Synthesis of Fischer-Type (Alkoxy)carbene Complexes Using Diphenylsulfonium Salts with Functionalized Alkyl Groups

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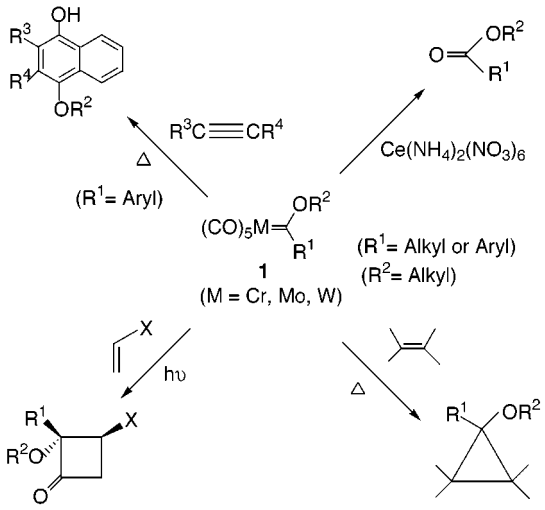
Received October 5, 1999

A new and general method for preparing Fischer-type alkoxycarbene complexes **1** is reported. This method involves the alkylation of acylate complexes **7** with alkyldiphenylsulfonium salts **10** with a variety of functionalized alkyl groups. The alkylation of tetramethylammonium pentacarbonyl-(1-oxyalkylidene)chromate(0) **7a**−**c**, tetramethylammonium pentacarbonyl(1-oxymethylidene)molybdate(0) **7d**, and pentacarbonyl(1-oxymethylidene)tungstate(0) **7e** with alkyldiphenylsulfonium salts **10** proceeded smoothly under mild conditions to give the corresponding alkoxycarbene complexes **12**−**39** in good to high yields. Competitive alkylation of **7a** with methyl-**11** and isopropyldiphenylsulfonium tetrafluoroborate **40** shows a higher reactivity of the isopropyl group, suggesting the participation of an S−O sulfurane intermediate **41**.

Introduction

Metal-stabilized carbene complexes, in particular Fischer-type (alkoxy)carbene complexes **1**, have attracted considerable attention as synthetically useful reagents since the first studies by Fischer et al.[1−3] Typical reactions of (alkoxy)carbene complex **1** are shown in Scheme 1. Complex **1** can be regarded as an ester equivalent, and the oxidation of **1** with molecular oxygen, pyridine *N*-oxide, ceric ammonium nitrate (CAN), etc., gives the corresponding ester in high yield.[4] Metal-coordinated carbene **1** can also be used as a building block for the synthesis of cyclopropane derivatives.[5] Photolytic reaction of **1** generates a ketene species which reacts with olefins to afford cyclobutanones as [2 + 2] cycloaddition products.[6] The addition of alkynes to complex **1**, which contains an aryl carbene ligand, leads to naphthol

Scheme 1



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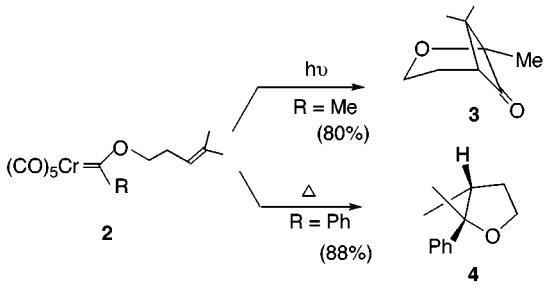
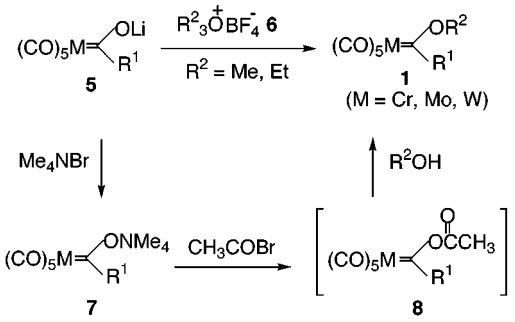
10.1021/jo991549n CCC: $19.00
Published on Web 07/07/2000

Scheme 2



Scheme 3

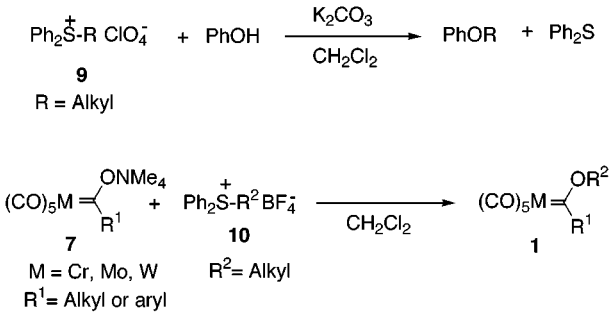


derivatives.[7] Furthermore, these reactions can be used for the synthesis of natural products such as vitamins,[8] steroids,[9] and antibiotics.[10]

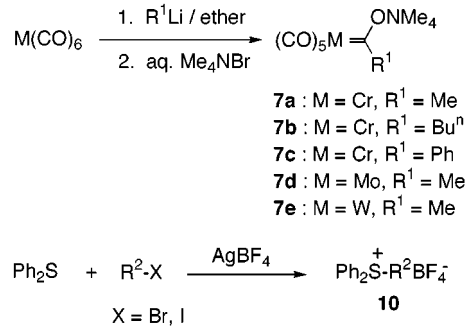
The intramolecular reaction of (alkoxy)carbene complexes containing functionalized alkyl or aryl groups is also useful for preparing key intermediates in organic synthesis. As shown in Scheme 2, photolysis of (alkenyloxy)(methyl)carbene complex **2** produced the bicyclic cyclobutanone **3** in good yield,[6a] whereas thermal intramolecular cyclopropanation of (alkenyl)(phenyl)carbene complex **2** gives the bicyclic cyclopropane **4**.[11]

Alkoxycarbene complexes are usually prepared by alkylating pentacarbonyl(1-oxyalkylidene)chromate(0), -molybdate(0), or -tungstate(0) with Meerwein oxonium salt **6**.[12] However, this method is limited to the preparation of alkoxycarbene complexes containing simple methoxy and ethoxy groups. The preparation of Fischer-type carbene complexes containing functionalized alkyl groups has been reported (Scheme 3).[6a,10a,11,13] However, the methods used to prepare alkoxy carbene complexes of chromium, molybdenum, and tungsten are still limited.[14,15]

Scheme 4



Scheme 5



In contrast to oxonium salts **6**, sulfonium salts with a variety of functionalized alkyl groups are readily available[16] and react with nucleophiles such as phenolate and carboxylate ions to produce the corresponding ethers and esters. As shown in Scheme 4, diphenylsulfonium salts **9**, which possess a good leaving group, Ph_2S, react with nucleophiles such as phenol under mild conditions to give alkylated products in good yields.[17] Keeping these results in mind, we developed a new and general method for preparing Fischer-type alkoxycarbene complexes **1** using the alkylation of tetramethylammonium acylate complexes **7** with alkyldiphenylsulfonium salt **10** (Scheme 4). We previously reported our preliminary findings in the alkylation of tetramethylammonium acylate complexes using sulfonium salt.[18] In this paper, we describe in detail the successful synthesis of alkoxycarbene complexes using a variety of alkyldiarylsulfonium salts, together with some related reactions.

