Generation of Reactive Species by One-Electron Reduction of Fischer-Type Carbene Complexes of Group 6 Metals and Their Use for Carbon–Carbon Bond Formation

Kohei Fuchibe[a, c] and Nobuharu Iwasawa*[b]

Abstract: Carbon–carbon bond-forming reactions mediated by one-electron reduction of Fischer-type carbene complexes of Group 6 metals were investigated. In the case of aryl- or silylcarbene complexes of tungsten, the anion radical species generated by one-electron reduction smoothly underwent addition reaction to ethyl acrylate. One-electron reduction of α,β-unsaturated carbene complexes afforded biscarbene complexes by dimerization of the corresponding anion radical species at the position γ to the metal center. In contrast, one-electron reduction of chromium phenyl- or alkylcarbene complexes gave, via carbonyl insertion, α-methoxyacylchromate complexes, which further underwent conjugate addition to various electron-poor olefins to give the corresponding α-methoxyketones.

Keywords: carbene ligands · chromium · radical ions · reduction · tungsten

Introduction

Since their first synthesis reported by Fischer and Maasböl,[1] Fischer-type carbene complexes of Group 6 metals have attracted much interest, not only from complex chemists but also from organic chemists due to their unique characteristics. In particular, over the last two decades, these carbene complexes have found increasing use as synthetic reagents by exploiting their unique reactivities,[2] and various useful reactions, including benzannulation[2a] and ketene formation,[2b] have been developed.

One of the most important properties of these complexes is their high electrophilicity. As the Fischer-type carbene complexes of Group 6 metals usually contain five carbonyl ligands which behave as strong π acids, the carbon–metal double bond is highly polarized, so that the carbene carbon atom is electrophilic (Figure 1). The carbon–metal double bond exhibits similar properties to the carbonyl group, and alkoxy-substituted Fischer-type carbene complexes behave like esters.

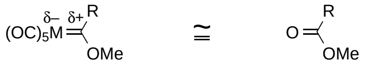

Figure 1. Similarity of Fischer-type carbene complexes to esters. M = Group 6 metal.

For example, various nucleophiles such as amines[3] and organolithium reagents[4] perform nucleophilic attack on the carbene carbon atom of complexes **1** to give tetrahedral intermediates **2**, which usually expel methanol to afford nucleophile-substituted carbene complexes **3**, which are further converted to demetalated products should they be unstable.[2f, 4d] Furthermore, alkyl-substituted carbene complexes **4** are readily deprotonated with various bases to give stable anionic species **5**,[5] which react like ester enolates with electrophiles such as alkyl halides (or pseudohalides)[6] and aldehydes[7] to give α-substituted carbene complexes **6** (Scheme 1).

It has also been reported that when phenylcarbene complexes **7** (M = Cr, W) were treated with Na/K in THF/HMPA at −78 °C, one-electron reduction of **7** took place to yield the stable anion radical **8**, which corresponds to ketyl radical formation from carbonyl compounds (Scheme 2).[8]

Although these anion radical species possess a unique structure in which a carbon-centered radical is substituted by a pentacarbonylmetal moiety, they have never been employed in further carbon–carbon bond forming reactions.

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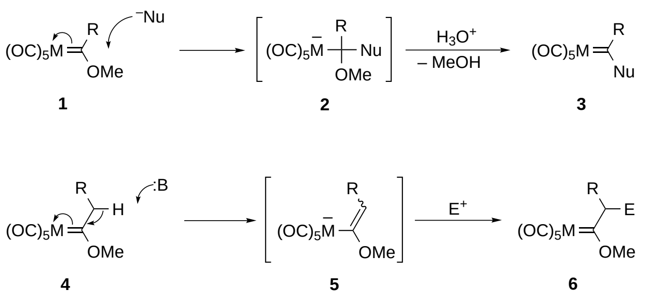
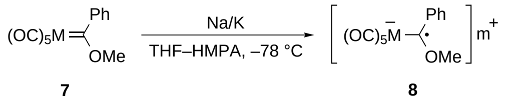


Scheme 1. Characteristic behavior of Fischer-type carbene complexes of Group 6 metals. M = Group 6 metal.

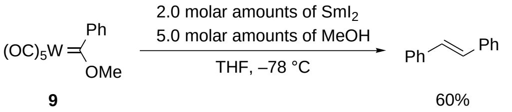


Scheme 2. One-electron reduction of phenylcarbene complexes with alkali metals. M = Group 6 metal, m = Na or K.

Here we report details of our investigations on the development of carbon–carbon bond forming reactions utilizing the novel reactive species generated by samarium(II) iodide-mediated one-electron reduction of Fischer-type carbene complexes of Group 6 metals.[9]

Results and Discussion

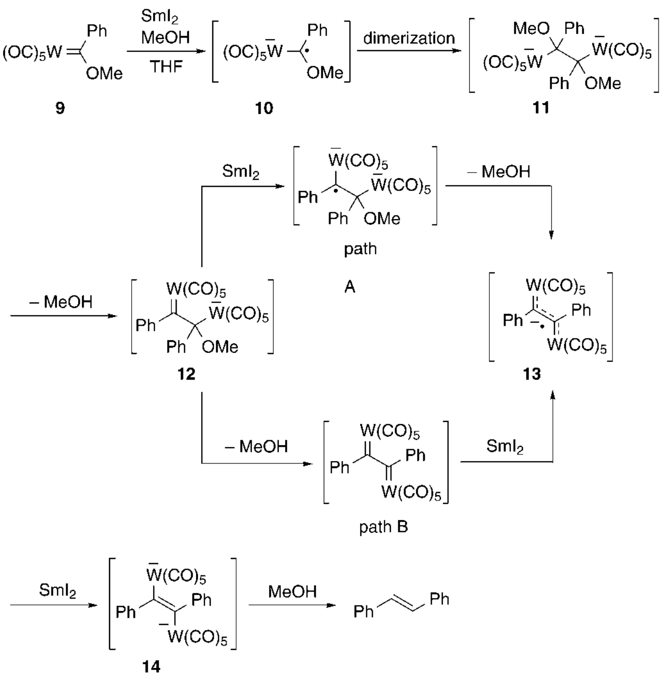
One-electron reduction of tungsten aryl- or silylcarbene complexes and their coupling reaction with ethyl acrylate: We first examined the possibility of using samarium(II) iodide as a one-electron reductant[10] for Fischer-type carbene complexes. When the phenylcarbene tungsten complex **9** was treated with 2.0 molar amounts of samarium(II) iodide in the presence of 5.0 molar amounts of methanol at –78 °C in THF, the characteristic red color of **9** disappeared within a few minutes and *trans*-stilbene was formed in 60% yield (Scheme 3).



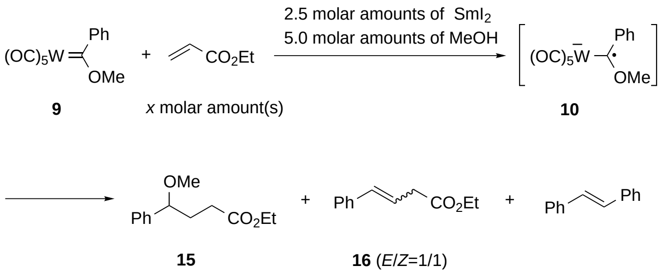
Scheme 3. One-electron reduction of phenylcarbene complex **9**.

The reaction is presumed to proceed as follows (Scheme 4): one-electron reduction of **9** gives anion radical **10**, which dimerizes to give dianion intermediate **11**. Dianion **11** is then protonated at the oxygen atom of the methoxyl group, and elimination of methanol gives monoanion intermediate **12**, which leads to anion radical intermediate **13** by a reduction/elimination (path A) or by an elimination/reduction (path B). The dimerized intermediate **13** is further reduced to give alkenylditungsten intermediate **14**, and protonation of **14** with methanol yields *trans*-stilbene.

As samarium(II) iodide was effective in reducing **9**, we next examined the reaction in the presence of an electron-poor olefin as a radical acceptor (Scheme 5). When **9** was treated with 2.5 molar amounts of samarium(II) iodide in the presence of an equimolar amount of ethyl acrylate and 5.0 molar amounts of methanol at –78 °C in THF, the colors of samarium(II) iodide and **9** disappeared within a few minutes, and methyl ether **15** and olefin **16** were obtained, albeit in low yields (9% each). These coupling products were accompanied by *trans*-stilbene in 30% yield, but this stilbene formation was completely suppressed by using an excess of ethyl acrylate (6.1 molar amounts), to give **15** and **16** in 38 and 34% yield, respectively.



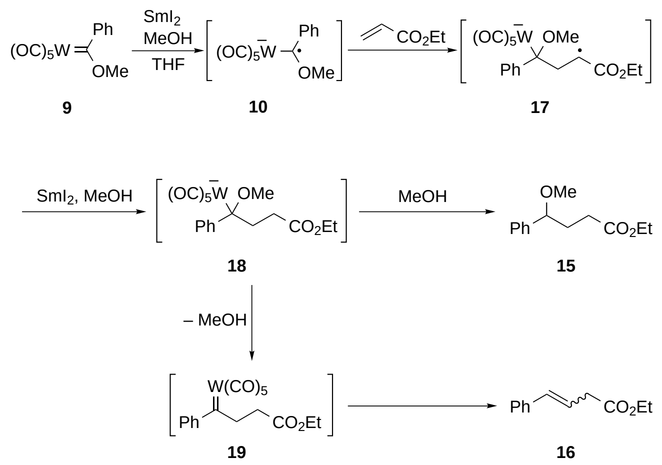
Scheme 4. Proposed mechanism for formation of *trans*-stilbene. The cation $[SmI_2]^+$ is omitted for clarity.



	15	16	
x=1.0	9%	9%	30%
x=6.1	38%	34%	–

Scheme 5. Coupling of **9** with ethyl acrylate. The cation $[SmI_2]^+$ is omitted for clarity.

