241 (33), 183 (69), 171 (67), 155 (51), 146 (28), 137 (100), HRMS calcd for $C_{18}H_{20}O_4$ *m*/*z* 300.1356, measd 300.1361.

4.3. 1-o-Xyleneacetal-2-isopropoxy-2-phenyl-cyclopropane (25)

This compound was isolated in 76% yield as a colorless liquid using the procedure described above with 216 mg (0.32 mmol) of pentacarbonyl-[isopropoxybenzylidene]-chromium (0) **11c**, 12 mL of THF and 90 mg (0.64 mmol) of ketene acetal. The reaction was performed at 50 °C under 640 psi CO for 69 h. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.07 (d, 3H, CH(CH_3)$_2$), 1.19 (d, 3H, CH(CH_3)$_2$), 1.57 (d, 1H, CH_2, $J = 7$ Hz), 1.84 (d, 1H, CH_2, $J = 7$ Hz), 3.81 (hept, 1H, $CH(CH_3)_2$, $J = 6$ Hz), 4.51 (m, allylic CH_2, 2H), 5.10 (m, allylic CH_2, 2H), 7.01 (d, Ar–CH, 1H), 7.1–7.5 (m, Ar–CH, 8H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 23.0 (C-3,$J_{CH} = 159$ Hz), 23.5, 69.2, 70.4, 70.4, 71.9, 95.7, 127.2, 127.2, 127.3, 127.3, 127.4, 128.0, 137.8, 138.6, 138.9 (1 aryl C not located); IR (thin film, cm^{-1}) 2972s, 1496m, 1447s, 1424m, 1380m, 1369s. Anal. Calc. for $C_{20}H_{22}O_3$: C, 77.39; H, 7.14. Found: C, 77.41; H, 7.29%.

4.4. 1-o-Xyleneacetal-2-cyclohexyloxy-2-phenyl-cyclopropane (26)

Colorless oil, 77% yield. Spectral data for **26**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.84–0.96 (m, 1H), 1.10–1.56 (m, 6H), 1.62 (d, $J = 7.0$ Hz, 1H), 1.64–1.80 (m, 2H), 1.87 (d, $J = 7.0$ Hz, 1H), 1.88–1.98 (m, 1H), 3.45–3.55 (m, 1H), 4.39 (d, $J = 14.2$ Hz, 1H), 4.64 (d, $J = 14.0$ Hz, 1H), 5.04 (d, $J = 14.2$ Hz, 1H), 5.20 (d, $J = 14.2$ Hz, 1H), 7.02 (d, $J = 7.2$ Hz, 1H), 7.15–7.25 (m, 3H), 7.25–7.42 (m, 3H), 7.55 (d, $J = 7.7$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.0, 24.4, 25.6, 33.2, 33.5, 69.0, 70.4, 71.9, 76.4, 95.8, 127.0, 127.1, 127.2, 127.8, 127.83, 138.0, 138.5, 138.9 (three carbons not located). Anal. Calc. for $C_{23}H_{26}O_3$: C, 78.83; H, 7.48. Found: C, 78.99; H, 7.21%.

4.5. 1-o-Xyleneacetal-2-isopropoxy-2-butyl-cyclopropane (27)

Cyclopropanone acetal **27** was isolated in 48% yield as a yellow liquid using the procedure described above with 200 mg (0.62 mmol) of pentacarbonyl-[isopropoxy-butylidene]-chromium (0) **18c**, 8 mL of THF and 111 mg (0.69 mmol) of ketene acetal **20**. The reaction was performed at 75 °C under 500 psi CO for 92 h. TLC (SiO_2, 4:1/Hexanes:EtOAc, $R_f = 0.28$). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.89 (m, 4H), 1.21 (m, 7H), 1.36 (m, 2H), 1.52 (m, 2H), 1.67 (m, 2H), 3.81 (sept, 1H, $J = 6.2$ Hz, $CH(CH_3)_2$), 4.69–5.05 (m, 4H, OCH_2), 7.04–7.22 (m, Ar–CH, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.3 (butyl-CH_3), 23.1, 23.9, 24.0, 24.2, 27.9, 30.7, 68.4 (C-2), 70.4 ($OCH(CH_3)_2$), 70.7 (OCH_2), 71.6 (OCH_2), 97.2 (C-1), 127.3 (Ar–C), 127.4 (Ar–C), 127.5 (Ar–C), 138.8 (C_{ipso}), 139.2 (C_{ipso}); IR (thin film, cm^{-1}) 2957s, 2928s, 2861s, 1446m, 1367m, 1213w, 1168s, 1152s, 1069s, 1039s, 745m; mass spectrum (FAB) *m*/*z* (% rel. int.) 289 (8), 247 (14), 231 (10), 185 (8), 154 (51), 136 (36), 135 (34), 104 (100), HRMS calcd for $C_{18}H_{26}O_3$ *m*/*z* 289.1803, measd 289.1803.

