Addition of Et$_3$B to α,β-Unsaturated Alkoxychromium(0) Carbene Complexes
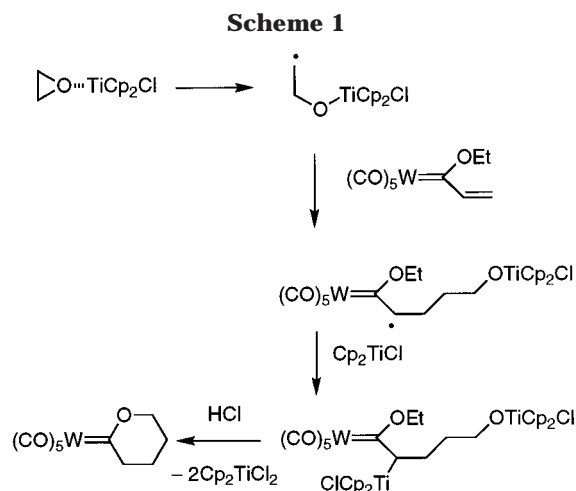
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Summary: Reactions of the α,β-unsaturated alkoxychromium(0) carbenes **1**, **2**, **5**, *and* **6** *with Et$_3$B in THF solution at room temperature, in the presence of oxygen as radical initiator, generate the products derived from 1,4-radical addition. The reaction can be interpreted through the initial formation of the delocalized intermediate radical* **11**, *from which either addition products or a competitive polymerization process are obtained.*

Scheme 1

The isolobal analogy principle[1] states that α,β-unsaturated alkoxychromium(0) carbenes should behave as α,β-unsaturated organic esters in processes taking place outside of the coordination sphere of the metal.[2] This is the case for most of the nucleophilic additions to these systems.[3] Recently, we[4] and others[5] have shown that the metal can play a key role in the reactions of α,β-unsaturated alkoxychromium(0) carbene complexes with nucleophiles. In the course of our work in these and related processes,[6] we realized that the additions of radicals to chromium(0) carbene complexes were practically unknown, in clear contrast with the plethora of papers describing the reactivity of these substrates toward charged nucleophiles.[3] Merlic in his pioneering work reported the stoichiometric generation of alkyl radicals from epoxides and [Cp$_2$TiCl]$_2$ and subsequent trapping by α,β-unsaturated alkoxytungsten(0) carbenes (Scheme 1).[7] This approach has been used recently by Dötz to prepare carbohydrate-modified fused pyranosylidene tungsten(0) and chromium(0) carbene complexes, by addition of epoxides to monosaccharide-derived vinylcarbene complexes catalyzed by [Cp$_2$TiCl]$_2$.[8] The use of other, more conventional methodologies for radical additions to group 6 (Fischer) carbene complexes may be thwarted by the ability of these complexes to react with the reagents used for the generation of the radicals. Thus, for example, carbene insertion into Sn−H[9] and Si−H[10] bonds precludes the use of these types of reagents for radical generation. Other methods to generate radicals usually employ

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harsh reaction conditions which are incompatible with the organometallic substrate.[11]

With these premises in hand and in a search for methodologies to effect radical additions to chromium-(0) carbene complexes, we focused our interest on two well-established reagents in radical chemistry, namely alkylboranes[12] and Barton esters.[13] In both cases, the reactions require very mild thermal (alkylboranes) or photochemical (Barton esters) conditions which may, in principle, warrant their compatibility with the organometallic substrate. Reported herein is the successful implementation of the first approach: the uncatalyzed transfer of an ethyl group from Et$_3$B to α,β-unsaturated alkoxychromium(0) carbenes under conditions that maintain the integrity of the metal−carbene bond.