Results and Discussion

The tetramethylammonium acylate complex **7** was prepared by treating $M(CO)_6$ (M = Cr, Mo, W) with organolithium reagent and then adding tetramethylammonium bromide ($Me_4N^+Br^-$) as described in the literature[12a] (Scheme 5). Alkyldiphenylsulfonium tetrafluoroborates **10** were obtained in yields of 53−83% by

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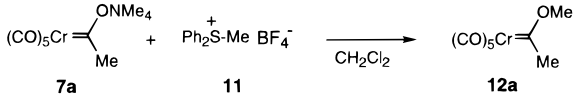
Table 1. Preparation of Carbene Complex 12a from Ammonium Salt 7a and Sulfonium Salt 11[a]



7a **11** **12a**

run	additive (mmol)	Yield (%) of **12a**
1	none	84
2	K_2CO_3	73
3	pyridine (1.2)	0 [b]
4	2,6-lutidine (1.2)	52

a) **7a** (1 mmol), **11** (1 mmol), CH_2Cl_2 (5 mL).
b) $(CO)_5$Cr-pyridine was obtained (15%). [12c]

reacting a large excess of Ph_2S with alkyl halides in the presence of $AgBF_4$ (Scheme 5).[19]

Reaction of tetramethylammonium pentacarbonyl(1-oxymethyliden)chromate(0) (**7a**) with methyldiphenylsulfonium tetrafluoroborate (**11**) in CH_2Cl_2 was carried out under an argon atmosphere at room temperature, and the results are summarized in Table 1. Alkylation of **7a** with **11** readily gave pentacarbonyl[(methoxy)-methylcarbene]chromium (**12a**) in high yield (run 1). The (alkoxy)carbene complexes obtained are unstable under acidic conditions. We considered that it may be necessary to control the pH of the reaction solution because the sulfonium salt **11** is acidic, like the oxonium salt **6**, and the resulting carbene complex **12a** may decompose under these reaction conditions. Therefore, alkylations of **7a** with **11** were attempted in the presence of a base (runs of 2−4). However, as seen in Table 1, in each case the use of base decreased the yield of carbene complex **12a**. This result implies that sulfonium salts are mild and useful alkylating reagents for preparing (alkoxy)carbene complex **12a**. Thus, subsequent alkylation with sulfonium salts was performed under the conditions used in run 1.

Alkylation of tetramethylammonium chromium (acylate) complexes **7a**−**c** was investigated using diphenylsulfonium salt **10** with various alkyl groups. As shown in Table 2, chromium (alkoxy)carbene complexes **12**−**23** were obtained in moderate to high yields. For example, the total yields of carbene complexes by two-steps (yields for the preparation of sulfonium salts **10** and then alkylation of **7** with **10**) are as follows: **12a**, 69%; **14**, 68%; and **22a**, 69%. The present method using sulfonium salts has the following advantages: (1) While a longer reaction time (12 h) is needed than that in the known method[12] using oxonium salts **6**, a variety of functionalized alkyl groups with a secondary carbon can be effectively introduced. (2) This reaction can be carried out at room temperature, although the known method using acyloxy intermediate **8** gives enol esters at room temperature when α-hydrogens next to the carbene carbon atom are present.[14] (3) The present method is particularly useful for preparing carbene complexes **18** with a hydroxyl group, since the known method via acyloxy intermediate **8** gives a mixture of **18** and a biscarbene complex like **20**. (4) The use of diphenylsulfonium salt as an alkylating reagent makes it possible to obtain the novel biscarbene complex **20**.

The chromium (alkoxy)carbene complexes **12**−**23** were identified by examining ^{1}H NMR, ^{13}C NMR, IR, and MS spectral data. The ^{13}C NMR spectra of complexes **12**−**23** are particularly informative and show signals due to carbene carbons in a low-field position from 350 to 370 ppm. Most of the chromium complexes were stable below −20 °C and can be stored in a freezer. However, complexes **15a**−**c** containing an ether group, and **17c**, **19a**,**b**, and **23a** containing an ester group, slowly decomposed in a freezer. Complexes **19a**−**c** decomposed when they were purified by column chromatography on silica gel.

Molybdenum carbene complexes are usually less stable in a freezer than the corresponding chromium and tungsten complexes. There are few studies on the preparation of molybdenum carbene complexes and their application to organic synthesis.[5d,15,20]

Alkylation of tetramethylammonium molybdenum (acylate) complex **7d** with sulfonium salts **10** was attempted in a manner similar to that for preparing chromium complexes (Table 3). This method gave molybdenum (alkoxy)-carbene complexes **24**−**31** containing various functionalized alkoxy groups in moderate to good yields (Table 3). Although the yields of molybdenum complexes **24**−**31** are less than those of chromium compounds **12**−**23**, molybdenum (alkoxy)carbene complexes with various functional groups could be obtained using this method.

Molybdenum (alkoxy)carbene complexes **24**−**31** also exhibit characteristic carbon signals in a low-field position from 340 to 360 ppm. Complexes **29** and **31** were stable in nonpolar solvents, but decomposed gradually at room temperature in the absence of solvent. Complexes **26**−**28** slowly decomposed in a freezer.

Similarly, tungsten complexes **32**−**39** were successfully prepared from acylate complex **7e** and diphenylsulfonium salts **10** (Table 4). Most of the tungsten (alkoxy)carbene complexes **32**−**39** were stable, like the corresponding chromium complexes. Compound **38** with a hydroxy group was very unstable in the absence of solvent. Complexes **36** and **39** slowly decomposed in a freezer.

For the alkylation of acylate ion from **7** with alkyldiphenylsulfonium salts **10**, there are at least three posssible routes: (1) via an S_N2 reaction, (2) via an S−O sulfurane intermediate, and (3) via single-electron transfer (Figure 1).

The alkylation of carboxylate anions with alkylsulfonium salts has been suggested to proceed via sulfurane intermediates on the basis of the relative reactivities of the alkyl groups in sulfonium salts.[21,22] To explore the mechanism of the alkylation in the present study, the competitive alkylation of **7a** (1 mmol) with methyldiphenylsulfonium tetrafluoroborate **11** (5 mmol) and isopropyldiphenylsulfonium tetrafluoroborate **40** (5 mmol) was carried out (Scheme 6). From this reaction, the relative

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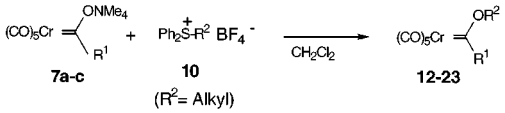
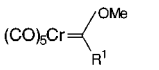
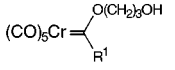
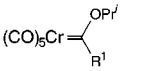
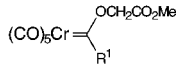
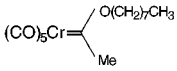
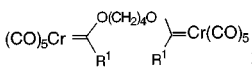
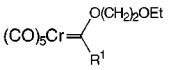
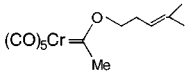
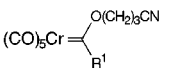
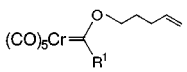
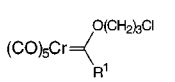
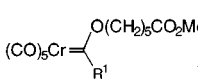
Table 2. Preparation of Chromium (Alkoxy)carbene Complexes



7a-c 10 (R^2 = Alkyl) 12-23

Product (%) [a]		Product (%) [a]	
	**12** a: R^1 = Me (84) b: Bu^n (82) c: Ph (85)		**18** a: R^1 = Me (41) b: Bu^n (31)
	**13** a: R^1 = Me (92) b: Bu^n (94) c: Ph (90)		**19** a: R^1 = Me (90) b: Bu^n (93) c: Ph (57)
	**14** (91)		**20** a: R^1 = Me (60) b: Bu^n (61) c: Ph (26)
	**15** a: R^1 = Me (68) b: Bu^n (71) c: Ph (66)		**21** (55)
	**16** a: R^1 = Me (84) b: Bu^n (79) c: Ph (67)		**22** a: R^1 = Me (87) b: Bu^n (88) c: Ph (92)
	**17** a: R^1 = Me (89) b: Bu^n (83) c: Ph (83)		**23** a: R^1 = Me (66) b: Bu^n (86) c: Ph (93)

a) Isolated yield.