4.6. 1,1-Dimethoxy-2-mentholoxy-2-phenyl-cyclopropane (28)

This cyclopropanone acetal **28** was isolated in 98% yield as a colorless oil using the procedure described above with 160 mg (0.37 mmol) of pentacarbonyl-[(1*R*,2*S*,5*R*)-(−)-menthyloxybenzylidene]-chromium (0) **11f**, 5 mL of THF and 65 mg (0.74 mmol) of dimethoxy ketene acetal **21**. The reaction was performed at 80 °C under 380 psi CO for 24 h. Acetal **28** was isolated as a 2:1 mixture of isomers which could be separated by preparative TLC with a 1:1:20 mixture of ether, methylene chloride and hexanes. Major isomer: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.66 (d, 3H), 0.77 (d, 3H), 0.92 (d, 3H), 0.6–1.6 (m, 10H), 2.33 (m, 1H), 3.13 (s, 3H), 3.21 (m, 1H), 3.52 (s, 3H), 7.2–7.4 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.9, 19.7, 21.4, 22.9, 23.1, 24.7, 31.6, 34.4, 42.4, 48.3, 52.9, 54.3, 69.4, 78.2, 94.1, 126.8, 127.5, 127.7, 139.7; IR (neat, cm^{-1}) 2954s, 2933s, 2870m, 1448m, 1225m; mass spectrum *m*/*z* (% rel. int.) 219 ($M^+ - C_{10}H_{19}$, 3), 193 (68), 169 (8), 131 (11), 105 (100) (thick colorless oil). Minor isomer: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.42 (d, 3H, $J = 7$ Hz), 0.7–1.6 (m, 9H), 0.85 (d, 3H, $J = 7$ Hz), 0.88 (d, 3 H, $J = 7$ Hz), 2.2–2.7 (m, 2H), 3.07 (m, 1H), 3.19 (s, 3H), 3.61 (s, 3H), 7.3–7.4 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.6, 21.3, 22.6, 22.7, 25.0, 31.3, 34.4, 40.8, 48.0, 52.7, 54.3, 67.9, 75.5, 91.4, 127.6, 128.1, 129.4, 136.3 (1 aliphatic C not located); IR (neat, cm^{-1}) 2954s, 2933s, 2870m, 1448m, 1224m.

4.7. 1-o-Xyleneacetal-2-mentholoxy-2-phenyl-cyclopropane (30)

Major isomer, 33% yield, colorless oil. Spectral data for **30** (major): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.72 (d, $J = 6.6$ Hz, 3H), 0.83 (d, $J = 6.9$ Hz, 3H), 0.99 (d, $J = 7.1$ Hz, 3H), 0.90–1.32 (m, 3H), 1.36–1.48 (m, 1H), 1.52–1.70 (m, 4H), 1.60 (d, $J = 7.7$ Hz, 1H), 1.85 (d, $J = 7.7$ Hz, 1H), 2.45 (pd, $J = 7.1$, 2.8 Hz, 1H), 3.30 (td, $J = 10.4$, 3.8 Hz, 1H),4.33 (*d*, $J = 14.0$ Hz, 1H),4.54 (d,