The reactions of chromium(0) carbene complexes **1** and **2** and ester **3** (Figure 1) were studied first under different conditions. Irradiation (300 W, tungsten lamp, Pyrex) of equimolar mixtures of the corresponding metal carbene and the ester **3** in Cl$_2$CH$_2$ at 0 °C consistently resulted in the disappearance of **3** and the recovering of unreacted metal−carbene complex. The use of different temperatures, solvents, or source of light (sunlight) did not give any other result except for the presence, in some cases, of variable amounts of the ester derived from the oxidation of the Fischer carbene.
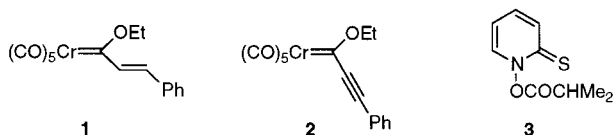

Figure 1.

With these disappointing results, we turned our attention to Et$_3$B, since it is well-known that this reagent adds to α,β-unsaturated carbonyl derivatives at room temperature or below.[12] Thus, the reaction of complex **1** and Et$_3$B (3 mol/mol of complex **1**) in dry THF and under an argon atmosphere yielded the new chromium(0) carbene complex **4**, which was isolated as pure material in 31% yield after column chromatography.[14]

The solvent was used without previous degasification to maintain traces of oxygen (see below), but an argon atmosphere was required to avoid the slow oxidation of the complex. Furyl- and thienyl-substituted chromium-(0) carbene complexes **5** and **6** also yielded the corresponding addition products **7** and **8** in 23% and 26% yields, respectively (Scheme 2). The less reactive aminocarbene complex **9** was recovered unaltered under these reaction conditions.

Scheme 2
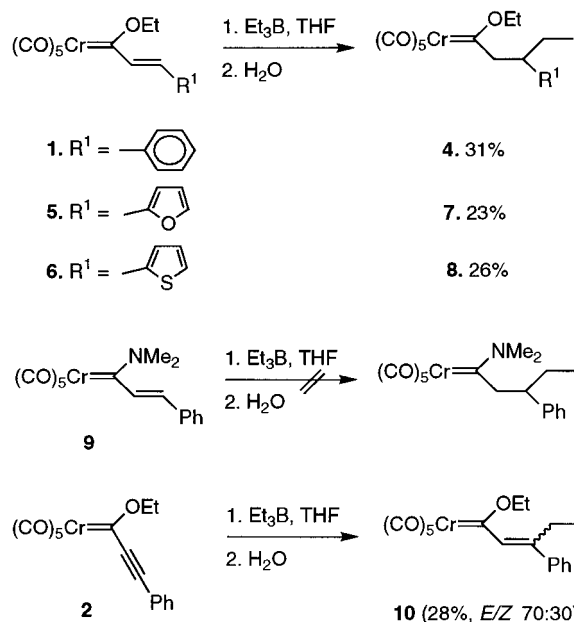
The reaction of chromium carbene **2** was assayed next. In this case, higher amounts of Et$_3$B (up to 6 mol/mol of complex **2**) were needed to obtain acceptable conversions, and complex **10** was isolated in 28% yield as an inseparable 7:3 mixture of *E/Z* isomers (Scheme 2).[14] Lower amounts of Et$_3$B resulted in the recovery of unreacted starting material, together with variable quantities of ethyl phenylpropiolate derived from the oxidation of the starting complex.

To interpret these results, we could consider the initial conjugate addition of an ethyl radical (produced from Et$_3$B by the traces of oxygen in the solvent[12]) to the C=C double bond of the carbene complex, leading to the formation of the radical intermediate **11** (Scheme 3). This species can be described by means of two extreme forms, a chromium-centered radical and a carbon-centered radical. The reaction of the chromium-centered radical **11** with an excess of Et$_3$B would form the enolate-like chromium−boron intermediate **12**, together with a new ethyl radical. Protonation of **12** would yield the isolated addition products. The presence of substantial amounts of polymeric material in the crude reaction mixtures could be explained by competitive addition of the carbon-centered intermediate **11** to a new molecule of the starting carbene, which would initiate a vinyl-like polymerization.[15]

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(12) For an excellent review on the use of organoboranes in free-radical displacement reactions, see: (a) Brown, H. C.; Midland, M. M. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 692. For recent examples on the use of Et$_3$B as an ethyl-transfer reagent in radical processes, see: (b) Liu, J.-T.; Jang, Y.-J.; Shih, Y.-K.; Hu, S.-R.; Chu, Ch.-M.; Yao, Ch.-F. *J. Org. Chem.* **2001**, *66*, 6021 and pertinent references therein.