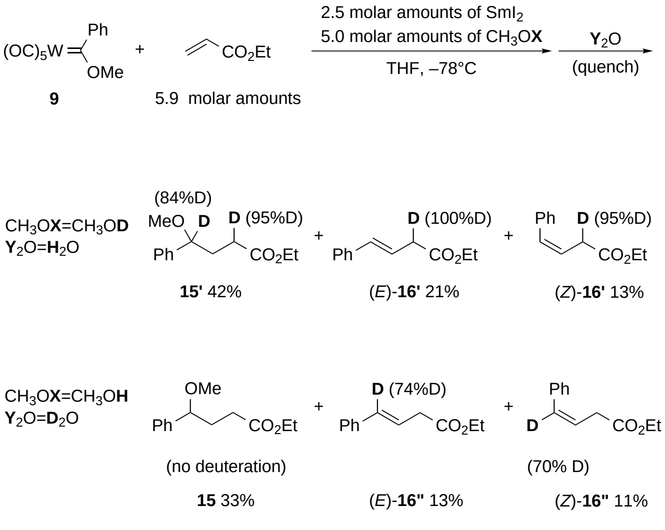
Scheme 6 shows a plausible mechanism for this reaction. Radical anion **10**, generated by one-electron reduction of **9**, undergoes radical addition to ethyl acrylate. The resulting radical anion intermediate **17** is further reduced by samarium(II) iodide and then protonated by methanol to give alkyltungsten intermediate **18**. Methyl ether **15** is produced by protonation of the carbon–tungsten bond of the intermediate



Scheme 6. A plausible mechanism for the formation of **15** and **16**. The cation $[SmI_2]^+$ is omitted for clarity.

18, while the olefin **16** is thought to be produced by 1,2-hydrogen migration of the unstable carbene intermediate **19**, which is generated from **18** by elimination of methanol.

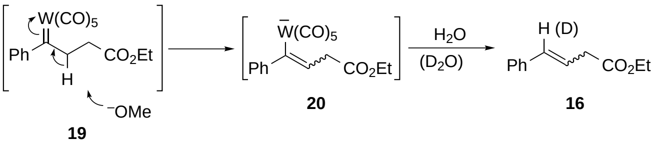
To confirm the mechanism described above, deuterium-labeling experiments were carried out. First, we carried out the reaction in the presence of CH_3OD as a deuterium source and performed workup with H_2O (pH 7 phosphate buffer, Scheme 7). The methyl ether **15** was deuterated at the position α to the ethoxycarbonyl group and α to the methoxyl group (**15′**, 95 and 84 % D, respectively), while the *E* and *Z* isomers of olefin **16** were deuterated only at the position α to the ethoxycarbonyl group ((*E*)-**16′** and (*Z*)-**16′**, 100 and 95 % D, respectively).



Scheme 7. Deuterium-labeling experiments.

On the other hand, when the same reaction was carried out in the presence of CH_3OH and workup was performed with D_2O, the (*E*)- and (*Z*)-**16** were deuterated at the position α to the phenyl group ((*E*)-**16″** and (*Z*)-**16″**, 74 and 70 % D, respectively), while the methyl ether **15** was not deuterated at all.

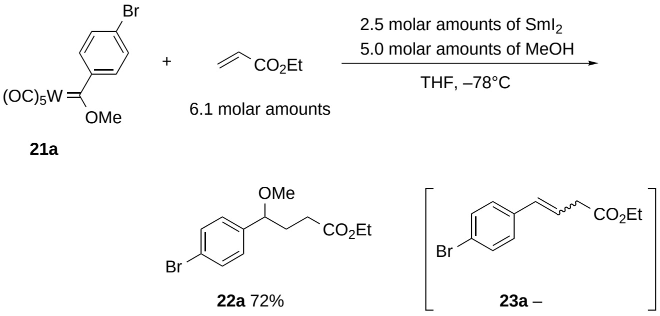
On the basis of these results, we now believe that methyl ether **15** is produced by protonation of the carbon–tungsten bond of the intermediate **18** by the methanol in the reaction mixture, while olefin **16** is produced by deprotonation of the unstable carbene intermediate **19**,[5] followed by direct protonation of the carbon–tungsten bond of the resulting alkenyltungsten intermediate **20**, not by the methanol in the reaction medium, but by the water employed for workup (Scheme 8).[11]



Scheme 8. Mechanism for formation of **16**. The cation $[SmI_2]^+$ is omitted for clarity.

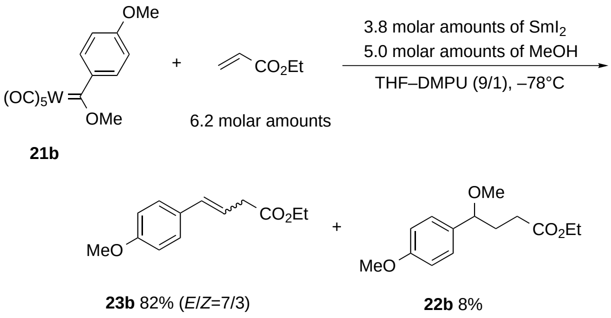
This reaction is applicable to arylcarbene complexes bearing electron-withdrawing or electron-donating groups at the *para* position of the phenyl group.

One-electron reduction of *p*-bromophenylcarbene complex **21a** went to completion within a few minutes at –78 °C to give methyl ether **22a** in 72 % yield without formation of the olefin **23a** (Scheme 9).



Scheme 9. Reaction of *p*-bromophenylcarbene complex **21a**.

The reaction of *p*-methoxyphenylcarbene complex **21b** was slow in THF, but use of the mixed solvent THF/DMPU (9/1) enabled the reaction to proceed smoothly, and in this case olefin **23b** was obtained as the major product (82 % yield) accompanied by methyl ether **22b** (8 % yield) (Scheme 10).[12]



Scheme 10. Reaction of *p*-methoxyphenylcarbene complex **21b**.

The effect of the *para* substituent on the product distribution can be explained as follows (Figure 2): the bromine atom in intermediate **24a** retards elimination of methanol and makes protonation of the carbon–tungsten bond of **24a** relatively faster to give the methyl ether **22a** as the sole product. On the other hand, the methoxyl group at the *para* position in **24b** accelerates elimination of methanol, and this results in selective formation of olefin **23b**.

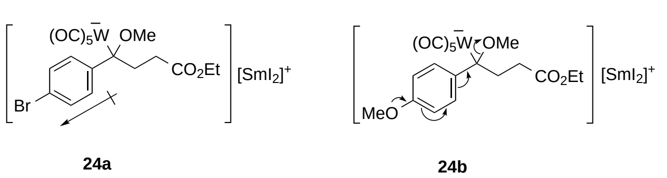
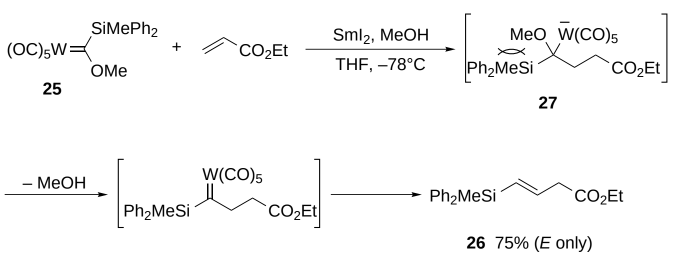


Figure 2. The substituent effect of a bromine atom and a methoxyl group at the *para* position on the intermediate **24a** or **24b**.

Reaction of silylcarbene complex **25** also proceeded smoothly, and vinylsilane derivative **26** was obtained in 75 % yield exclusively as the *E* isomer (Scheme 11). Probably, the bulky silyl group accelerates elimination of methanol from intermediate **27**.



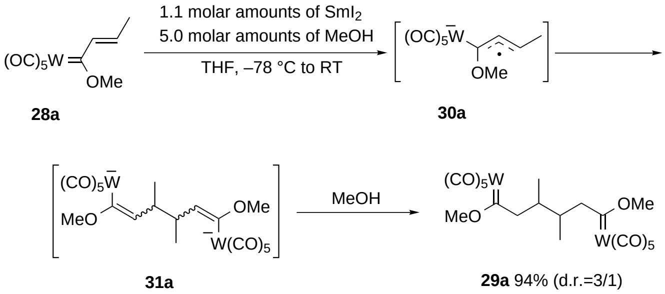
Scheme 11. Reaction of silylcarbene complex **25** with ethyl acrylate. The cation $[SmI_2]^+$ is omitted for clarity. **25**/ethyl acrylate/SmI_2/MeOH = 1/22/3/5.

However, a similar reaction of the phenylcarbene complex **9** with methyl crotonate failed, and only *trans*-stilbene was obtained in 52 % yield. This suggests that the rate of addition of anion radical **10** is greatly decreased by the presence of the β-methyl group of the crotonate.[13] Furthermore, reaction of a butylcarbene complex of tungsten (with a butyl group instead of the phenyl group in **9**) with ethyl acrylate also failed, and no addition products were obtained. Samarium(II) iodide was consumed in the reduction of ethyl acrylate when the reaction mixture was warmed to room temperature, and the carbene complex was recovered in 56 % yield. Thus, the present method for the generation and reaction of tungsten-containing radical species is limited to aryl- and silylcarbene complexes.

These samarium(II) iodide-mediated one-electron reductions of Fischer-type carbene complexes can be regarded as an umpolung of the carbene complexes. The carbene carbon atom of Fischer-type carbene complexes of Group 6 metals is highly electrophilic. One-electron reduction of the complexes makes the carbene carbon atom a nucleophilic radical center, which preferably adds to electron-poor olefins.[14]

Reductive dimerization of α,β-unsaturated carbene complexes: synthesis of biscarbene complexes: We next examined one-electron reduction of α,β-unsaturated carbene complexes in the expectation that dimerization of anion radical species at the position γ to the metal center would give novel biscarbene complexes.[15]

When the *trans*-propenylcarbene tungsten complex **28a** was treated with 1.1 molar amounts of samarium(II) iodide in the presence of 5.0 molar amounts of methanol at −78 °C in THF (Scheme 12), reduction went to completion within a few minutes to give the desired biscarbene complex **29a** in 94 % yield. Thus, dimerization of **30a** selectively occurred at the position γ to the metal center.[16, 17]

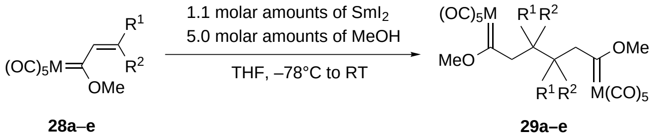


Scheme 12. One-electron reduction of *trans*-propenylcarbene complex **28a**. The cation $[SmI_2]^+$ is omitted for clarity.