$J = 13.7$ Hz, 1H), 4.88 (d, $J = 14.2$ Hz, 1H), 5.19 (d, $J = 14.0$ Hz, 1H), 7.03 (d, $J = 6.9$ Hz, 1H), 7.14–7.40 (m, 6H), 7.48–7.54 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.8, 21.3, 22.3, 22.9, 24.9, 31.5, 34.4, 42.0, 48.2, 68.6, 70.8, 72.3, 77.6, 96.7, 126.5, 126.6, 127.2, 127.4, 127.6, 127.8, 138.8, 139.2, 139.8 (1 aryl and 1 alkyl C not located); IR (film) 632, 644, 737, 764, 898, 990, 1028, 1063, 1074, 1129, 1144, 1181, 1262, 1329, 1370, 1447, 1495, 2868, 2918, 2953 cm^{-1}. Anal. Calc. for $C_{27}H_{34}O_3$: C, 79.76; H, 8.43. Found: C, 80.02; H, 8.22%. *Minor isomer*. Colorless oil, 8% yield. Spectral data for **30** (minor): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.50 (d, $J = 6.9$ Hz, 3H), 0.89 (d, $J = 2.5$ Hz, 3H), 0.91 (d, $J = 1.9$ Hz, 3H),0.70–1.70 (m, 8H),1.54 (d, $J = 7.1$ Hz, 1H), 1.88 (d, $J = 7.1$ Hz, 1H),2.24–2.32 (*m*,1H),2.36 (*pd*, $J = 6.9$,4.4 Hz, 1H),3.25 (td, $J = 10.4$, 4.4 Hz, 1H), 4.53 (d, $J = 14.0$ Hz, 1H), 4.74 (d, $J = 14.0$ Hz, 1H), 5.04 (d, $J = 14.0$ Hz, 1H), 5.24 (d, $J = 14.2$ Hz, 1H), 7.04 (d, $J = 6.9$ Hz, 1H), 7.16–7.24 (m, 3H), 7.30–7.42 (m, 3H), 7.44–7.50 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.8, 21.3, 22.5, 22.8, 24.3, 25.0, 31.3, 34.3, 40.9, 48.1, 67.8, 70.0, 72.0, 75.7, 94.2, 127.1, 127.3, 127.31, 127.6, 128.1, 129.2, 136.1, 138.6, 138.9 (1 aryl C not located); IR (film) 642, 700, 745, 764, 909, 982, 1001, 1034, 1063, 1134, 1183, 1262, 1345, 1360, 1447, 1495, 2853, 2923, 2953, cm^{-1}. Anal. Calc. for $C_{27}H_{34}O_3$: C, 79.76; H, 8.43. Found: C, 79.88; H, 8.21%.

*4.8. 1-o-Xyleneacetal-2-(9-phenylmentholoxy)-2-phenylcyclopropane (**31**)*

Major isomer, 20% yield, colorless oil. Spectral data for **31** (major): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.60–1.00 (m, 3H), 0.75 (d, $J = 6.6$ Hz, 3H), 1.15–1.50 (m, 3H), 1.46 (s, 3H), 1.72 (d, $J = 7.7$ Hz, 1H), 1.74 (s, 3H), 1.85 (d, $J = 7.7$ Hz, 1H), 1.90–2.00 (m, 2H), 3.50 (td, $J = 10.4$, 3.8 Hz, 1H), 4.50 (q, $J = 13.7$ Hz, 2H), 4.84 (d, $J = 14.0$ Hz, 1H), 5.16 (d, $J = 14.0$ Hz, 1H), 7.03 (d, $J = 6.8$ Hz, 1H), 7.10–7.55 (m, 13H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.9, 22.0, 22.4, 27.9, 30.9, 31.5, 34.8, 40.8, 41.9, 52.1, 67.1, 70.3, 72.0, 78.9, 96.6, 124.9, 126.1, 126.4, 126.8, 127.1, 127.3, 127.6, 127.7, 138.7, 140.5, 151.8 (2 aryl C not located); IR (film) 632, 644, 737, 764, 898, 990, 1028, 1063, 1074, 1129, 1144, 1181, 1262, 1329, 1370, 1447, 1495, 2868, 2918, 2953 cm^{-1}. Anal. Calc. for $C_{33}H_{38}O_3$: C, 82.12; H, 7.94. Found: C, 82.01; H, 8.02%. *Minor isomer*. 4% yield, colorless oil. Spectral data for **31** (minor): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.65–1.45 (m, 6H), 0.90 (d, $J = 6.6$ Hz, 3H), 1.30 (s, 3H), 1.54 (d, $J = 7.1$ Hz, 1H), 1.63 (s, 3H), 1.83 (d, $J = 7.1$ Hz, 1H), 1.90–2.00 (m, 1H), 2.45–2.55 (m, 1H), 3.42 (td, $J = 10.4$, 4.2 Hz, 1H), 4.78 (q, $J = 14.0$ Hz, 2H), 4.92 (d, $J = 14.2$ Hz, 1H), 5.20 (d, $J = 14.2$ Hz, 1H), 7.04 (d, $J = 6.9$ Hz, 1H), 7.10–7.60 (m, 13H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.4, 22.44, 25.0, 27.5, 31.2, 31.7, 34.6, 41.0, 41.1, 51.5, 66.3, 69.5, 71.3, 77.5, 93.5, 124.9, 125.7, 126.8, 127.1, 127.9, 128.1, 129.9, 135.4, 138.4, 138.6, 152.1 (3 aryl C not located); IR (film) 642, 700, 745, 764, 909, 982, 1001, 1034, 1063, 1134, 1183, 1262, 1345, 1360, 1447, 1495, 2853, 2923, 2953, 3025 cm^{-1}. Anal. Calc. for $C_{33}H_{38}O_3$: C, 82.12; H, 7.94. Found: C, 81.88; H, 8.21%.