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(14) Complexes **4**, **7**, **8**, and **10** were obtained as the sole identifiable products, together with considerable amounts of colored polymeric materials of unknown structure. The yields on complexes **4, 7, 8**, and **10** were estimated to be close to 50% in the reaction mixtures before purification (¹H NMR). No other organic materials were recovered in these reactions.

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Scheme 3
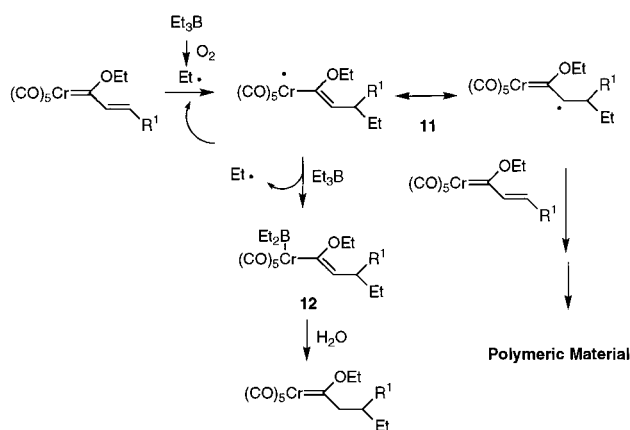
Two facts are remarkable in the reactions disclosed here. First, we have observed the conjugated uncatalyzed addition of an ethyl radical derived from Et₃B to a β-substituted double bond. This is significant, since it is known that uncatalyzed additions of Et₃B to β-substituted α,β-unsaturated aldehydes or ketones hardly occur.[12] Furthermore, conjugated esters are not suitable substrates for these types of reactions. In fact, we have found that *trans*-ethylcinnamate is recovered unaltered after being treated with an excess of Et₃B (6 equiv) in THF, at room temperature for 72 h. Our results demonstrate one more time the exceptional reactivity of α,β-unsaturated group 6 Fischer carbene complexes in comparison to their organic counterparts. The main shortcoming of the radical additions described here is that the reaction products are obtained in low yield, possibly due to a competitive radical polymerization. Finally, the reasons that radicals derived from Barton ester **3** fail to add to α,β-unsaturated alkoxychromium(0) carbene complexes **1** and **2** under the conditions described are not clear at the moment.

In conclusion, a new process of conjugate addition of radicals to α,β-unsaturated alkoxychromium(0) carbene complexes has been reported. Both alkenyl- and alkynylchromium(0) carbenes are reactive toward Et₃B, yielding products derived from the 1,4-radical addition. The reaction could be interpreted through the initial formation of a delocalized intermediate radical, from which either the addition process or a competitive polymerization reaction is obtained. Further work in the search for other radical precursors compatible with the M=C bond is currently underway in our laboratories.

Experimental Section

General Considerations. ¹H NMR and ¹³C NMR spectra were obtained in CDCl₃, on Varian XL-300S (299.94 MHz for ¹H and 75.43 MHz for ¹³C), Bruker 250-AC (250.13 MHz for ¹H and 62.90 MHz for ¹³C), Bruker 200-AC (200.13 MHz for ¹H and 50.03 for ¹³C MHz), and Bruker Avance-300 (300.13 MHz for ¹H and 75.48 MHz for ¹³C) spectrometers. Chemical shifts are given in ppm relative to TMS (¹H, 0.0 ppm) or CDCl₃ (¹³C, 77.0 ppm). IR spectra were taken on a Perkin-Elmer 781 spectrometer. Merck silica gel (230−400 mesh) was used as the stationary phase for purification of crude reaction mixtures by flash chromatography. Identification of products was made by TLC (Kiesegel 60F-254), and UV light (λ = 254 nm) or iodine was used to develop the plates. All commercially available compounds were used without further purification.