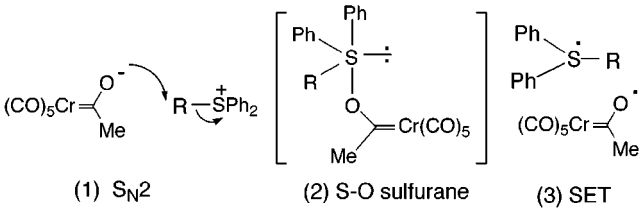
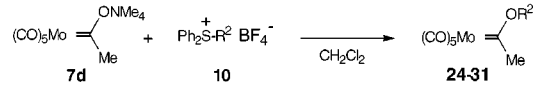
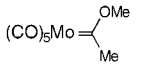
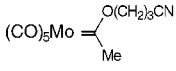
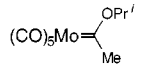
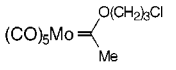
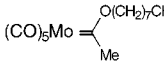
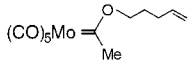
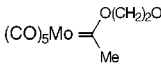
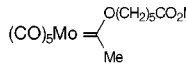


Figure 1. Possible alkylation processes of metal acylate ion.

Table 3. Preparation of Molybdenum (Alkoxy)carbene Complexes



7d 10 24-31

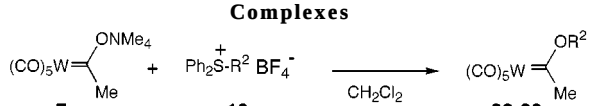
Product (%) [a]			
	**24** (85)		**28** (42)
	**25** (74)		**29** (67)
	**26** (66)		**30** (67)
	**27** (57)		**31** (65)

a) Isolated yield.

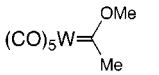
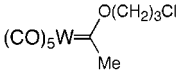
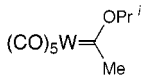
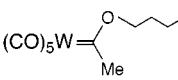
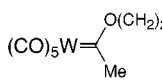
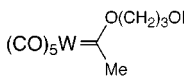
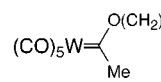
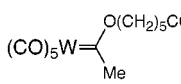
reactivity of the methyl and isopropyl groups was found to be 1:9, based on the yields of **12a** and **13a**. This result shows that the secondary alkyl group is more reactive than the primary alkyl group. A similar reactivity (Me: Bu-*s* = 1:2) for the alkylation of carboxylate anions has been reported in the literature.[21a,23] The relative reactivities of the methyl, ethyl, and isopropyl groups in alkyl

(23) Umemura, K.; Matsuyama, H.; Kamigata, N. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 2593.

Table 4. Preparation of Tungsten (Alkoxy)carbene Complexes

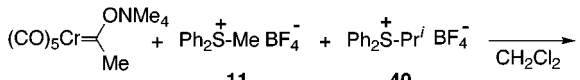


7e 10 32-39

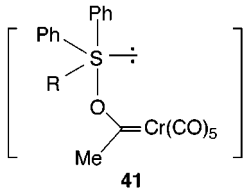
Product (%) [a]			
	**32** (93)		**36** (90)
	**33** (95)		**37** (91)
	**34** (85)		**38** (48)
	**35** (69)		**39** (85)

a) Isolated yield.

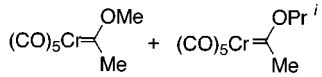
Scheme 6



7a 11 40



41



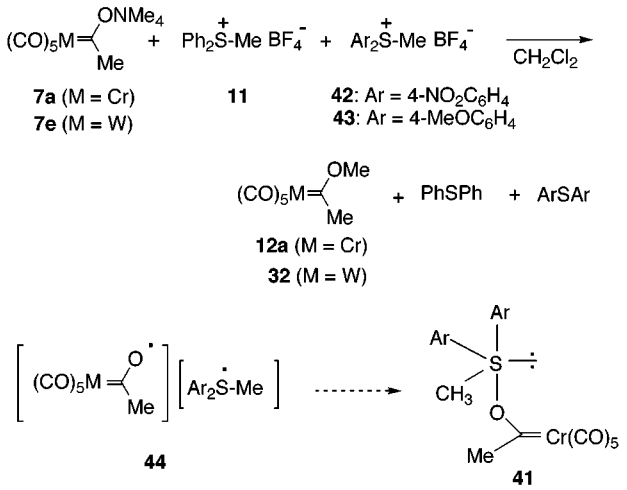
12a 13a

8% 72%

1 : 9

halides toward several nucleophiles via an S_N2 reaction have been reported to be 1.0, 0.05, and 0.001, respectively.[24] Accordingly, the reaction mechanism of the present alkylation is not a simple S_N2-type reaction, and

Scheme 7



the reaction may proceed *via* an S−O sulfurane intermediate **41**. One possible explanation for the ratio of isopropylated and methylated products posutulates a transition state in which the S−C bond is broken before alkylation of acylate ion from **7**.

Other competitive alkylation experiments suggested another possible mechanism (Scheme 7). In the methylation of **7a** (0.5 mmol) with methyldiphenylsulfonium tetrafluoroborate **11** (1.5 mmol) and methyl(4,4′-dinitrodiphenyl)sulfonium tetrafluoroborate **42** (1.5 mmol) [or methyl(4,4′-dimethoxydiphenyl)sulfonium tetrafluoroborate **43** (1.5 mmol)], the relative reactivities of sulfonium salts were estimated, again based on the yields of the resulting diaryl sulfides, since the yields of methylation are almost equal to those of the sulfides. The results are as follows: 4-$NO_2C_6H_4$:C_6H_5:4-$MeOC_6H_4$ = 6.9:1.00:0.38 (M = Cr) and 4-$NO_2C_6H_4$:C_6H_5:4-$MeOC_6H_4$ = 6.3:1.00:0.26 (M = W). These results show that sulfonium salts with an electron-withdrawing substituent (4-$NO_2C_6H_4$) react much faster than those with an electron-donating substituent (4-$MeOC_6H_4$). Taking into account the reactivities of **11**, **42**, and **43** for acylate complexes **7**, a possible pathway for the formation of methoxycarbene complex may include an electron-transfer reaction.[25,26] Thus, the reaction of **7** with sulfonium salts **11**, **42**, and **43** forms the radical pair **44** via electron transfer, followed by bond formation to produce the S−O sulfurane intermediate **41**.[27,28] Electron transfer from **7** to **42** is expected to be faster than that from **7** to **11**, whereas electron transfer from **7** to **43** is slow. Although the rho (ρ) value of the Hammett relationship might suggest nucleophilic attack of acylate ion to sulfonium salts (S_N2 mechanism), the S_N2 reaction can be ruled out from the results shown in Scheme 6. Since electron transfer between **7** and **40** might take place to form **41** faster than that between **7** and **11** due to an isopropyl group, electron transfer can also explain the relative reactivities of alkyl groups in sulfonium salts.

In conclusion, alkylation with diphenylsulfonium salts was found to be a simple and general method for synthesizing Fischer-type chromium, molybdenum, and tungsten (alkoxy)carbene complexes with various functionalized alkoxy groups. It may be possible to develop new intra- and intermolecular reactions of the resulting carbene complexes using the functional groups in these complexes.

Experimental Section

^{1}H NMR spectra were recorded at 400 MHz and ^{13}C NMR spectra were recorded at 100 MHz. Mass and high-resolution mass spectra were determined at an inoizing voltage of 70 eV. Column chromatography was performed with Daisogel 1001w containing 10% water. Gel permeation chromatograpy was performed with two JAIGEL-1H columns (20 mm × 600 mm) with chloroform as eluent. Dry solvents were purified as follows. Dichloromethane was distilled over CaH_2; ether was distilled from sodium benzophenone ketyl immediately before use. Tetramethylammonium pentacarbonyl(1-oxymethylidene)-chromate(0) (**7a**), tetramethylammonium pentacarbonyl(1-oxybutylidene)chromate(0) (**7b**), tetramethylammonium pentacarbonyl(1-oxyphenylidene)chromate(0) (**7c**), tetramethylammonium pentacarbonyl(1-oxymethylidene)molybdate(0) (**7d**), and tetramethylammonium pentacarbonyl(1-oxymethylidene)-tungstate(0) (**7e**) were prepared according to the literature.[12,13] Alkyl iodides were prepared from commercially available alkyl bromides and KI (3 equiv) in refluxing acetone.