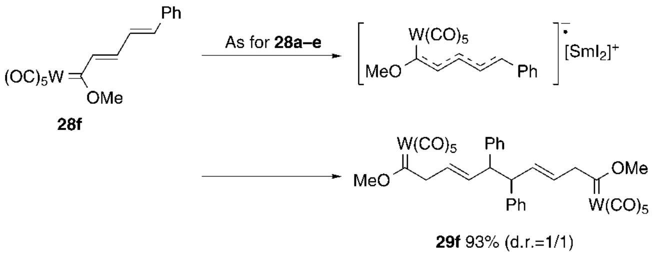
Various kinds of α,β-unsaturated carbene complexes, including β,β-dimethyl-substituted carbene complex **28b**, yielded the corresponding biscarbene complexes in good yields (Table 1). Chromium complexes were also suitable for this reaction.[18]

Furthermore, dienylcarbene complex **28f** also underwent reductive dimerization at the terminal position to give biscarbene complex **29f** in 93 % yield (Scheme 13).

Table 1. Synthesis of biscarbene complexes.



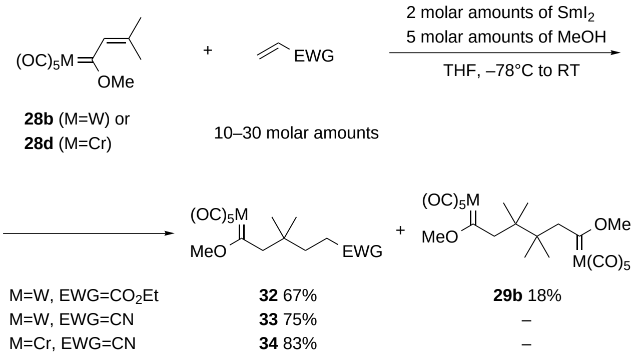
M	R^1	R^2	**28**	Yield of **29** [%] (d.r.)
W	Me	H	**a**	94 (3/1) (**29a**)
W	Me	Me	**b**	83 (**29b**)
W	Ph	H	**c**	67 (1/1) (**29c**)
Cr	Me	Me	**d**	60 (**29d**)
Cr	Me	H	**e**	72 (4/1) (**29e**)



Scheme 13. Reductive dimerization of dienylcarbene complex **28f**.

Although various kinds of biscarbene complexes have previously been synthesized,[19] and recently some of them have been utilized as synthetic reagents,[20] general routes to this type of biscarbene complexes are still limited.[21] This reductive dimerization of α,β-unsaturated carbene complexes can be utilized as a general, efficient, and easy method for the synthesis of symmetrical biscarbene complexes.

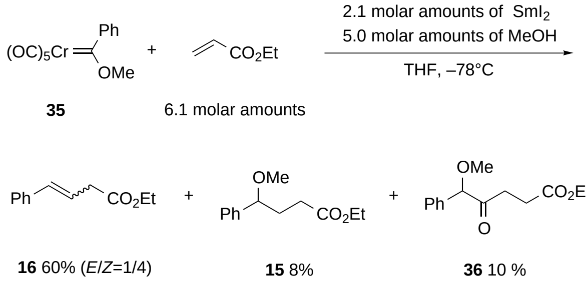
Furthermore, functionalized carbene complexes can be prepared by reductive coupling of α,β-unsaturated carbene complexes with electron-poor olefins. When **28b** or **28d** was treated with 2 molar amounts of samarium(II) iodide in the presence of a large excess of an electron-poor olefin and 5 molar amounts of methanol, the functionalized carbene complexes **32**–**34** were obtained in good yields (Scheme 14).



Scheme 14. Reductive coupling of **28b** or **28d** with electron-poor olefins. EWG = electron-withdrawing group.

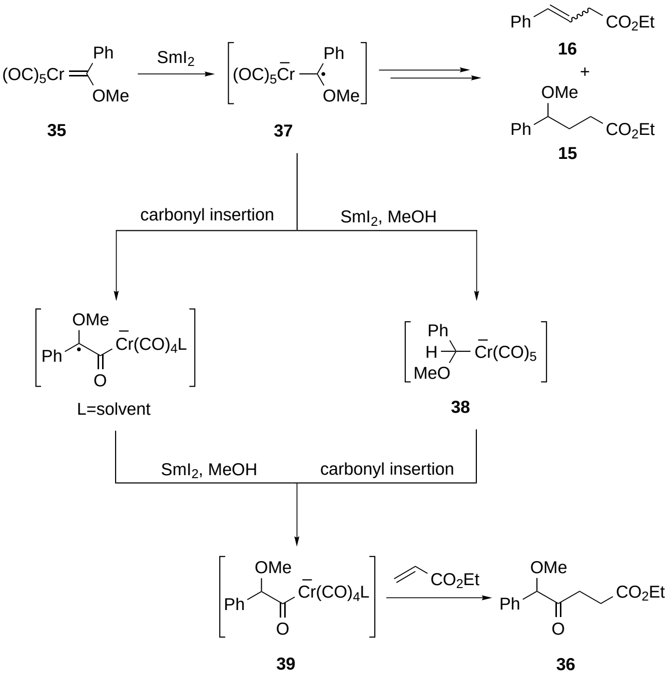
Generation of α-methoxyacylchromate complexes by one-electron reduction of chromium carbene complexes: As described in Scheme 5, one-electron reduction of tungsten phenylcarbene complex **9** yielded anion radical **10**, which underwent addition to ethyl acrylate. We next examined the one-electron reduction of chromium phenylcarbene complex **35** and found that an α-methoxyacylchromate complex was produced by carbonyl insertion.

Complex **35** was treated with 2.1 molar amounts of samarium(II) iodide in the presence of 6.1 molar amounts of ethyl acrylate and 5.0 molar amounts of methanol at $-78\,^{\circ}C$ in THF. The rate of reduction was slower than that of tungsten complex **9**, but **35** was completely consumed after a few hours to give the olefin **16** and the methyl ether **15** in 60 and 8% yield, respectively. Interestingly, formation of a small amount of α-methoxyketone **36** was detected in this reaction of chromium complex **35** (Scheme 15).



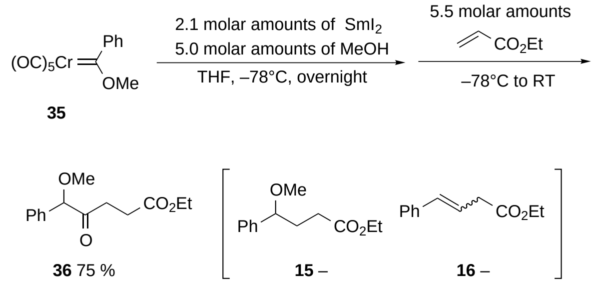
Scheme 15. Reaction of phenylcarbene complex of chromium **35**.

Formation of α-methoxyketone **36** suggests that insertion of a carbonyl ligand into the anion radical **37** or its reduced form **38** took place to give α-methoxyacylchromate complex **39** competitively with the direct addition of **37** to the acrylate (Scheme 16). It is presumed that **39** then undergoes conjugate addition to ethyl acrylate to give the α-methoxyketone **36**.[22]



Scheme 16. Supposed mechanism for reaction of the chromium complex **35**. The cation $[SmI_2]^+$ is omitted for clarity.

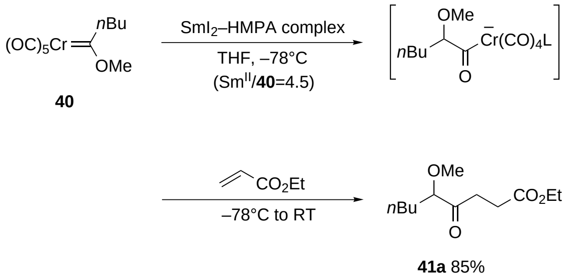
As acylchromate complexes are known to be stable,[23] we examined the possibility of adding the acrylate after reduction of the carbene complex **35** (Scheme 17). Thus, complex **35** was treated with 2.1 molar amounts of samarium(II) iodide in the presence of 5.0 molar amounts of methanol at $-78\,^{\circ}C$ in THF, and after stirring overnight the reaction mixture was treated with 5.5 molar amounts of ethyl acrylate and warmed to room temperature. Usual workup of the reaction mixture gave the desired α-methoxyketone **36** in 75% yield without formation of **15** or **16**.[24]



Scheme 17. Selective formation of **36**.

Thus, chromium carbene complex **35** underwent carbonyl insertion, while the corresponding tungsten complex **9** gave *trans*-stilbene in 60% yield when treated with samarium(II) iodide in the absence of ethyl acrylate. This characteristic difference between tungsten and chromium complexes is probably due to the difference in electronegativity of these metals. As chromium is more electropositive than tungsten (Pauling electronegativities: Cr 1.6, W 1.7), and migratory insertion of a carbonyl ligand is facilitated by the nucleophilicity of the migrating alkyl group, chromium complexes are expected to be more prone to carbonyl insertion than the corresponding tungsten complexes.[25]

We next applied this reaction to alkyl-substituted carbene complexes. Butylcarbene complex **40** was, however, not reduced by samarium(II) iodide even under reflux in THF, probably due to the electron-donating property of the butyl group. This inertness was overcome by using samarium(II) iodide–HMPA complex as the one-electron reductant.[26] As shown in Scheme 18, samarium(II) iodide–HMPA complex reduced **40** smoothly at −78 °C, and treatment of the resulting solution with ethyl acrylate afforded the corresponding α-methoxyketone **41a** in 85 % yield.