*4.9. Reaction of complex **11a** with ketal acetal **20** at room temperature*

Carbene complex **11a** (0.1159 g) was dissolved in 7.4 mL THF with 1.0 eq of **20.** The solution was deoxygenated by the freeze–thaw method (three cycles). The solution was then stirred at room temperature until the complete consumption of the carbene complex was observed (5 days). The crude mixture was then purified by chromatography. *Ortho* ester **34** was isolated in 54% (*cis*:*trans* = 10:1) yield along with α-methoxystyrene (not quantified) and **36** in 25% yield. *cis*-**34**: ^{1}H NMR ($CDCl_3$) δ 2.46 (dd, 1H, $J = 6.2$, 13.2 Hz), 2.70 (t, 1H, $J = 12.8$ Hz), 3.58 (s, 3H), 4.09–4.14 (m, 1H, d), 5.41 (d, 1H, $J = 13.7$ Hz), 5.65 (d, 1H, $J = 9.2$ Hz), 6.13 (d, 1H, $J = 7.6$ Hz), 6.75 (t, 1H, $J = 7.4$ Hz), 6.95–7.04 (m, 7 H); ^{13}C NMR ($CDCl_3$) δ 42.2, 47.9, 51.3, 65.5, 85.0, 122.6, 126.35, 126.43, 126.56, 126.97, 127.85 (2 carbons), 127.88, 137.0, 138.5, 139.4; IR (CH_2Cl_2) 1640m, 1574m, 1318m, 1304s, 1286s cm^{-1}; mass spectrum *m*/*z* (% rel. int.) M^+ 282 (3), 251 (2), 208 (41), 163 (35), 149 (7), 121 (100), 104 (27). Anal. Calc. for $C_{18}H_{18}O_3$: C, 76.56; H, 6.43. Found: C, 76.31; H, 6.51%. White solid, mp 70 °C (dec.). *trans*-**34**: ^{1}H NMR ($CDCl_3$) δ 2.25 (dd, 1H, $J = 9.3$, 12.1 Hz), 2.67 (dd, 1H, $J = 8.7$, 12.0 Hz), 3.44–3.49 (m, 1H), 3.59 (s, 3H), 4.50 (d, 1H, $J = 14.0$ Hz), 5.24 (d, 1H, $J = 4.1$ Hz), 5.40 (d, 1H, $J = 14.0$ Hz), 6.90–6.91 (m, 1H), 7.10–7.36 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 43.0, 52.26, 52.33, 65.6, 87.4, 122.5, 125.5, 126.9, 127.0, 127.4, 127.5, 127.6, 129.0, 136.4, 142.4, 143.8; IR (CH_2Cl_2) 1446m cm^{-1}; mass spectrum *m*/*z* (% rel. int.) M^+ 282 (5), 264 (14), 200 (50), 162 (42), 122 (30), 121 (100), 120 (28), 119 (98). White solid, mp 67 °C (dec.). Compound **36**: ^{1}H NMR ($CDCl_3$) δ 5.7 (s, 4H), 7.5 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 74.9, 128.3, 130.4, 135.6, 216.7, 221.9, 268.7; IR (CH_2Cl_2) 2064s, 1998br,s cm^{-1}; mass spectrum *m*/*z* (% rel. int.) 340 M^+ (25), 312 (5), 256 (12), 228 (52), 220 (20), 200 (100), 199 (95), 201 (27). Anal. Calc. for $C_{14}H_8CrO_7$: C, 49.42; H, 2.37. Found: C, 49.32; H, 2.56%. Pale yellow solid: mp 126.5 °C (dec.).

*4.10. Reaction of complex **11a** with ketal acetal **20** at room temperature under 1000 psi of carbon monoxide*

A solution of 0.1410 g of **11a** and 0.0744 g of **20** in 8.4 mL THF was prepared under an argon atmosphere and then transferred to the Parr reactor under inert atmosphere. The reactor was then charged to a pressure of 1000 psi of CO. The reaction was then set aside for five days at room temperature. After the pressure was released from the reactor, the crude mixture was then purified on silica gel to give a 78% yield of **34** (*cis*:*trans* = 7:1) and a 17% yield of **35**. Spectral data for **35**: ^{1}H NMR ($CDCl_3$)

δ 1.5 (d, 1H, $J = 7$ Hz), 1.7 (d, 1H, $J = 7$ Hz), 3.3 (s, 3H), 4.5 (m, 2H), 5.1 (m, 2H), 7.1–7.5 (m, 9H); ^{13}C NMR ($CDCl_3$) δ 23.2 ($J_{CH} = 160$ Hz), 54.6, 71.2, 72.0, 72.7, 98.0, 128.23, 128.26, 128.32, 128.37, 128.44, 128.94, 129.0, 137.2, 139.9, 140.2 (colorless oil).