Tetramethylammonium pentacarbonyl(1-oxymethylidene) molybdate(0) (7d): 50% yield; yellow crystals; mp 120.0 °C (dec); ^{1}H NMR (CD_2Cl_2) δ 2.31 (s, 3H), 3.34 (s, 12H); ^{13}C NMR (CD_2Cl_2) δ 53.9, 54.5, 199.5, 210.0, 217.3, 296.6; IR (KBr) 2050, 1888 cm^{-1}.

Tetramethylammonium pentacarbonyl(1-oxybutylidene) tungstate(0) (7e): 64% yield; yellow needles; mp 131.8 °C (dec); ^{1}H NMR (CD_2Cl_2) δ 2.38 (s, 3H), 3.35 (s, 12H); ^{13}C NMR (CD_2Cl_2) δ 54.5, 56.3, 202.2, 207.2, 282.3; IR (KBr) 2052, 1878, 1071 cm^{-1}.

Diphenylsulfonium Tetrafluoroborate 10.[16,19] To silver tetrafluoroborate $AgBF_4$ (2.93 g, 15 mmol), under ice bath cooling, was added dropwise a mixture of diphenyl sulfide (27.9 g, 0.15 mol) and alkyl halides (18 mmol). The mixture was covered with aluminum foil and stirred at room temperature for 3 days. Then the mixture was passed through a short column of silica gel and eluted with acetone. The eluate was concentrated in vacuo. After being washed with ether, the residue was dried under reduced pressure or was recrystallized from CH_2Cl_2−ether.

Methyldiphenylsulfonium tetrafluoroborate: 82% yield; mp 51.0−53.0 °C; ^{1}H NMR (CD_3OD) δ 3.69 (s, 3H), 7.62−7.73 (m, 6H), 7.94−7.96 (m, 4H).

Isopropyldiphenylsulfonium tetrafluoroborate: 53% yield; mp 126.0−127.0 °C; ^{1}H NMR (CD_3OD) δ 1.50 (d, J = 6.35 Hz, 6H), 4.91 (m, 1H), 7.72−7.84 (m, 6H), 8.11−8.13 (m, 4H); ^{13}C NMR (CD_3OD) δ 19.3, 52.4, 125.9, 133.0, 133.3, 136.7.

1-Octyldiphenylsulfonium tetrafluoroborate: 75% yield; oil; ^{1}H NMR (CD_3OD) δ 0.85 (t, J = 6.84 Hz, 3H), 1.23−1.30 (m, 8H), 1.55 (quintet, J = 7.33 Hz, 2H), 1.74 (quintet, J = 7.57 Hz, 2H), 4.20 (t, J = 7.57 Hz, 2H), 7.69−7.80 (m, 6H), 8.04 (d, J = 7.33 Hz, 4H); ^{13}C NMR (CD_3OD) δ 15.1, 24.2, 26.2, 29.6, 30.5, 33.2, 45.8, 127.0, 132.2, 133.1, 136.2.

(2-Ethoxyethyl)diphenylsulfonium tetrafluoroborate: 79% yield; mp 68.3−69.6 °C; ^{1}H NMR (CD_3OD) δ 1.05 (t, J = 7.08 Hz, 3H), 3.41 (t, J = 7.00 Hz, 2H), 3.83 (t, J = 5.37 Hz, 2H), 4.46 (t, J = 5.37 Hz, 2H), 7.70 (t, J = 7.82 Hz, 4H), 7.77 (t, J = 6.84 Hz, 2H), 8.02 (d, J = 8.30 Hz, 4H); ^{13}C NMR (CD_3OD) δ 15.7, 47.2, 65.1, 68.3, 126.8, 132.2, 132.9, 136.0.

(5-Methoxycarbonylpentyl)diphenylsulfonium tetrafluoroborate: 80% yield; mp 77.8−78.4 °C; ^{1}H NMR (CD_3OD)

(24) Okamoto, K.; Nitta, I.; Imoto, T.; Singu, H. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 1905.
(25) Andrieux, C. P.; Robert, M.; Saeva, F. D.; Saveant, J.-M. *J. Am. Chem. Soc.* **1994**, *116*, 7864.
(26) Saeva, F. D.; Brestin, D. T.; Martic, P. A. *J. Am. Chem. Soc.* **1989**, *111*, 1328.
(27) Fountain, K. R.; Kamlesh, D. P. *J. Org. Chem.* **1997**, *62*, 4795.
(28) Tetramethylammonium pentacarbonyl(1-oxidoalkylidene)chromium(0) complexes are oxidized with manganese(III) 2-pyridinecarboxylate to generate carbon-centered radicals which react with various olefins giving the intermolecular addition products. See, Narasaka, K.; Sakurai, H. *Chem. Lett.* **1993**, 1269.

δ 1.59−1.62 (m, 4H), 1.73−1.77 (m, 2H), 2.30 (t, J = 6.84 Hz, 2H), 3.62 (s, 3H), 4.21 (t, J = 7.57 Hz, 2H), 7.70−7.81 (m, 6H), 8.01−8.04 (m, 4H); ^{13}C NMR (CD_3OD) δ 24.7, 24.9, 27.9, 44.7, 51.9, 125.8, 131.3, 132.2, 135.4, 175.0. Anal. Calcd for $C_{19}H_{23}O_2SBF_4$: C, 56.67; H, 5.76. Found: C, 56.24; H, 5.54.

(3-Hydroxypropyl)diphenylsulfonium tetrafluoroborate: 73% yield; mp 78.1−79.6 °C; ^{1}H NMR (CD_3OD) δ 1.98 (quintet, J = 6.35 Hz, 2H), 3.77 (t, J = 5.86 Hz, 2H), 4.25 (t, J = 7.08 Hz, 2H), 4.72 (s, 1H), 7.69−7.80 (m, 6H), 7.99−8.01 (m, 4H); ^{13}C NMR (CD_3OD) δ 27.9, 42.7, 59.9, 125.8, 130.9, 132.0, 135.1. Anal. Calcd for $C_{15}H_{17}OSBF_4$: C, 54.24; H, 5.16. Found: C, 54.12; H, 5.14.

(3-Chloropropyl)diphenylsulfonium tetrafluoroborate: 76% yield; mp 107.3−108.5 °C; ^{1}H NMR (acetone-d_6) δ 2.23 (quintet, J = 6.84 Hz, 2H), 3.76 (t, J = 6.35 Hz, 2H), 4.33 (t, J = 7.33 Hz, 2H), 7.71−7.82 (m, 6H), 8.03−8.05 (m, 4H); ^{13}C NMR (acetone-d_6) δ 28.8, 42.7, 43.2, 126.0, 131.8, 132.5, 135.8. Anal. Calcd for $C_{15}H_{16}ClSBF_4$: C, 51.38; H, 4.59. Found: C, 50.97; H, 4.52.

(4-Methy-3-pentenyl)diphenylsulfonium tetrafluoroborate: 30% yield; colorless oil; ^{1}H NMR (CD_3OD) δ 1.39 (s, 3H), 1.65 (s, 3H), 2.49−2.52 (m, 2H), 4.24 (t, J = 7.08 Hz, 2H), 5.18 (m, 1H), 7.66−7.76 (m, 6H), 7.99−8.02 (m, 4H); ^{13}C NMR (CD_3OD) δ 24.1, 27.6, 34.8, 45.7, 119.1, 125.8, 130.1, 131.3, 135.3, 136.5.