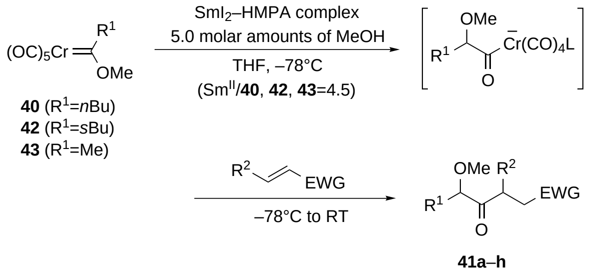


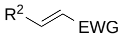
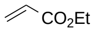
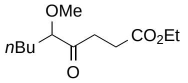
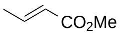
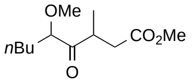
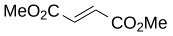
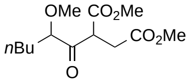
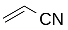
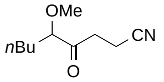
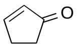
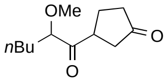
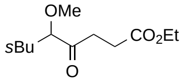
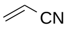
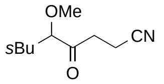
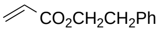
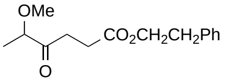
Scheme 18. Reaction of butylcarbene complex **40** with SmI$_2$-HMPA complex.

Table 2 shows the generality of this reaction. The α-methoxyacylchromate complex derived from butylcarbene complex **40** reacted not only with acrylate esters but also with acrylonitrile and cyclopentenone to give the corresponding α-methoxyketones. The reaction could also be applied to *sec*-butyl- and methylcarbene complexes (**42** and **43**).

Söderberg et al. reported that acyl(pentacarbonyl)chromate complexes undergo conjugate addition to electron-poor olefins under thermal (refluxing in THF) or photochemical conditions.[22] It is believed that liberation of one carbonyl ligand from the complex is necessary for olefin coordination to occur. On the other hand, our reaction proceeded between −78 °C and room temperature. This is probably due to facile coordination of the electron-poor olefins to chromium, as only a weakly coordinating solvent molecule occupies the vacant site generated by the carbonyl insertion.[27]

Table 2. Preparation of α-methoxyketones.



R^1		α-methoxyketone	Yield of **41** [%] (d.r.)
*n*Bu (**40**)			85 (**41a**)
*n*Bu (**40**)			46 (81/19) (**41b**)
*n*Bu (**40**)			61 (53/47) (**41c**)
*n*Bu (**40**)			69 (**41d**)
*n*Bu (**40**)			51 (51/49) (**41e**)
*s*Bu (**42**)			65 (55/45) (**41f**)
*s*Bu (**42**)			56 (56/44) (**41g**)
Me (**43**)			55 (**41h**)

Conclusion

The anion radical species generated by one-electron reduction of Fischer-type carbene complexes of tungsten and chromium are suitable for carbon–carbon bond-forming reactions. In the case of aryl- or silylcarbene complexes of tungsten, the anion radicals underwent addition to electron-poor olefins. In contrast, anion radicals derived from chromium carbene complexes gave α-methoxyacylchromate complexes by carbonyl insertion, which further underwent conjugate addition to electron-poor olefins. Furthermore, α,β-unsaturated carbene complexes gave dimerized biscarbene complexes in good yields. Thus, the anion radical species of Fischer-type carbene complexes exhibit distinctive behavior that depends on the nature of the central metal atom and the substituent on the carbene carbon atom.[30]

Experimental Section

General: All reactions were carried out under an argon atmosphere. All materials were purified by distillation or recrystallization before use. NMR spectra were recorded on Bruker DRX500 (500 MHz for ^{1}H, 125 MHz for ^{13}C), JEOL Lambda400 (400 MHz for ^{1}H, 100 MHz for ^{13}C), JEOL AL400 (400 MHz for ^{1}H, 100 MHz for ^{13}C), or JEOL Lambda300 (300 MHz for ^{1}H, 75 MHz for ^{13}C) instruments. Chemical shifts δ for ^{1}H are referenced to residual chloroform ($\delta = 7.24$ ppm) as internal standard. Chemical shifts δ for ^{13}C are referenced to a solvent signal (CDCl$_3$, $\delta = 77.0$ ppm) as internal standard. IR spectra were recorded on JASCO FT/IR-200 or JASCO FT/

IR460PLUS instruments. High-resolution mass spectrometry (HRMS) was conducted with 70 eV electron impact ionization on a JEOL JMS-SX102A instrument with perfluorokerosene as standard. Flash column chromatography and preparative thin layer chromatography (preparative TLC) were conducted on silica gel (Merck Kieselgel 60 Art 7734 and Wako gel B-5F, respectively).

Preparation of carbene complexes: Aryl-, alkyl-, and silylcarbene complexes and α,β-unsaturated carbene complexes, except for **28c** and **28f**, were prepared according to reference [28]. Complexes **28c** and **28f** were prepared according to the method reported by Aumann and Heinen.[7b]

Preparation of samarium(II) iodide: Samarium(II) iodide was prepared from freshly distilled diiodomethane and samarium metal.[10b]

One-electron reduction of tungsten phenylcarbene complex 9 with samarium(II) iodide: A THF solution of samarium(II) iodide (6.4 mL, 0.10 M, 0.64 mmol) was added to a THF solution (1.5 mL) of **9** (140 mg, 0.315 mmol) and methanol (50 μL) at −78 °C. After the mixture was stirred for 2 h, the reaction was quenched with pH 7 phosphate buffer at this temperature. The product was extracted with ethyl acetate four times, and the combined organic phase was dried over anhydrous magnesium sulfate. After evaporation of the solvent, the crude product was purified by preparative TLC (hexane) to give *trans*-stilbene (18 mg, 60%). The spectral data of the product were in complete agreement with those of the authentic sample, which is commercially available.

Reaction of tungsten phenylcarbene complex 9 with ethyl acrylate: A THF solution of samarium(II) iodide (6.8 mL, 0.10 M, 0.68 mmol) was added to a THF solution (3.8 mL) of **9** (120 mg, 0.270 mmol), methanol (53 μL), and ethyl acrylate (162 mg, 1.62 mmol) at −78 °C. After the mixture was stirred for 30 min, the reaction was quenched with pH 7 phosphate buffer at this temperature. The products were extracted with ethyl acetate four times, and the combined organic phase was dried over anhydrous magnesium sulfate. After evaporation of the solvent, the crude product was purified by preparative TLC (hexane/ethyl acetate 8/1) to give ethyl 4-methoxy-4-phenylbutanoate (**15**, 24 mg, 38%) and ethyl 4-phenylbut-3-enoate (**16**, 17 mg, 33%, $E/Z = 47/53$).

Ethyl 4-methoxy-4-phenylbutanoate (15): ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta = 1.22$ (t, ^{3}J(H,H) = 7.2 Hz, 3H; CH$_3$), 1.89–2.11 (m, 2H; CH$_2$), 2.35 (t, ^{3}J(H,H) = 7.4 Hz, 2H; CH$_2$), 3.23 (s, 3H; CH$_3$), 4.09 (q, ^{3}J(H,H) = 7.2 Hz, 2H; CH$_2$), 4.13 (dd, ^{3}J(H,H) = 5.7, 7.8 Hz, 1H; CH), 7.24–7.36 ppm (m, 5H; ArH); ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C): $\delta = 14.2$, 30.6, 33.1, 56.7, 60.3, 82.8, 126.6, 127.7, 128.4, 141.5, 173.5 ppm; IR (neat): $\tilde{\nu} = 2982$, 1735 (C=O), 1106, 702 cm^{-1}; HRMS calcd for $C_{13}H_{18}O_3$ (222.27): 221.1178 $[M-\mathrm{H}]^+$; found: 221.1179 $[M-\mathrm{H}]^+$.

Ethyl 4-phenylbut-3-enoate (16): ^{1}H NMR spectra were in complete agreement with those in the literature.[29]

Deuterium-labeling experiments: The spectral data of the compounds **15′**, **16′**, and **16″** are given below. The percentages of deuterium incorporation were determined by the relative intensity of the peaks versus the methyl signal of the methyl ether moiety for **15′** and versus the methylene signal of the ethyl ester moiety for **16′** and **16″**.

15′: ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta = 1.22$ (t, ^{3}J(H,H) = 7.2 Hz, 3H; CH$_3$), 1.89–2.11 (m, 2H; CH$_2$), 2.32–2.39 (m, 1.05H; CHD, 95% D), 3.23 (s, 3H; CH$_3$), 4.08–4.16 (m, 2.16H; CH$_2$ + CD, 84% D), 7.24–7.36 ppm (m, 5H; ArH).

(*E*)-16′: ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta = 1.28$ (t, ^{3}J(H,H) = 7.2 Hz, 3H; CH$_3$), 3.16–3.22 (m, 1H; CHD, 100% D), 4.17 (q, ^{3}J(H,H) = 7.2 Hz, 2H; CH$_2$), 6.30 (dd, ^{3}J(H,H) = 7.1, 11.8 Hz, 1H; CH), 6.50 (d, ^{3}J(H,H) = 11.8 Hz, 1H; CH), 7.21–7.40 ppm (m, 5H; ArH).

(*Z*)-16′: ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta = 1.26$ (t, ^{3}J(H,H) = 7.2 Hz, 3H; CH$_3$), 3.29–3.38 (m, 1.05H; CHD, 95%D), 4.17 (q, ^{3}J(H,H) = 7.2 Hz, 2H; CH$_2$), 5.90 (dd, ^{3}J(H,H) = 6.3, 7.9 Hz, 1H; CH), 6.64 (d, ^{3}J(H,H) = 7.9 Hz, 1H; CH), 7.23–7.41 ppm (m, 5H; ArH).

(*E*)-16″: ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): $\delta = 1.28$ (t, ^{3}J(H,H) = 7.2 Hz, 3H; CH$_3$), 3.17 (d, ^{3}J(H,H) = 6.7 Hz, 2H; CH$_2$), 4.17 (q, ^{3}J(H,H) = 7.2 Hz, 2H; CH$_2$), 6.24–6.37 (m, 1H; CH), 6.50 (d, ^{3}J(H,H) = 11.8 Hz, 0.26H; CD, 74% D), 7.21–7.40 ppm (m, 5H; ArH).