The following products were prepared according to literature methods: pentacarbonyl[ethoxy(phenylethenyl)carbene]chromium(0),[16] pentacarbonyl[ethoxy[2-(2-furyl)ethenyl]carbene]chromium(0),[16] pentacarbonyl[ethoxy[2-(2-thienyl)ethenyl]carbene]chromium(0),[16] and pentacarbonyl[ethoxy(phenylethynyl)carbene]chromium(0).[17]

General Procedure for the Reaction of Complexes 1, 2, 5, and 6 with Et₃B. To a solution of the corresponding complex under argon in anhydrous (nondegasified) THF at room temperature was added by syringe 1.0 equiv of Et₃B (1.0 M in THF) over a period of 10 min. This solution was stirred for 8 h before another portion of Et₃B (1.0 equiv) was added, and the stirring was continued overnight. Finally, to the resulting mixture was added another portion of Et₃B (1.0 equiv.) until complete disappearance of the starting material (checked by TLC). The reaction was quenched with water (2.0 equiv.), concentrated under vacuo and diluted with Et₂O. The insoluble materials were filtered off through Celite, and the residue was purified by flash column chromatography.

Reaction of Pentacarbonyl[ethoxy(phenylethenyl)-carbene]chromium(0) (1) with Et₃B. 4 was prepared by the general procedure with 310 mg (0.88 mmol, 1 equiv) of **1** and 2.64 mL (2.64 mmol, 3 equiv) of Et₃B in 6 mL of THF. After 24 h of reaction the crude mixture was quenched, filtered, and concentrated under reduced pressure, and the residue was purified by chromatography on silica gel (hexane to AcOEt) to afford 102.6 mg (31%) of **4** as a deep yellow oil. ¹H NMR: δ 0.69 (t, *J* = 7.3 Hz, 3H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.54 (dq, *J* = 7.3 Hz, *J* = 7.2 Hz, 2H), 2.94 (dt overlapped, *J* = 7.2 Hz, 1H), 3.59 (m, 2H), 4.84 (q, *J* = 7.1 Hz, 2H), 7.05−7.23 (m, 5H). ¹³C NMR: δ 358.9, 222.6, 216.2, 143.6, 128.2, 127.4, 126.2, 77.8, 69.5, 45.2, 29.2, 14.5, 12.0. IR (film): 2062, 1940 cm⁻¹. Anal. Calcd for C₁₈H₁₈O₆Cr: C, 56.55; H, 4.75. Found: C, 56.35; H, 4.83.

Reaction of Pentacarbonyl[ethoxy[2-(2-furyl)ethenyl]carbene]chromium(0) (5) with Et₃B. 7 was prepared by following the general procedure with 100 mg (0.29 mmol, 1 equiv) of **5** and 0.87 mL (0.87 mmol, 3 equiv) of Et₃B in 3 mL of THF. After 24 h of reaction the crude mixture was quenched, filtered, and concentrated under reduced pressure, and the residue was purified by chromatography on silica gel (hexane to AcOEt) to afford 24.6 mg (23%) of **7** as a deep yellow oil. ¹H NMR: δ 0.77 (t, *J* = 7.3 Hz, 3H), 1.42−1.58 (m, 5H), 3.01−3.15 (m, 1H), 3.42−3.67 (m, 2H), 4.94 (q, *J* = 7.0 Hz, 2H), 5.87 (m, 1H), 6.18 (m, 1H), 7.19 (m, 1H). ¹³C NMR: δ 358.1, 223.8, 216.4, 157.0, 141.0, 110.0, 105.3, 78.0, 66.9, 38.4, 27.2, 14.9, 12.0. IR (film): 2062, 1936 cm⁻¹. Anal. Calcd for C₁₆H₁₆O₇Cr: C, 51.62; H, 4.33. Found: C, 51.48; H, 4.45.