(4-pentenyl)diphenylsulfonium tetrafluoroborate: 79% yield; colorless oil; NMR (CD_3OD) δ 1.86 (quintet, J = 7.45 Hz, 2H), 2.32 (q, J = 7.00 Hz, 2H), 4.17 (t, J = 7.81 Hz, 2H), 5.03 (d, J = 10.3 Hz, 1H), 5.09 (d, J = 17.1 Hz, 1H), 5.76 (ddt, J = 17.1, 10.3, 6.78 Hz, 1H), 7.71 (t, J = 7.82 Hz, 4H), 7.78 (t, J = 7.33 Hz, 2H), 8.03 (d, J = 8.30 Hz, 4 H); ^{13}C NMR (CD_3-OD) δ 25.2, 33.0, 45.2, 118.1, 126.2, 131.9, 132.9, 136.1, 137.1.

Bistetrafluoroborate salt of 1,4-bis(diphenylsulfonio)-butane: 83% yield; colorless oil; ^{1}H NMR (CD_3OD) δ 2.02 (br s,4H), 4.22 (br s, 4H), 7.68 (t, J = 7.82 Hz, 8H), 7.76 (t, J = 7.33 Hz, 4H), 7.97 (d, J = 7.32 Hz, 8H); ^{13}C NMR (CD_3OD) δ 23.7, 43.7, 125.4, 131.2, 132.2, 135.5.

(3-Cyanopropyl)diphenylsulfonium tetrafluoroborate: 80% yield; colorless oil; ^{1}H NMR (CD_3OD) δ 2.14 (quintet, J = 7.45 Hz, 2H), 2.80 (t, J = 7.33 Hz, 2H), 4.27 (t, J = 7.57 Hz, 2H), 7.68−7.80 (m, 6H), 8.01−8.03 (m, 4H); ^{13}C NMR (CD_3OD) δ 16.7, 22.4, 44.1, 120.5, 125.8, 132.0, 133.0, 136.3.

(Methoxycarbonylmethyl)diphenylsulfonium tetrafluoroborate: 66% yield; mp 94.0−94.8 °C; ^{1}H NMR (acetone-d_6) δ 3.73 (s, 3H), 5.53 (s, 2H), 7.71 (t, J = 7.57 Hz, 4H), 7.79 (t, J = 7.57 Hz, 2H), 8.16 (d, J = 7.81 Hz, 4H); ^{13}C NMR (acetone-d_6) δ 47.7, 54.7, 125.8, 131.6, 132.4, 135.7, 165.0.

Preparation of Diarylmethylsulfonium Tetrafluoroborates 42 and 43. To silver tetrafluoroborate (2.14 g, 11 mmol) was added dropwise a mixture of diaryl sulfide (10 mmol) and methyl iodide (8 mL, 129 mmol) under ice-cooling. The mixture was covered with aluminum foil and stirred at room temperature for 3 days. The mixture was passed through a short column of silica gel and eluted with acetone. The eluate was concentrated in vacuo. After being washed with ether, the residue was dried under reduced pressure or was recrystallized from acetone.

Methyl(4,4′-Dinitrodiphenyl)sulfonium tetrafluoroborate (42): 60% yield; mp 151.6−154.2 °C; ^{1}H NMR (acetone-d_6) δ 4.20 (s, 3H), 8.51(d, J = 9.00 Hz, 4H), 8.57(d, J = 9.00 Hz, 4H). Anal. Calcd for $C_{13}H_{11}N_2O_4SBF_4$: C, 41.29; H, 2.93; N, 7.40. Found: C, 40.95; H, 2.84; N, 7.30.

Methyl(4,4′-Dimethoxydiphenyl)sulfonium tetrafluoroborate (43): 96% yield; mp 99.0−100.0 °C; ^{1}H NMR (acetone-d_6) δ 3.83 (s, 3H), 3.91 (s, 6H), 7.26 (d, J = 9.15 Hz, 4H), 8.03 (d, J = 9.15 Hz, 4H). Anal. Calcd for $C_{15}H_{17}O_2SBF_4$: C, 51.75; H, 4.92. Found: C, 51.68; H, 4.76.

Preparation of (Alkoxy)carbene Complex 12a. A mixture of ammonium acylate complex **7a** (0.311 g, 1.0 mmol) and methyldiphenylsulfonium tetrafluoroborate **10** (0.288 g, 1.0 mmol) in CH_2Cl_2 (5 mL) was stirred for 12 h at room temperature under Ar. The solvent was removed under reduced pressure at 0 °C, and the residue was dissolved into ether. The ether solution was passed through a short column of silica gel and concentrated in vacuo. The product was separated by gel permeation chromatography with chloroform. The results are summarized in Table 1.

Run 1: The reaction was carried out under the conditions described above, and carbene complex **12a** (0.21 g, 84% yield) and diphenyl sulfide (0.19 g, 100% yield) were obtained.

Run 2: The reaction was carried out in the presence of potassium carbonate (0.14 g, 1.0 mmol), and carbene complex **12a** (0.18 g, 73% yield) and diphenyl sulfide (0.178 g, 95% yield) were obtained.

Run 3: The reaction was carried out in the presence of pyridine (0.1 mL, 1.2 mmol). However, carbene complex **12a** was not obtained. $(CO)_5Cr$−pyridine complex[12c] [15% yield; yellow needles; mp 96.5−98 °C; MS m/z 415 (M^+)] and diphenyl sulfide (0.152 g, 81% yield) were obtained.

Run 4: The reaction was carried out in the presence of 2,6-lutidine (0.14 mL, 1.2 mmol). Carbene complex **12a** (0.13 g, 52% yield) and diphenyl sulfide (0.19 g, 100% yield) were obtained.

General Procedure for Preparation of Chromium (Alkoxy)carbene Complexes 12−23. A mixture of ammonium acylate complexes **7a**−**c** (3.0 mmol) and diphenylsulfonium tetrafluoroborate **10** (3.0 mmol) in CH_2Cl_2 (15 mL) was stirred at room temperature for 12 h under Ar. The solvent was removed under reduced pressure at 0 °C, and the residue was dissolved into ether. The ether solution was passed through a short column of silica gel and concentrated in vacuo. The product was separated by gel permeation chromatography using chloroform or by column chromatography on silica gel using a mixed solvent of hexane and ether as eluent. The results are summarized in Table 2.

12a: 84% yield; yellow needles; mp 33.4−34.0 °C [lit.[12a] mp 34 °C]; ^{1}H NMR ($CDCl_3$) δ 2.94 (s, 3H), 4.70 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 49.6, 67.3, 216.5, 223.5, 360.5; MS m/z 250 (M^+), 233, 222.

12b: 82% yield; orange oil; ^{1}H NMR ($CDCl_3$) δ 0.91 (s, 3H), 1.34 (s, 2H), 1.46 (s, 2H), 3.30 (s, 2H), 4.76 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 13.9, 22.5, 28.4, 62.9, 67.6, 216.5, 223.2, 363.9; MS m/z 292 (M^+), 279, 264; HRMS cacld for $C_{11}H_{12}O_6Cr$: 292.0039, found: 291.9992.

12c: 85% yield; red needles; mp 47.0−48.3 °C [lit.[12a] mp 46 °C]; ^{1}H NMR ($CDCl_3$) δ 4.65 (s, 3H), 7.28 (s, 3H), 7.38(s, 2H); ^{13}C NMR ($CDCl_3$) δ 67.2, 123.1, 128.3, 130.4, 153.8, 216.3, 224.2, 351.1; MS m/z 312 (M^+), 284, 256.

13a: 92% yield; yellow needles; mp 54.0−55.1 °C; ^{1}H NMR ($CDCl_3$) δ 1.55 (d, J = 5.37 Hz, 6H), 2.90 (s, 3H), 5.82 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 22.5, 50.3, 87.2, 216.6, 223.5, 352.2; MS m/z 279 (M^+ + 1), 251, 223; HRMS calcd for $C_{10}H_{10}O_6Cr$: 277.9882, found: 277.9882.