(*Z*)-16″: ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): $\delta = 1.26$ (t, ^{3}J(H,H) = 7.2 Hz, 3H; CH$_3$), 3.32 (d, ^{3}J(H,H) = 7.5 Hz, 2H; CH$_2$), 4.17 (q, ^{3}J(H,H) = 7.2 Hz, 2H; CH$_2$), 5.83–5.94 (m, 1H; CH), 6.64 (d, ^{3}J(H,H) = 7.9 Hz, 0.30H; CD, 70% D), 7.23–7.41 ppm (m, 5H; ArH).

Reaction of (*p*-bromophenyl)carbene complex 21a with ethyl acrylate: The reaction was carried out in a similar manner as for the reaction of tungsten phenylcarbene complex **9**.

Ethyl 4-(4-bromophenyl)-4-methoxybutanoate (22a): ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta = 1.22$ (t, ^{3}J(H,H) = 7.1 Hz, 3H; CH$_3$), 1.85–2.12 (m, 2H; CH$_2$), 2.34 (t, ^{3}J(H,H) = 7.7 Hz, 2H; CH$_2$), 3.18 (s, 3H; CH$_3$), 4.05–4.13 (m, 3H; CH, CH$_2$), 7.14 (d, ^{3}J(H,H) = 11.0 Hz, 2H; ArH), 7.46 ppm (d, ^{3}J(H,H) = 11.0 Hz, 2H; ArH); ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C): $\delta =$ 14.2, 30.4, 33.0, 56.8, 60.3, 82.1, 121.4, 128.3, 131.6, 140.7, 173.2 ppm; IR (neat): $\tilde{\nu} = 2931$, 1732 (C=O), 1108, 823 cm^{-1}; elemental analysis (%) calcd for $C_{13}H_{17}O_3Br$ (301.2): C 51.84, H 5.69; found C 51.90, H 5.91.

Reaction of *p*-methoxyphenylcarbene complex 21b with ethyl acrylate: A THF solution of samarium(II) iodide (8.0 mL, 0.085 M, 0.68 mmol) was added to a THF solution (3.5 mL) of the tungsten *p*-methoxyphenylcarbene complex **21b** (84 mg, 0.18 mmol), ethyl acrylate (112 mg, 1.12 mmol), methanol (35 μL), and DMPU (0.35 mL) at −78 °C. The blue color of samarium(II) iodide disappeared immediately, and the reaction mixture became heterogeneous. The reaction mixture was stirred for 30 min at this temperature and quenched with pH 7 phosphate buffer. The products were extracted with ethyl acetate four times, and the combined organic phase was dried over anhydrous magnesium sulfate. After evaporation of the solvent, the crude product was purified by preparative TLC (hexane/ethyl acetate 8/1) to give ethyl (*Z*)-4-(4-methoxyphenyl)but-3-enoate ((*Z*)-**23b**, 9.9 mg, 25%), ethyl (*E*)-4-(4-methoxyphenyl)but-3-enoate ((*E*)-**23b**, 22.6 mg, 57%), and ethyl 4-methoxy-4-(4-methoxyphenyl)butanoate (**22b**, 3.6 mg, 8%).

Ethyl (*Z*)-4-(4-methoxyphenyl)but-3-enoate ((*Z*)-23b): ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): $\delta = 1.25$ (t, ^{3}J(H,H) = 7.2 Hz, 3H; CH$_3$), 3.31 (dd, ^{3}J(H,H) = 7.2 Hz, ^{4}J(H,H) = 1.6 Hz, 2H; CH$_2$), 3.80 (s, 3H; CH$_3$), 4.15 (q, ^{3}J(H,H) = 7.2 Hz, 2H; CH$_2$), 5.79 (dt, ^{3}J(H,H) = 7.2, 12.0 Hz, 1H; CH), 6.55 (d, ^{3}J(H,H) = 12.0 Hz, 1H; CH), 6.86 (d, ^{3}J(H,H) = 9.0 Hz, 2H; ArH), 7.20 ppm (d, ^{3}J(H,H) = 9.0 Hz, 2H; ArH); ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C): $\delta = 14.2$, 34.2, 55.3, 60.7, 113.7, 121.8, 129.2, 129.9, 131.4, 158.6, 171.9 ppm; IR (neat): $\tilde{\nu} = 2980$, 1735 (C=C), 1610, 1515, 1180 cm^{-1}; HRMS calcd for $C_{13}H_{16}O_3$ (220.26): 220.1100 $[M]^+$; found: 220.1078 $[M]^+$.

Ethyl (*E*)-4-(4-methoxyphenyl)but-3-enoate ((*E*)-23b): ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): $\delta = 1.26$ (t, ^{3}J(H,H) = 7.2 Hz, 3H; CH$_3$), 3.19 (dd, ^{3}J(H,H) = 7.2 Hz, ^{4}J(H,H) = 1.2 Hz, 2H; CH$_2$), 3.78 (s, 3H; CH$_3$), 4.15 (q, ^{3}J(H,H) = 7.2 Hz, 2H; CH$_2$), 6.14 (dt, ^{3}J(H,H) = 7.2, 16.0 Hz, 1H; CH), 6.41 (d, ^{3}J(H,H) = 16.0 Hz, 1H; CH), 6.82 (d, ^{3}J(H,H) = 9.2 Hz, 2H; ArH), 7.29 ppm (d, ^{3}J(H,H) = 9.2 Hz, 2H; ArH); ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C): $\delta = 14.2$, 38.5, 55.3, 60.7, 113.9, 119.6, 127.4, 129.7, 132.7, 159.1, 171.8 ppm; IR (neat): $\tilde{\nu} = 2985$, 1735 (C=C), 1606, 1511, 1250 cm^{-1}; elemental analysis (%) calcd for $C_{13}H_{16}O_3$ (220.3): C 70.89, H 7.32; found: C 70.92, H 7.54.

Reaction of methyldiphenylsilylcarbene complex 25 with ethyl acrylate: The reaction was carried out in a similar manner to the reaction of tungsten phenylcarbene complex **9** using 3.0 molar amounts of samarium(II) iodide and 22 molar amounts of ethyl acrylate.

Ethyl (*E*)-4-(methyldiphenylsilyl)but-3-enoate (26): ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C): $\delta = 0.62$ (s, 3H; CH$_3$), 1.23 (t, ^{3}J(H,H) = 7.5 Hz, 3H; CH$_3$), 3.21 (dd, ^{3}J(H,H) = 6.5 Hz, ^{4}J(H,H) = 1.5 Hz, 2H; CH$_2$), 4.13 (q, ^{3}J(H,H) = 7.5 Hz, 2H; CH$_2$), 6.10 (dt, ^{3}J(H,H) = 18.5 Hz, ^{4}J(H,H) = 1.5 Hz, 1H; CH), 6.22 (dt, ^{3}J(H,H) = 6.5, 18.5 Hz, 1H; CH), 7.32–7.39 (m, 6H; ArH), 7.50–7.55 ppm (m, 4H; ArH); ^{13}C NMR (125 MHz, CDCl$_3$, 25 °C): $\delta = -3.9$, 14.2, 42.2, 60.6, 127.8, 129.3, 130.5, 134.8, 136.3, 141.6, 171.1 ppm; IR (neat): $\tilde{\nu} = 2980$, 1734 (C=C), 1430, 1112 cm^{-1}; elemental analysis (%) calcd for $C_{19}H_{22}O_2Si$ (310.5): C 73.50, H 7.14; found: C 73.20, H 7.19.

Reductive dimerization of α,β-unsaturated carbene complexes: A typical procedure is described for tungsten *trans*-propenylcarbene complex (**28a**).

A solution of samarium(II) iodide (4.0 mL, 0.089 M, 0.36 mmol) in THF was added to a solution of the tungsten *trans*-propenylcarbene complex **28a** (116 mg, 0.284 mmol) in THF (3.0 mL) and methanol (56 μL) at −78 °C. After stirring for 15 min at this temperature, the reaction mixture was exposed to an oxygen atmosphere (1 atm) for a few minutes at −78 °C to quench remaining samarium(II) iodide. When the blue color of samarium(II) iodide had disappeared, the oxygen atmosphere was replaced by argon, and the reaction mixture warmed to room temperature. The solvent was evaporated and the reaction mixture was filtered using a small amount of silica gel and dichloromethane. Purification by column chromatography (hexane/ethyl acetate 10/1) yielded biscarbene complex **29a** (110 mg, 94%) as a yellow solid.

1,6-Dimethoxy-3,4-dimethylhexa-1,6-diylidenebis(pentacarbonyltungsten(0)) (29a, 3:1 mixture of diastereomers): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 0.80$ (d, $^3J(\mathrm{H,H}) = 6.8$ Hz, 6H × 0.75; CH_3), 0.83 (d, $^3J(\mathrm{H,H}) = 6.8$ Hz, 6H × 0.25; CH_3), 2.03–2.15 (m, 2H; CH), 2.96–3.25 (m, 4H; CH_2), 4.61 (s, 6H × 0.75; CH_3), 4.62 ppm (s, 6H × 0.25; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 15.4$, 17.0, 36.2, 36.9, 68.5, 69.8, 70.5, 196.9, 202.7, 337.1, 337.4 ppm; IR (neat): $\tilde{\nu} = 2061$, 1908 (br), 1446, 1273, 665 cm^{-1}; elemental analysis (%) calcd for $C_{20}H_{18}O_{12}W_2$ (817.9): C 29.37, H 2.22; found: C 29.67, H 2.46.

Spectral data of compounds listed in Table 1:

1,6-Dimethoxy-3,3,4,4-tetramethylhexa-1,6-diylidenebis(pentacarbonyltungsten(0)) (29b): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 0.99$ (s, 12H; CH_3), 3.29 (s, 4H; CH_2), 4.64 ppm (s, 6H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 22.6$, 44.2, 69.8, 70.5, 197.4, 203.3, 343.2 ppm; IR (neat): $\tilde{\nu} = 2070$, 1920 (br), 1450, 1255, 570 cm^{-1}; elemental analysis (%) calcd for $C_{22}H_{22}O_{12}W_2$ (846.0): C 31.23, H 2.62; found: C 31.25, H 2.83.