Repeating the reaction under the same conditions in hexane as solvent gave a 60% yield of **34** as a 7:1 mixture of *cis*:*trans* isomers. Less than <1% yield of **35** was observed by ^{1}H NMR. Repeating the reaction under the same conditions in acetonitrile as solvent gave a 56% yield of **34** as an 8:1 mixture of *cis*:*trans* isomers along with a 6% yield of **35**.

When the reaction was carried out as described above in THF in the presence of of 10 eq of CD_3OD the products were purified to give **34** in 26% yield which contained less than 5% deuterium in the methoxyl group and a 62% yield of **35** which contained less than 10% deuterium in the methoxyl group.

4.11. Reaction of the para-methoxyl complex *38* with ketene acetal *20*

A sample of 0.0738 g of **20** was allowed to react with 0.1679 g of carbene complex **38** in 14 mL THF at 70 °C under 800 psi CO for 50 h. The reaction mixture was directly purified on silica gel to give a 31% yield of the cyclic orthoester **41** and a 40% yield of the cyclopropananone acetal **42**. The orthoester **41** was formed as a single diastereomer (*cis*:*trans* $\geqslant$ 10:1). Spectral data for **41**: ^{1}H NMR ($CDCl_3$) δ 2.40 (dd, 1H), 2.69 (dd, 1H), 3.67 (s, 3H), 3.71 (s, 3H), 4.07 (m, 1H), 4.48 (d, 1H, $J = 17$ Hz), 5.42 (d, 1H, $J = 17$ Hz), 5.62 (d, 1H, $J = 9$ Hz), 6.17 (d, 1H, $J = 7$ Hz), 6.53 (d, 2H, $J = 7$ Hz), 6.80 (t, 1H, $J = 7$ Hz), 6.85 (d, 1H, $J = 7$ Hz), 6.95–7.05 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 42.1, 47.1, 51.6, 54.6, 65.6, 85.4, 112.9, 114.8, 122.2, 122.6, 126.3, 126.5, 126.9, 128.0, 129.9, 131.2, 136.9, 137.5, 158.9; IR (CH_2Cl_2) 1612w, 1513m cm^{-1} (colorless oil). Spectral data for **42**: 40% yield, ^{1}H NMR ($CDCl_3$) δ 1.44 (d, 1H, $J = 7$ Hz), 1.68 (d, 1H, $J = 7$ Hz), 3.27 (s, 3H), 3.83 (s, 3H), 4.55 (d, 1H, $J = 18$ Hz), 4.67 (d, 1H, $J = 18$ Hz), 5.05 (d, 1H, $J = 17$ Hz), 5.13 (d, 1H, $J = 17$ Hz), 6.93 (d, 2H, $J = 7$ Hz), 7.06 (d, 1H, $J =$ Hz), 7.15–7.25 (m, 3H), 7.38 (d, 2H, $J = 7$ Hz); ^{13}C NMR ($CDCl_3$) δ 22.6, 54.6, 55.3, 63.0, 70.7, 72.1, 96.9, 113.7, 127.3, 127.4, 127.5, 127.6, 129.0, 129.3, 138.6, 138.7, 159.0; IR (neat) 1610m, 1513s, 1459m, 1431m, 1302m, 1247s, 1176s cm^{-1}. Anal. Calc. for $C_{19}H_{20}O_4$: C, 73.06; H, 6.45. Found: C, 73.01; H, 6.41%. Colorless oil.

4.12. Cross-over experiment with complexes *37* and *38*

A mixture of 0.1405 g of carbene complex **37** and 0.0842 g of carbene complex **38** was reacted with 0.7432 mmol of ketene acetal **20** in a 0.05 M solution of THF under 800 psi CO at 70 °C for 36 h. The crude reaction mixture was purified to give a 7% yield of **40**, a 29% yield **42**, a 60% yield of **39** and a 23% yield of **41**. Compounds **42** and **39** were not separable and the yields were calculated from the ^{1}H NMR spectrum. The ^{1}H NMR integration of the OCH_3 on the sp^3-carbon in each product was used to calculate the percentage of methoxyl group exchange during the reaction. Compounds **39** and **40** contained greater than 95% deuterium and compounds **41** and **42** contained less than 5% deuterium. Other than the deuterated methoxyl group, the ^{1}H NMR spectrum of **39** and **40** were identical to those of their protio analogs *cis*-**34** and **35**, respectively.

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