13b: 94% yield; yellow needles; mp 37.9−38.3 °C; ^{1}H NMR ($CDCl_3$) δ 0.91 (s, 3H), 1.54 (br s, 10H), 3.23 (s, 2H), 5.82 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 13.9, 22.4, 28.3, 63.0, 87.1, 216.6, 223.5, 355.3; MS m/z 320 (M^+), 292, 264; HRMS calcd for $C_{13}H_{16}O_6Cr$: 320.0352, found: 320.0430.

13c: 90% yield; red needles; mp 39.2−39.7 °C; ^{1}H NMR ($CDCl_3$) δ 1.55 (s, 6H), 5.63 (s, 1H), 7.35 (s, 5H); ^{13}C NMR ($CDCl_3$) δ 22.6, 85.8, 122.5, 128.2, 129.8, 153.8, 216.3, 224.5, 345.6; MS m/z 340 (M^+), 312, 284; HRMS calcd for $C_{15}H_{12}O_6Cr$: 340.0040, found: 340.0078.

14: 91% yield; orange oil; ^{1}H NMR ($CDCl_3$) δ 0.90 (s, 3H), 1.31(s, 10H), 1.50 (s, 2H), 1.98 (s, 2H), 2.93 (s, 3H), 4.93 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 25.9, 29.2, 29.3, 31.7, 49.9, 82.0, 216.6, 223.5, 357.4; MS m/z 348 (M^+), 320, 292; HRMS calcd for $C_{15}H_{20}O_6Cr$: 348.0665, found: 348.0637.

15a: 68% yield; orange oil; ^{1}H NMR ($CDCl_3$) δ 1.25 (s, 3H), 2.98 (s, 3H), 3.61 (s, 2H), 3.95 (s, 2H), 5.02 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 15.1, 49.6, 67.2, 68.4, 80.1, 216.5, 223.5, 359.5; MS m/z 308 (M^+), 252, 224; HRMS calcd for $C_{11}H_{12}O_7Cr$: 307.9988, found: 308.0046.

15b: 71% yield; orange oil; ^{1}H NMR ($CDCl_3$) δ 0.91 (s, 3H), 1.24 (s, 3H), 1.34 (s, 2H), 1.48 (s, 2H), 3.32 (s, 2H), 3.60 (s, 2H), 3.94 (s, 2H), 5.09 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 13.9, 15.1, 22.4, 28.5, 62.9, 67.0, 68.4, 80.6, 216.4, 223.3, 362.4; MS m/z 350 (M^+), 294, 266; HRMS calcd for $C_{14}H_{18}O_7Cr$: 350.0457, found: 350.0417.

15c: 66% yield; dark red oil; ^{1}H NMR ($CDCl_3$) δ 1.24 (s, 3H), 3.60 (s, 2H), 3.95 (s, 2H), 4.92 (s, 2H), 7.26−7.39 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 15.1, 67.0, 68.4, 79.8, 122.9, 128.2, 130.1, 153.5, 216.2, 224.4, 350.2; MS *m*/*z* 370 (M^+), 314, 286; HRMS calcd for $C_{16}H_{14}O_7Cr$: 370.0145, found: 370.0088.

16a: 84% yield; yellow crystals; mp 40.8−42.0 °C; ^{1}H NMR ($CDCl_3$) δ 2.37 (s, 2H), 2.64 (s, 2H), 2.99 (s, 3H), 4.96 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 14.4, 25.5, 49.2, 76.0, 118.5, 216.3, 223.4, 360.6; MS *m*/*z* 303 (M^+), 275, 247; HRMS calcd for $C_{11}H_9O_6NCr$: 302.9835, found: 302.9753.

16b: 79% yield; orange oil; ^{1}H NMR ($CDCl_3$) δ 0.92 (s, 3H), 1.36 (s, 2H), 1.47 (s, 2H), 2.37 (s, 2H), 2.61 (s, 2H), 3.33 (s, 2H), 5.07 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 13.8, 14.4, 22.4, 25.6, 28.6, 62.9, 78.3, 118.3, 216.2, 223.0 363.9; MS *m*/*z* 345 (M^+), 317, 289; HRMS calcd for $C_{14}H_{15}O_6NCr$: 345.0304, found: 345.0271.

16c: 67% yield; dark red oil; ^{1}H NMR ($CDCl_3$) δ 2.35 (s, 2H), 2.66 (s, 2H), 4.80 (s, 2H), 7.18 (s, 2H), 7.42 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 14.3, 25.6, 62.7, 118.3, 122.1, 128.4, 130.2, 153.4, 215.9, 224.1, 351.8; MS *m*/*z* 365 (M^+), 309, 281; HRMS calcd for $C_{16}H_{11}O_6NCr$: 364.9992, found: 365.0084.

17a: 89% yield; orange oil; ^{1}H NMR ($CDCl_3$) δ 2.45 (s, 2H), 2.97 (s, 3H), 3.77 (s, 2H), 5.03 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 32.0, 40.7, 49.3, 76.1, 126.4, 223.4, 359.5; MS *m*/*z* 312 (M^+, ^{35}Cl), 283, 255; HRMS calcd for $C_{10}H_9O_6ClCr$: 311.9492, found: 311.9425.

17b: 83% yield; orange oil; ^{1}H NMR ($CDCl_3$) δ 0.91 (s, 3H), 1.35 (s, 2H), 1.46 (s, 2H), 2.45 (s, 2H), 3.32 (s, 2H), 3.74 (s, 2H), 5.12 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 13.9, 22.5, 28.5, 32.2, 40.7, 62.9, 77.6, 216.3, 223.2, 362.8; MS *m*/*z* 354 (M^+, ^{35}Cl), 326, 298; HRMS calcd for $C_{13}H_{15}O_6ClCr$: 353.9962, found: 353.9962.

17c: 83% yield; dark red oil; ^{1}H NMR ($CDCl_3$) δ 2.42−2.45 (m, 2H), 3.78 (t, J = 6.10 Hz, 2H), 4.89 (s, 2H), 7.20 (br s, 2H), 7.40−7.41 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 32.1, 40.7, 76.7, 122.2, 128.3, 130.1, 153.6, 216.1, 224.3, 351.0; MS *m*/*z* 374 (M^+, ^{35}Cl), 346, 290; HRMS calcd for $C_{15}H_{11}O_6ClCr$: 373.9649, found: 373.9726.

18a: 41% yield; orange oil; ^{1}H NMR ($CDCl_3$) δ 2.24 (s, 2H), 2.96 (s, 3H), 3.68 (s, 1H), 3.89 (s, 2H), 5.01 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 32.0, 49.7, 58.7, 77.7, 216.5, 223.4, 358.4; MS *m*/*z* 295 ($M^+ + 1$), 239, 221; HRMS calcd for $C_{10}H_{10}O_7Cr$: 293.9832, found: 293.9783.

18b: 31% yield; orange oil; ^{1}H NMR ($CDCl_3$) δ 0.91 (s, 3H), 1.36 (s, 4H), 2.22 (s, 2H), 3.30 (s, 3H), 3.86 (s, 2H), 5.10 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 13.8, 22.3, 28.3, 32.2, 58.8, 62.8, 78.5, 216.4, 223.2, 361.3; IR (neat) 3354, 2052, 1915 cm^{-1}; MS *m*/*z* 336 (M^+), 294, 280; HRMS calcd for $C_{13}H_{16}O_7Cr$: 336.0301, found: 336.0241.

19a: 90% yield; orange oil; ^{1}H NMR ($CDCl_3$) δ 3.06 (s, 3H), 3.86 (s, 3H), 5.59 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 49.3, 52.9, 74.7, 166.8, 215.8, 223.1, 363.4; MS *m*/*z* 308 (M^+), 280, 252; HRMS calcd for $C_{10}H_8O_8Cr$: 307.9624, found: 307.9583.