1,6-Dimethoxy-3,4-diphenylhexa-1,6-diylidenebis(pentacarbonyltungsten(0)) (29c, 1:1 mixture of diastereomers): ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): $\delta = 2.82$ (dd, $^2J(\mathrm{H,H}) = 16.0$ Hz, $^3J(\mathrm{H,H}) = 3.0$ Hz, 2H × 0.5), 3.35 (m, 2H × 0.5), 3.42–3.50 (m, 2H), 3.66–3.72 (m, 2H × 0.5), 3.79–3.87 (m, 2H × 0.5), 4.29 (s, 6H × 0.5; CH_3), 4.37 (s, 6H × 0.5; CH_3), 6.85–6.86 (m, 4H × 0.5; ArH), 7.01–7.04 (m, 2H × 0.5; ArH), 7.07–7.10 (m, 4H × 0.5; ArH), 7.20–7.23 (m, 6H × 0.5; ArH), 7.30–7.33 ppm (m, 4H × 0.5; ArH); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): $\delta = 48.1$, 48.5, 68.6, 69.7, 70.0, 70.2, 126.5, 127.2, 127.9, 128.0, 128.3, 128.8, 140.7, 141.5, 197.0, 202.8, 334.1, 335.3 ppm; IR (neat): $\tilde{\nu} = 2920$, 2075, 1910 (br), 1455, 1260 cm^{-1}; elemental analysis (%) calcd for $C_{30}H_{22}O_{12}W_2$ (942.1): C 38.24, H 2.35; found: C 38.53, H 2.62.

1,6-Dimethoxy-3,3,4,4-tetramethylhexa-1,6-diylidenebis(pentacarbonylchromium(0)) (29d): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 0.96$ (s, 12H; CH_3), 3.42 (s, 4H; CH_2), 4.83 ppm (s, 6H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 22.4$, 44.2, 67.7, 68.5, 216.3, 223.2, 369.8 ppm; IR (neat): $\tilde{\nu} = 2060$, 1992, 1901 (br), 1449, 1249 cm^{-1}; elemental analysis (%) calcd for $C_{22}H_{22}O_{12}Cr_2$ (582.4): C 45.37, H 3.81; found: C 45.07, H 3.86.

1,6-Dimethoxy-3,4-dimethyhexa-1,6-diylidenebis(pentacarbonylchromium(0)) (29e, 4:1 mixture of diastereomers): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 0.72$–0.81 (m, 6H; CH_3), 1.95–2.10 (m, 2H; CH), 3.10–3.38 (m, 4H; CH_2), 4.79 (s, 6H × 0.2; CH_3), 4.80 ppm (s, 6H × 0.8; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 15.1$, 16.8, 35.8, 36.4, 66.9, 67.8, 68.2, 216.30, 216.33, 222.96, 222.98, 364.3, 364.6 ppm; IR (neat): $\tilde{\nu} = 2060$, 1936 (br), 1445, 1259, 664 cm^{-1}; elemental analysis (%) calcd for $C_{20}H_{18}O_{12}Cr_2$ (554.3): C 43.33, H 3.27; found: C 43.61, H 3.56.

(*E*,*E*)-1,10-Dimethoxy-5,6-diphenyldeca-3,7-diene-1,10-diylidenebis(pentacarbonyltungsten(0)) (29f, 1:1 mixture of diastereomers): ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): $\delta = 3.56$ (dd, $^2J(\mathrm{H,H}) = 15.0$ Hz, $^3J(\mathrm{H,H}) = 6.0$ Hz, 2H + 2H × 0.5; CH, CH_2), 3.70 (dd, $^2J(\mathrm{H,H}) = 14.5$ Hz, $^3J(\mathrm{H,H}) = 7.0$ Hz, 2H × 0.5; CH_2), 3.84 (dd, $^2J(\mathrm{H,H}) = 15.0$ Hz, $^3J(\mathrm{H,H}) = 7.0$ Hz, 2H × 0.5; CH_2), 3.91 (dd, $^2J(\mathrm{H,H}) = 15.0$ Hz, $^3J(\mathrm{H,H}) = 7.0$ Hz, 2H × 0.5; CH_2), 4.35 (s, 6H × 0.5; CH_3), 4.53 (s, 6H × 0.5; CH_3), 5.09 (quintet, $^3J(\mathrm{H,H}) = 7.0$ Hz, 2H × 0.5; CH), 5.31 (quintet, $^3J(\mathrm{H,H}) = 7.0$ Hz, 2H × 0.5; CH), 5.53 (dd, $^3J(\mathrm{H,H}) = 5.5$, 14.0 Hz, 2H × 0.5; CH), 5.85 (dd, $^3J(\mathrm{H,H}) = 6.5$, 14.0 Hz, 2H × 0.5; CH), 6.92–7.32 ppm (m, 10H; ArH); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): $\delta = 54.7$, 67.6, 68.0, 70.3, 123.7, 124.3, 126.1, 126.4, 128.1, 128.2, 128.35, 128.39, 136.0, 136.4, 142.38, 142.40, 197.07, 197.11, 203.0, 203.2, 332.1, 332.3 ppm; IR (neat): $\tilde{\nu} = 2956$, 2069, 1915, 1450, 1245 cm^{-1}; HRMS calcd for $C_{34}H_{26}O_{12}W_2$ (994.15): 994.0444 $[M]^+$; found: 994.0490 $[M]^+$.

Reaction of *α,β*-unsaturated carbene complexes with electron-poor olefins: A typical procedure is described for the reaction of tungsten isobutenylcarbene complex **28b** with acrylonitrile.

A THF solution of samarium(II) iodide (6.1 mL, 0.10 M, 0.61 mmol) was added to a solution (3.0 mL) of tungsten isobutenylcarbene complex **28b** (123 mg, 0.291 mmol), acrylonitrile (462 mg, 8.71 mmol), and methanol (57 µL) at −78 °C. The reaction mixture was stirred overnight at this temperature and then exposed to an oxygen atmosphere (1 atm) to quench remaining samarium(II) iodide. After a few minutes, the blue color of samarium(II) iodide had disappeared, and the oxygen atmosphere was replaced with argon, and the reaction mixture warmed to room temperature. Evaporation of the solvent and purification by column chromatography (hexane/ethyl acetate 10/1) gave coupling product **33** (104 mg, 75%) as a yellow oil.

5-Cyano-1-methoxy-3,3-dimethylpent-1-ylidene(pentacarbonyl)tungsten(0) (33): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 0.99$ (s, 6H; CH_3), 1.72 (t, $^3J(\mathrm{H,H}) = 8.0$ Hz, 2H; CH_2), 2.26 (t, $^3J(\mathrm{H,H}) = 8.0$ Hz, 2H; CH_2), 3.19 (s, 2H; CH_2), 4.64 ppm (s, 3H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 12.5$, 27.5, 36.6, 38.1, 70.5, 73.4, 119.9, 197.2, 203.1, 339.7 ppm; IR (neat): $\tilde{\nu} = 2962$, 2070, 1913, 1451, 1259 cm^{-1}; elemental analysis (%) calcd for $C_{14}H_{15}O_6NW$ (477.1): C 35.24, H 3.17, N 2.94; found: C 35.51, H 3.31, N 2.87.

5-Ethoxycarbonyl-1-methoxy-3,3-dimethylpent-1-ylidene(pentacarbonyl)tungsten(0) (32): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 0.95$ (s, 6H; CH_3), 1.22 (t, $^3J(\mathrm{H,H}) = 8.0$ Hz, 3H; CH_3), 1.62 (t, $^3J(\mathrm{H,H}) = 8.0$ Hz, 2H; CH_2), 2.21 (t, $^3J(\mathrm{H,H}) = 8.0$ Hz, 2H; CH_2), 3.18 (s, 2H; CH_2), 4.09 (q, $^3J(\mathrm{H,H}) = 8.0$ Hz, 2H; CH_2), 4.61 ppm (s, 3H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 14.1$, 27.8, 29.7, 36.8, 37.8, 60.4, 70.4, 74.1, 173.7, 197.4, 203.3, 341.0 ppm; IR (neat): $\tilde{\nu} = 2960$, 2070, 1920, 1740 (C=C), 1450, 1260 cm^{-1}; elemental analysis (%) calcd for $C_{16}H_{20}O_8W$ (588.1): C 36.66, H 3.85; found: C 36.91, H 4.03.

5-Cyano-1-methoxy-3,3-dimethylpent-1-ylidene(pentacarbonyl)chromium(0) (34): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 0.87$ (s, 6H; CH_3), 1.61 (t, $^3J(\mathrm{H,H}) = 7.8$ Hz, 2H; CH_2), 2.15 (t, $^3J(\mathrm{H,H}) = 7.8$ Hz, 2H; CH_2), 3.25 (s, 2H; CH_2), 4.74 ppm (s, 3H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 12.6$, 27.4, 36.6, 38.1, 67.7, 71.6, 119.8, 215.7, 222.4, 365.6 ppm; IR (neat): $\tilde{\nu} = 2964$, 2063, 1923, 1455, 1261 cm^{-1}; HRMS calcd for $C_{14}H_{15}O_6NCr$ (345.27): 345.0304 $[M]^+$; found: 345.0288 $[M]^+$.

One-electron reduction of chromium phenylcarbene complex 35: A solution of samarium(II) iodide (14.0 mL, 0.10 M, 1.40 mmol) in THF was added to a THF solution (6.0 mL) of chromium phenylcarbene complex **35** (204 mg, 0.654 mmol) and methanol (129 µL) at −78 °C. The mixture was stirred overnight at this temperature, and then a solution of ethyl acrylate (361 mg, 3.60 mmol) in THF was added. When addition was complete, the reaction mixture was warmed to room temperature and stirred for an additional hour. The reaction was quenched with pH 7 phosphate buffer at room temperature, and the product extracted with ethyl acetate. The combined organic phase was dried over anhydrous magnesium sulfate, and the solvent evaporated. The crude product was filtered using a small amount of silica gel and dichloromethane and purified by preparative TLC (hexane/ethyl acetate 4/1) to give ethyl 5-methoxy-4-oxo-5-phenylpentanoate (**36**, 123 mg, 75%) as a colorless oil.