Reaction of Pentacarbonyl[ethoxy[2-(2-thienyl)ethenyl]carbene]chromium(0) (6) with Et₃B. 8 was prepared by following the general procedure with 250 mg (0.70 mmol, 1 equiv) of **6** and 2.10 mL (2.10 mmol, 3 equiv) of Et₃B in 6 mL of THF. After 24 h of reaction the crude mixture was quenched, filtered, and concentrated under reduced pressure, and the residue was purified by chromatography on silica gel (hexane to AcOEt) to afford 69.4 mg (26%) of **8** as a deep yellow oil. ¹H NMR: δ 0.78 (t, *J* = 7.2 Hz, 3H), 1.45 (t, *J* = 7.1 Hz, 3H), 1.57 (m, 2H), 3.29 (dt overlapped, *J* = 7.2 Hz, 1H), 3.60 (d, *J* = 7.2 Hz, 2H), 4.93 (q, *J* = 7.1 Hz, 2H), 6.67 (m, 1H), 6.83 (m, 1H), 7.04 (m, 1H). ¹³C NMR: δ 357.2, 223.7, 216.2, 145.1, 126.4, 123.6, 122.8, 78.0, 70.1, 40.1, 30.3, 14.6, 12.0. IR (film): 2062, 1927 cm⁻¹. Anal. Calcd for C₁₆H₁₆O₆SCr: C, 49.48; H, 4.15. Found: C, 49.29; H, 4.25.

Reaction of Pentacarbonyl[ethoxy(phenylethynyl)-carbene]chromium(0) (2) with Et₃B. To a solution of 50 mg (0.14 mmol, 1 equiv) of **2** in anhydrous THF (3 mL) at room temperature was added by syringe 2.0 equiv of Et₃B (1.0 M in THF) over a period of 10 min. This solution was stirred for 30

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(17) Aumann, R.; Hinterding, P. *Chem. Ber.* **1993**, *126*, 421.

min, and then another 4.0 equiv was added (1.0 equiv every 30 min). After 3 h of reaction the crude mixture was quenched with water (2.0 equiv), concentrated under vacuum, diluted with Et$_2$O, and filtered through Celite. The ^{1}H NMR spectrum of the crude reaction mixture showed the presence of **10** as a 68:32 mixture of *E* and *Z* isomers. After chromatography on silica gel (hexane to AcOEt), compound **10 (**15 mg, 28%) was obtained as an inseparable mixture of *E* and *Z* isomers (70: 30) and as a bright red oil. ^{1}H NMR: δ 0.84 (t, J = 7.1 Hz, 2.4H), 0.95 (t, J = 7.5 Hz, 0.6H), 1.01 (t, J = 7.4 Hz, 2.4H), 1.64 (t, J = 7.1 Hz, 0.6H), 2.37 (q, J = 7.4 Hz, 1.6H), 2.53 (d, J = 7.5 Hz, 0.4H), 4.51 (q, J = 7.1 Hz, 1.6H), 5.04 (q, J = 7.1 Hz, 0.4H), 6.90−6.95 (m, 1H), 7.18−7.40 (m, 5H). ^{13}C NMR: δ 341.1, 340.7, 224.7, 217.3, 140.7, 140.1, 128.8, 128.6, 128.3, 128.1, 127.9, 127.4, 127.2, 76.8, 76.3, 32.4, 25.6, 15.0, 13.7, 13.6, 12.5. IR (film): 2058, 1942 cm^{-1}. Anal. Calcd for C$_{18}$H$_{16}$O$_6$Cr: C, 56.85; H, 4.24. Found: C, 56.72; H, 4.31.

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