19b: 93% yield; orange oil; ^{1}H NMR ($CDCl_3$) δ 0.92 (s, 3H), 1.38 (s, 2H), 1.56 (s, 2H), 3.40 (s, 2H), 3.86 (s, 3H), 5.65 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 13.9, 22.5, 28.8, 52.8, 63.4, 75.4, 166.9, 215.8, 222.9, 367.2; MS *m*/*z* 350 (M^+), 322, 294; HRMS calcd for $C_{13}H_{14}O_8Cr$: 350.0094, found: 350.0014.

19c: 57% yield; dark red crystals; mp 38.8−39.3 °C; ^{1}H NMR ($CDCl_3$) δ 3.82 (s, 3H), 5.41 (s, 2H), 7.29−7.40 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 52.8, 73.9, 122.9, 128.3, 130.5, 152.9, 166.9, 215.7, 224.3, 353.0; MS *m*/*z* 370 (M^+), 342, 314; HRMS calcd for $C_{15}H_{10}O_8Cr$: 369.9781, found: 369.9704.

20a: 60% yield; yellow needles; mp 77.5−80.4 °C; ^{1}H NMR ($CDCl_3$) δ 2.26 (s, 4H), 2.98 (s, 6H), 5.01 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 26.2, 49.8, 80.2, 216.5, 223.3, 359.0; MS *m*/*z* 526 (M^+), 469, 414; HRMS calcd for $C_{18}H_{14}O_{12}Cr_2$: 525.9296, found: 525.9358.

20b: 61% yield; yellow needles; mp 67.5−69.0 °C; ^{1}H NMR ($CDCl_3$) δ 0.92 (s, 6H), 1.36 (s, 4H), 1.48 (s, 4H), 2.23 (s, 4H), 3.32 (s, 4H), 5.08 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 13.9, 22.5, 26.3, 28.6, 63.0, 80.6, 216.5, 223.2, 362.2; MS *m*/*z* 610 (M^+), 418, 414; HRMS calcd for $C_{24}H_{26}O_{12}Cr_2$: 610.0234, found: 610.0204.

20c: 26% yield; red needles; mp 90.5−92.5 °C; ^{1}H NMR ($CDCl_3$) δ 2.28 (s, 4H), 4.89 (s, 4H), 7.21−7.40 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 26.4, 79.7, 122.5, 128.3, 130.2, 153.5, 216.1, 224.1, 350.2; MS *m*/*z* 650 (M^+), 454, 398; HRMS calcd for $C_{28}H_{18}O_{12}Cr_2$: 649.9609, found: 649.9522.

21: 55% yield; orange oil; ^{1}H NMR ($CDCl_3$) δ 1.74 (s, 6H), 2.68 (s, 2H), 2.94 (s, 3H), 4.89 (s, 2H), 5.21 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 17.9, 25.8, 28.3, 49.7, 81.2, 118.1, 136.0, 216.6, 223.4, 357.6; MS *m*/*z* 317 ($M^+ - 1$), 287, 271: HRMS calcd for $C_{13}H_{14}O_6Cr$: 318.0196, found: 318.0145.

22a:[6a] 87% yield; orange oil; ^{1}H NMR ($CDCl_3$) δ 2.10 (s, 2H), 2.31 (s, 2H), 2.94 (s, 3H), 4.94−5.12 (m, 4H), 5.86 (s, 1H).

22b: 88% yield; orange oil; ^{1}H NMR ($CDCl_3$) δ 0.91(s, 3H), 1.34 (s, 2H), 1.46 (s, 2H), 2.09 (s, 2H), 2.29 (s, 2H), 3.30 (s, 2H), 4.98 (s, 2H), 5.08 (s, 2H), 5.85 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 13.9, 22.5, 28.5, 28.6, 30.0, 63.0, 81.1, 116.2, 136.7, 216.5, 223.3, 361.0; MS *m*/*z* 346 (M^+), 290, 262.

22c:[11] 92% yield; orange oil; ^{1}H NMR ($CDCl_3$) δ 2.10 (s, 2H), 2.31 (s, 2H), 4.80 (s, 2H), 5.05−5.13 (m, 2H), 5.82 (s, 1H), 7.22 (s, 2H), 7.39 (s, 3H).

23a: 66% yield; orange oil; ^{1}H NMR ($CDCl_3$) δ 1.57 (s, 2H), 1.75 (s, 2H), 2.02 (s, 2H), 2.38 (s, 2H), 2.94 (s, 3H), 3.68 (s, 3H), 4.92 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 24.5, 25.5, 29.1, 33.8, 49.9, 51.6, 81.7, 173.9, 216.6, 223.4, 357.9; MS *m*/*z* 364 (M^+), 332, 308; HRMS calcd for $C_{14}H_{16}O_8Cr$: 364.0250, found: 364.0205.

23b: 86% yield; orange oil; ^{1}H NMR ($CDCl_3$) δ 0.91 (s, 3H), 1.34 (s, 2H), 1.45 (s, 2H), 1.55 (s, 2H), 1.75 (s, 2H), 2.01 (s, 2H), 2.37 (s, 2H), 3.29 (s, 2H), 3.68 (s, 3H), 4.98 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 13.9, 22.4, 24.5, 25.5, 28.4, 29.2, 33.8, 51.6, 63.0, 81.6, 173.8, 216.5, 223.3, 360.9; MS *m*/*z* 406 (M^+), 350, 322.

23c: 93% yield; dark red oil; ^{1}H NMR ($CDCl_3$) δ 1.58 (s, 2H), 1.73 (s, 2H), 2.03 (s, 2H), 2.36 (s, 2H), 3.66 (s, 3H), 4.81 (s, 2H), 7.23 (s, 2H), 7.39 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 24.5, 25.5, 29.3, 33.8, 51.6, 80.8, 122.6, 128.2, 130.1, 153.7, 173.8, 216.2, 224.3, 349.4; MS *m*/*z* 426 (M^+), 370, 342.

General Procedure for Preparation of Molybdenum (Alkoxy)carbene Complexes 24−31. A mixture of ammonium acylate complexe **7d** (3.0 mmol) and diphenylsulfonium tetrafluoroborate **10** (3.0 mmol) in CH_2Cl_2 (15 mL) was stirred at room temperature for 12 h under Ar. The results are summarized in Table 3.

24:[12b] 85% yield; yellow solids; mp 40.5−41.0 °C; ^{1}H NMR ($CDCl_3$) δ 2.90 (s, 3H), 4.68 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 50.1, 69.4, 205.7, 213.3, 352.2; MS *m*/*z* 294 (M^+), 266, 238.

25: 74% yield; yellow solids; mp 57.8−58.5 °C; ^{1}H NMR ($CDCl_3$) δ 1.53 (d, J = 6.34 Hz, 6H), 2.85 (s, 3H), 5.67 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 22.2, 50.5, 89.2, 205.7, 213.5, 343.6; MS *m*/*z* 322 (M^+), 294, 266.

26: 66% yield; orange oil; ^{1}H NMR ($CDCl_3$) δ 0.90 (t, J = 6.60 Hz, 3H), 1.30−1.38 (m, 8H), 1.46−1.52 (m, 2H), 1.97 (quintet, J = 7.08 Hz, 2H), 2.89 (s, 3H), 4.89 (br s, 2H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 25.9, 29.2, 29.3, 31.8, 50.2, 205.8, 213.4, 348.9; MS *m*/*z* 392 (M^+), 336, 308.

27: 57% yield; orange oil; ^{1}H NMR ($CDCl_3$) δ 1.25 (t, J = 6.84 Hz, 3H), 2.94 (s, 3H), 3.61 (q, J = 7.00 Hz, 2H), 3.95 (t, J = 4.40 Hz, 2H), 5.00 (br s, 2H); ^{13}C NMR ($CDCl_3$) δ 15.1, 50.4, 67.0, 68.3, 82.8, 205.7, 213.3, 350.9; MS *m*/*z* 352 (M^+), 324, 296.