Ethyl 5-methoxy-4-oxo-5-phenylpentanoate (36): ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 1.18$ (t, $^3J(\mathrm{H,H}) = 7.2$ Hz, 3H; CH_3), 2.48 (t, $^3J(\mathrm{H,H}) = 6.8$ Hz, 1H; CH_2), 2.49 (t, $^3J(\mathrm{H,H}) = 6.3$ Hz, 1H; CH_2), 2.68–2.89 (m, 2H; CH_2), 3.37 (s, 3H; CH_3), 4.06 (q, $^3J(\mathrm{H,H}) = 7.2$ Hz, 2H; CH_2), 4.70 (s, 1H; CH), 7.30–7.37 ppm (m, 5H; ArH); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 14.1$, 27.6, 32.4, 57.3, 60.6, 89.0, 127.0, 128.6, 128.8, 135.9, 172.6, 207.0 ppm; IR (neat): $\tilde{\nu} = 2980$, 1732 (C=C), 1202, 702 cm^{-1}; HRMS calcd for $C_{14}H_{18}O_4$ (250.28): 250.1205 $[M]^+$; found: 250.1215 $[M]^+$.

One-electron reduction of chromium alkylcarbene complexes: A typical procedure is described for the reaction of chromium butylcarbene complex **40** with ethyl acrylate.

A THF solution of samarium(II) iodide–HMPA complex (prepared by mixing HMPA (0.43 mL, 2.5 mmol) with a THF solution of samarium(II) iodide (8.5 mL, 0.10 M, 0.85 mmol) at room temperature) was added to a THF solution (2.7 mL) of chromium butylcarbene complex **40** (55 mg, 0.19 mmol) and methanol (38 µL) at −78 °C. The mixture was stirred for 20 min at this temperature and then a THF solution (1.5 mL) of ethyl acrylate (113 mg, 1.13 mmol) was added. When addition was complete, the reaction mixture was warmed to room temperature and stirred for an additional hour. The reaction was quenched with pH 7 phosphate buffer, and the product extracted with ethyl acetate. The combined organic phase was dried over anhydrous magnesium sulfate and purified by column chromatography (hexane/ethyl acetate 4/1) to give ethyl 5-methoxy-4-oxononanoate (**41a**, 36 mg, 85%) as a colorless oil.

Ethyl 5-methoxy-4-oxononanoate (41a): ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 0.87$ (t, $^3J(\mathrm{H,H}) = 6.8$ Hz, 3H; CH_3), 1.23 (t, $^3J(\mathrm{H,H}) = 7.1$ Hz, 3H; CH_3), 1.18–1.40 (m, 4H; CH_2CH_2), 1.61 (t, $^3J(\mathrm{H,H}) = 6.8$ Hz, 2H; CH_2), 2.56 (t, $^3J(\mathrm{H,H}) = 6.6$ Hz, 2H; CH_2), 2.71–2.89 (m, 2H; CH_2), 3.35 (s, 3H; CH_3), 3.59 (t, $^3J(\mathrm{H,H}) = 6.3$ Hz, 1H; CH), 4.10 ppm (q, $^3J(\mathrm{H,H}) = 7.1$ Hz, 2H; CH_2); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 13.9$, 14.2, 22.5, 27.2, 27.5, 31.8, 32.4, 58.2, 60.6, 87.2, 172.7, 211.5 ppm; IR (neat): $\tilde{\nu} = 2958$, 1733 (C=C), 1716 (C=C), 1205, 1099 cm^{-1}; HRMS calcd for $C_{12}H_{22}O_4$ (230.30): 185.1177 $[M - \mathrm{EtO}]^+$; found: 185.1179 $[M - \mathrm{EtO}]^+$.

Spectral data of the compounds listed in Table 2:

Methyl 5-methoxy-3-methyl-4-oxononanoate (41b, 81:19 mixture of diastereomers): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 0.88$ (t, ^3J(H,H) = 7.1 Hz, 3H; CH_3), 1.10 (d, ^3J(H,H) = 7.3 Hz, 3H × 0.81; CH_3), 1.11 (d, ^3J(H,H) = 7.4 Hz, 3H × 0.19; CH_3), 1.23–1.44 (m, 4H; CH_2CH_2), 1.52–1.62 (m, 1H; CH_2), 1.67–1.78 (m, 1H; CH_2), 2.30 (dd, ^2J(H,H) = 17.1 Hz, ^3J(H,H) = 5.7 Hz, 1H × 0.81; CH_2), 2.31 (dd, ^2J(H,H) = 16.8 Hz, ^3J(H,H) = 5.4 Hz, 1H × 0.19; CH_2), 2.76 (dd, ^2J(H,H) = 16.8 Hz, ^3J(H,H) = 9.0 Hz, 1H × 0.19; CH_2), 2.79 (dd, ^2J(H,H) = 17.1 Hz, ^3J(H,H) = 9.3 Hz, 1H × 0.81; CH_2), 3.17–3.45 (m, 1H; CH), 3.36 (s, 3H × 0.19; CH_3), 3.38 (s, 3H × 0.81; CH_3), 3.63 (s, 3H; CH_3), 3.76 (dd, ^3J(H,H) = 3.9, 8.1 Hz, 1H × 0.81; CH), 3.84 ppm (dd, ^3J(H,H) = 4.4, 7.6 Hz, 1H × 0.19; CH); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 13.9$, 16.9, 22.5, 22.6, 27.4, 27.7, 29.7, 30.8, 31.8, 36.4, 37.6, 37.8, 38.0, 51.6, 51.7, 58.1, 58.4, 86.0, 86.4, 172.5, 172.7, 213.5, 214.1 ppm; IR (neat): $\tilde{\nu} = 2957$, 1738 (C=C), 1715 (C=C), 1200, 1100 cm^{-1}; elemental analysis (%) calcd for $C_{12}H_{22}O_4$ (230.3): C 62.58, H 9.63; found: C 62.58, H 9.83.

Dimethyl 2-(2-methoxyhexanoyl)succinate (41c, 53:47 mixture of diastereomers): ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 0.86$ (m, 3H; CH_3), 1.10–1.40 (m, 4H; CH_2CH_2), 1.50–1.80 (m, 2H; CH_2), 2.70 (dd, ^2J(H,H) = 17.0 Hz, ^3J(H,H) = 6.0 Hz, 1H × 0.47; CH_2), 2.79 (dd, ^2J(H,H) = 17.4 Hz, ^3J(H,H) = 6.0 Hz, 1H × 0.53; CH_2), 2.90 (dd, ^2J(H,H) = 17.0 Hz, ^3J(H,H) = 8.4 Hz, 1H × 0.47; CH_2), 2.92 (dd, ^2J(H,H) = 17.4 Hz, ^3J(H,H) = 8.1 Hz, 1H × 0.53; CH_2), 3.33 (s, 3H × 0.53; CH_3), 3.36 (s, 3H × 0.47; CH_3), 3.64 (s, 6H × 0.53; CH_3), 3.69 (s, 6H × 0.47; CH_3), 3.74 (t, ^3J(H,H) = 6.0 Hz, 1H × 0.53; CH), 3.83 (dd, ^3J(H,H) = 6.0, 9.0 Hz, 1H × 0.47; CH), 4.21 (dd, ^3J(H,H) = 6.0, 8.1 Hz, 1H × 0.53; CH), 4.24 ppm (dd, ^3J(H,H) = 6.0, 8.4 Hz, 1H × 0.47; CH); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 13.8$, 22.4, 22.5, 26.8, 27.3, 30.7, 31.2, 31.9, 32.2, 49.7, 49.9, 52.0, 52.5, 52.6, 58.4, 58.5, 86.4, 86.5, 168.7, 169.1, 171.3, 171.6, 205.4, 205.9 ppm; IR (neat): $\tilde{\nu} = 2955$, 1740 (C=C), 1724 (C=C), 1437, 1162 cm^{-1}; HRMS calcd for $C_{13}H_{22}O_6$ (274.31): 243.1233 $[M - \mathrm{MeO}]^+$; found: 243.1223 $[M - \mathrm{MeO}]^+$.

5-Methoxy-4-oxononanenitrile (41d): ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 0.86$ (t, ^3J(H,H) = 7.1 Hz, 3H; CH_3), 1.20–1.40 (m, 4H; CH_2CH_2), 1.52–1.72 (m, 2H; CH_2), 2.56 (t, ^3J(H,H) = 6.8 Hz, 2H; CH_2), 2.81–2.99 (m, 2H; CH_2), 3.34 (s, 3H; CH_3), 3.60 ppm (t, ^3J(H,H) = 6.2 Hz, 1H; CH); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 11.1$, 13.8, 22.4, 26.9, 31.4, 33.4, 58.3, 86.8, 119.0, 209.2 ppm; IR (neat): $\tilde{\nu} = 2935$, 2250, 1721 (C=C), 1465, 1099 cm^{-1}; HRMS calcd for $C_{10}H_{17}O_2N$ (183.25): 183.1259 $[M]^+$; found: 183.1259 $[M]^+$.

3-(2-Methoxyhexanoyl)cyclopentan-1-one (41e, 50:50 mixture of diastereomers): ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): $\delta = 0.85$–0.90 (m, 3H; CH_3), 1.27–1.39 (m, 4H; CH_2CH_2), 1.61–1.69 (m, 2H; CH_2), 1.92–2.04 (m, 1H; cyclopentanone), 2.16–2.48 (m, 5H; cyclopentanone), 3.34 (s, 3H × 0.50; CH_3), 3.37 (s, 3H × 0.50; CH_3), 3.55–3.63 (m, 1H; cyclopentanone), 3.66–3.70 ppm (m, 1H; CH); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): $\delta = 13.8$, 22.47, 22.48, 26.1, 26.5, 27.0, 27.3, 30.9, 31.3, 37.46, 37.48, 40.7, 41.2, 42.7, 42.8, 58.2, 58.3, 86.81, 86.83, 213.1, 213.3, 216.50, 216.51 ppm; IR (neat): $\tilde{\nu} = 2956$, 1746 (C=C), 1713 (C=C), 1103 cm^{-1}; elemental analysis (%) calcd for $C_{12}H_{20}O_3$ (212.3): C 67.89, H 9.50; found C 67.69, H 9.60.

Ethyl 5-methoxy-6-methyl-4-oxooctanoate (41f, 55:45 mixture of diastereomers): ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): $\delta = 0.82$ (d, ^3J(H,H) = 7.4 Hz, 3H × 0.55; CH_3), 0.848 (d, ^3J(H,H) = 6.8 Hz, 3H × 0.45; CH_3), 0.849 (t, ^3J(H,H) = 7.5 Hz, 3H × 0.55; CH_3), 0.88 (t, ^3J(H,H) = 7.5 Hz, 3H × 0.45; CH_3), 1.19–1.29 (m, 1H; CH), 1.22 (t, ^3J(H,H) = 7.2 Hz, 3H; CH_3), 1.37–1.45 (m, 1H × 0.45; CH), 1.49–1.57 (m, 1H × 0.55; CH), 1.69–1.79 (m, 1H; CH), 2.54 (t, ^3J(H,H) = 6.8 Hz, 2H × 0.55; CH_2), 2.55 (t, ^3J(H,H) = 6.6 Hz, 2H × 0.45; CH_2), 2.69–2.88 (m, 2H; CH_2), 3.29 (d, ^3J(H,H) = 7.1 Hz, 1H × 0.55; CH), 3.33 (s, 3H × 0.55; CH_3), 3.37 (s, 3H × 0.45; CH_3), 3.47 (d, ^3J(H,H) = 5.0 Hz, 1H × 0.45; CH), 4.10 ppm (q, ^3J(H,H) = 7.2 Hz, 2H; CH_2); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): $\delta = 11.1$, 11.6, 14.1, 14.7, 24.4, 24.8, 25.8, 27.4, 27.6, 33.0, 33.5, 33.9, 37.2, 37.8, 58.8, 59.1, 60.55, 60.57, 90.3, 91.7, 172.7, 173.3, 211.4, 211.5 ppm; IR (neat): $\tilde{\nu} = 2965$, 1737 (C=C), 1517, 1205, 1097 cm^{-1}; HRMS calcd for $C_{12}H_{22}O_4$ (230.30): 185.1178 $[M - \mathrm{EtO}]^+$; found: 185.1180 $[M - \mathrm{EtO}]^+$.

5-Methoxy-6-methyl-4-oxooctanenitrile (41g, 56:44 mixture of diastereomers): ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 0.80$–0.93 (m, 6H; CH_3), 1.13–1.27 (m, 1H), 1.35–1.45 (m, 1H × 0.44), 1.47–1.56 (m, 1H × 0.56), 1.69–1.78 (m, 1H), 2.52–2.59 (m, 2H; CH_2), 2.74–2.97 (m, 2H; CH_2), 3.33 (d, ^3J(H,H) = 6.8 Hz, 1H × 0.56; CH), 3.34 (s, 3H × 0.56; CH_3), 3.36 (s, 3H × 0.44; CH_3), 3.46 ppm (d, ^3J(H,H) = 5.1 Hz, 1H × 0.44; CH); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 11.08$, 11.11, 11.5, 14.2, 14.7, 24.8, 25.6, 33.9, 34.5, 37.3, 38.0, 59.0, 59.4, 90.3, 91.3, 119.0, 128.4, 209.3, 209.7 ppm; IR (neat): $\tilde{\nu} = 2966$, 2250, 1720 (C=C), 1462, 1096; elemental analysis (%) calcd for $C_{10}H_{17}NO_2$ (183.2): C 65.56, H 9.35, N 7.65; found C 65.26, H 9.35, N 7.36.

Phenethyl 5-methoxy-4-oxohexanoate (41h): ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 1.30$ (d, ^3J(H,H) = 7.2 Hz, 3H; CH_3), 2.59 (t, ^3J(H,H) = 6.8 Hz, 2H; CH_2), 2.80–2.85 (m, 2H; CH_2), 2.93 (t, ^3J(H,H) = 7.1 Hz, 2H; CH_2), 3.37 (s, 3H; CH_3), 3.76 (q, ^3J(H,H) = 7.2 Hz, 1H; CH), 4.29 (t, ^3J(H,H) = 7.1 Hz, 2H; CH_2), 7.16–7.33 ppm (m, 5H; ArH); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 17.0$, 27.4, 31.9, 35.0, 57.5, 65.0, 82.6, 126.5, 128.4, 128.8, 137.7, 172.6, 211.0 ppm; IR (neat): $\tilde{\nu} = 2940$, 1736 (C=C), 1168, 702; elemental analysis calcd (%) for $C_{15}H_{20}O_3$ (248.3): C 68.16, H 7.63; found: C 67.86, H 7.55.

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[11] The alkenyltungsten intermediate **20** was not protonated by methanol at −78 °C. Even when the reaction was carried out in the presence of CH$_3$OD and stirred overnight, no incorporation of deuterium into the olefin **16** was observed.

[12] DMPU = *N,N'*-dimethylpropyleneurea. When the reaction was carried out in THF, about 50% yield of olefin **23b** and about 50% recovery of complex **21b** were obtained even after stirring overnight. DMPU is known to increase the rate of reduction with samarium(II) iodide: T. Mukhopadhyay, D. Seebach, *Helv. Chim. Acta* **1982**, *65*, 385.

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[15] α,β-Unsaturated esters are reduced by samarium(II) iodide to give azipates, products dimerized at the position β to the carbonyl group: J. Inanaga, Y. Handa, T. Tabuchi, K. Otsubo, M. Yamaguchi, T. Hanamoto, *Tetrahedron Lett.* **1991**, *32*, 6557.

[16] It is not clear whether **29a** is produced by direct radical coupling of **30a** or by radical addition of **30a** to **28a**.

[17] The reaction mixture was warmed to room temperature when reduction was complete. The yellow-green solution changed in color to red, and this suggests that protonation of the dianion intermediate **31a** by methanol took place.

[18] One-electron reduction of a (2-phenylethynyl)carbene complex of tungsten gave a complex mixture of products.

[19] M. A. Sierra, *Chem. Rev.* **2000**, *100*, 3591.

[20] E. Kuester, L. S. Hegedus, *Organometallics* **1999**, *18*, 5318.

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[22] a) B. C. Söderberg, D. C. York, T. R. Hoye, G. M. Rehberg, J. A. Suriano, *Organometallics* **1994**, *13*, 4501; b) B. C. Söderberg, D. C. York, E. A. Harriston, H. J. Caprara, A. H. Flurry, *Organometallics* **1995**, *14*, 3712.

[23] Acylchromate complexes produced by the reaction of hexacarbonylchromium with alkyl- or aryllithium reagents are isolable in the form of their tetramethylammonium salts: E. O. Fischer, A. Maasböl, *Chem. Ber.* **1967**, *100*, 2445.

[24] We previously reported that the α-methoxyketone **36** was accompanied by small amounts of methyl ether **15** and olefin **16** under similar conditions.[9] However, re-examination of this reaction afforded the α-methoxyketone **36** without formation of **15** or **16**.

[25] The lower bond energy of the chromium – carbon single bond may be responsible for this difference. The strength of the metal – methyl bond in [Cp(CO)$_3$CrMe] was estimated to be about 55 – 70% of that in the corresponding tungsten complex: D. C. McKean, G. P. McQuillan, A. R. Morrisson, I. Torto, *J. Chem. Soc. Dalton Trans.* **1985**, 1207. Facile insertion of a carbonyl ligand into the carbon – metal double bond of carbene complexes to give ketene complexes is well known for chromium, but not so common for tungsten.[2b, h] For example, the reaction of phenyl- or alkenylchromium carbene complexes with alkynes usually gives hydronaphthoquinone or hydroquinone derivatives, respectively, via carbon monoxide insertion (Dötz benzannulation reaction), whereas the similar reaction with the corresponding tungsten complexes usually gives indene or cyclopentadiene derivatives. These differences are usually explained by the lower bond energy of the chromium – CO bond relative to the tungsten – CO bond: W. D. Wulff, B. M. Bax, T. A. Brandvold, K. S. Chan, A. M. Gilbert, R. P. Hsung, *Organometallics* **1994**, *13*, 102; and ref. [2g]. In our case, however, it might not be appropriate to apply this difference in bond energy of the metal – carbonyl bond, as the carbonyl ligand is not liberated from the complexes.

[26] HMPA = *N,N,N',N',N'',N''*-hexamethylphosphoramide. HMPA is known to increase the rate of reduction: a) K. Otsubo, J. Inanaga, M. Yamaguchi, *Tetrahedron Lett.* **1986**, *27*, 5763; b) J. Inanaga, M. Ishikawa, M. Yamaguchi, *Chem. Lett.* **1987**, 1485; c) M. Shabangi, R. A. Flowers, II, *Tetrahedron Lett.* **1997**, *38*, 1137.

[27] Hydride reduction of the carbene complex [Ph(EtO)C=Cr(CO)$_5$] with *N*-methyl-1,4-dihydropyridine yielded the α-ethoxyacylchromate complex, which underwent conjugate addition to cyclopentenone to give an α-ethoxyketone under similar conditions to our reaction: a) H. Rudler, A. Parlier, B. Martin-Vaca, E. Garrier, J. Vaissermann, *Chem. Commun.* **1999**, 1439; b) H. Rudler, A. Parlier, T. Durand-Réville, B. Martin-Vaca, M. Audouin, E. Garrier, V. Certal, J. Vaissermann, *Tetrahedron* **2000**, *56*, 5001.

[28] W. D. Wulff, W. E. Bauta, R. W. Kaesler, P. J. Lankford, R. A. Miller, C. K. Murray, D. C. Yang, *J. Am. Chem. Soc.* **1990**, *112*, 3642.

[29] R. M. Gerkin, B. Rickborn, *J. Am. Chem. Soc.* **1967**, *89*, 5850.

[30] **Note added in proof** (26.12.2002): After submission of this manuscript, a paper by Sierra and co-workers appeared in which the reductive dimerization of α,β-unsaturated Fischer carbene complexes by using C$_8$K as a one-electron reductant was described: M. A. Sierra, P. Ramírez-López, M. Gómez-Gallego, T. Lejon, M. J. Mancheño, *Angew. Chem.* **2002**, *114*, 3592; *Angew. Chem. Int. Ed.* **2002**, *41*, 3442.

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