28: 42% yield; orange oil; ^{1}H NMR ($CDCl_3$) δ 2.37 (quintet, J = 6.47 Hz, 2H), 2.63 (t, J = 7.08 Hz, 2H), 2.94 (s, 3H), 4.99 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 14.5, 25.5, 50.4, 80.5, 118.4, 205.5, 213.1, 351.9; MS *m*/*z* 347 (M^+), 319, 291.

29: 67% yield; orange oil; ^{1}H NMR ($CDCl_3$) δ 2.44 (quintet, J = 6.11 Hz, 2H), 2.91 (s, 3H), 3.74 (t, J = 6.35 Hz, 2H), 5.03 (br s, 2H); ^{13}C NMR ($CDCl_3$) δ 32.0, 40.7, 50.3, 79.8, 205.6, 213.3, 350.9; MS *m*/*z* 356 (M^+, ^{35}Cl), 328, 300.

30: 67% yield; orange oil; ^{1}H NMR ($CDCl_3$) δ 2.08 (quintet, J = 6.84 Hz, 2H), 2.28 (q, J = 7.16 Hz, 2H), 2.89 (s, 3H), 4.90 (br s, 2H), 5.06 (d, J = 9.28 Hz, 1H), 5.10 (d, J = 16.1 Hz, 1H), 5.85 (ddt, J = 17.1, 10.3, 6.78 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 28.4, 30.0, 50.2, 83.3, 116.1, 136.7, 205.8, 213.4, 349.4; MS *m*/*z* 348 (M^+), 292, 264.

31: 65% yield; orange oil; ^{1}H NMR ($CDCl_3$) δ 1.55 (quintet, J = 7.81 Hz, 2H), 1.74 (quintet, J = 7.57 Hz, 2H), 2.00 (quintet, J = 7.08 Hz, 2H), 2.38 (t, J = 7.33 Hz, 2H), 2.89 (s, 3H), 3.68

(s, 3H), 4.89 (br s, 2H); ^{13}C NMR ($CDCl_3$) δ 24.5, 25.5, 29.0, 33.8, 50.3, 51.6, 83.8, 173.8, 205.7, 213.3, 349.3; MS *m*/*z* 410 (M^+), 354, 326.

General Procedure for Preparation of Tungsten (Alkoxy)carbene Complexes 32−39. A mixture of ammonium acylate complexe **7e** (3.0 mmol) and diphenylsulfonium tetrafluoroborate **10** (3.0 mmol) in CH_2Cl_2 (15 mL) was stirred at room temperature for 12 h under Ar. The results are summarized in Table 4.

32: 93% yield; yellow needles; mp 52.3−53.0 °C [lit.[13] mp 52 °C]; ^{1}H NMR ($CDCl_3$) δ 2.89 (s, 3H), 4.59 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 52.1, 70.3, 197.2, 203.5, 333.3; MS *m*/*z* 382 (M^+), 354, 339.

33: 95% yield; yellow needles; mp 67.1−67.8 °C; ^{1}H NMR ($CDCl_3$) δ 1.52 (d, J = 6.34 Hz, 6H), 2.86 (s, 3H), 5.60−5.67 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 22.2, 52.6, 89.9, 197.1, 203.5, 325.5; MS *m*/*z* 410 (M^+), 365, 337.

34: 85% yield; orange oil; ^{1}H NMR ($CDCl_3$) δ 1.25 (t, J = 6.84 Hz, 3H), 2.92 (s, 3H), 3.61 (q, J = 7.00 Hz, 2H), 3.94 (t, J = 4.64 Hz, 2H), 4.90 (br s, 2H); ^{13}C NMR ($CDCl_3$) δ 15.1, 52.5, 67.0, 68.2, 83.5, 197.3, 203.5, 332.0; MS *m*/*z* 440 (M^+), 412, 384.

35: 69% yield; orange oil; ^{1}H NMR ($CDCl_3$) δ 2.35 (quintet, J = 6.47 Hz, 2H), 2.62 (t, J = 6.84 Hz, 2H), 2.90 (s, 3H), 4.88 (br s, 2H); ^{13}C NMR ($CDCl_3$) δ 14.5, 25.3, 52.3, 81.3, 118.4, 197.0, 203.4, 332.5; MS *m*/*z* 435 (M^+), 407, 379.

36: 90% yield; orange oil; ^{1}H NMR ($CDCl_3$) δ 2.44 (quintet, J = 6.11 Hz, 2H), 2.89 (s, 3H), 3.75 (t, J = 6.11 Hz, 2H), 4.93 (br s, 2H); ^{13}C NMR ($CDCl_3$) δ 31.9, 40.7, 52.3, 80.5, 197.1, 203.5, 331.8; MS *m*/*z* 444 (M^+, ^{35}Cl), 416, 388.

37: 91% yield; orange oil; ^{1}H NMR ($CDCl_3$) δ 2.08 (quintet, J = 6.84 Hz, 2H), 2.28 (q, J = 7.00 Hz, 2H), 2.88 (s, 3H), 4.80 (br s, 2H), 5.05−5.12 (m, 2H), 5.84 (ddt, J = 17.1, 10.3, 6.65 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 28.2, 30.0, 52.3, 84.0, 116.1, 136.7, 197.3, 203.5, 330.7; MS *m*/*z* 436 (M^+), 380, 352.

38: 48% yield; orange oil; ^{1}H NMR ($CDCl_3$) δ 2.13 (br s, 1H), 2.23 (quintet, J = 6.11 Hz, 2H), 2.89 (s, 3H), 3.88 (t, J = 6.10 Hz, 2H), 4.93 (br s, 2H); ^{13}C NMR ($CDCl_3$) δ 31.9, 52.3, 58.9, 81.4, 197.3, 203.6, 331.0; MS *m*/*z* 426 (M^+), 398, 370.

39: 85% yield; orange oil; ^{1}H NMR ($CDCl_3$) δ 1.52−1.58 (m, 2H), 1.74 (quintet, J = 7.57 Hz, 2H), 1.99 (quintet, J = 7.08 Hz, 2H), 2.37 (t, J = 7.32 Hz, 2H), 2.88 (s, 3H), 3.68 (s, 3H), 4.80 (br s, 2H); ^{13}C NMR ($CDCl_3$) δ 24.5, 25.5, 28.9, 33.8, 51.6, 52.3, 84.5, 173.8, 197.3, 203.5, 330.6; MS *m*/z 496 (M^+), 440, 412.

Competitive Alkylation of Tetramethylammonium pentacarbonyl(1-oxymethylidene)chromate(0) (7a) with 11 and 40. A mixture of ammonium acylate complexe **7a** (1 mmol) and methyldiphenylsulfonium tetrafluoroborate **11** (5 mmol) and isopropyldiphenylsulfonium tetrafluoroborate **40** (5 mmol) in CH_2Cl_2 (30 mL) was stirred at room temperature for 12 h under Ar. The product was separated by gel permeation chromatography, and **12a** (8%) and **13a** (72%) were obtained (see Scheme 6).

Competitive Methylation of Tetramethylammonium pentacarbonyl(1-oxymethylidene)chromate(0) (7a) or Tetramethylammonium pentacarbonyl(1-oxymethylidene)tungstate(0) (7e) with 11 and 42 (or 43). (a) A mixture of ammonium acylate complex **7a** (0.5 mmol), methyldiphenylsulfonium tetrafluoroborate **11** (1.5 mmol), and methyl(4,4′-dinitrodiphenyl)sulfonium tetrafluoroborate **42** (1.5 mmol) in CH_2Cl_2 (5 mL) was stirred at room temperature for 24 h under Ar, and a mixture of **12a** (62%), diphenyl sulfide (10%), and 4,4′-dinitrodiphenyl sulfide (69%) was obtained (see Scheme 7).

(b) Similarly, a mixture of ammonium acylate complex **7a** (0.5 mmol), methyldiphenylsulfonium tetrafluoroborate **11** (1.5 mmol), and methyl(4,4′-dimethoxydiphenyl)sulfonium tetrafluoroborate **43** (1.5 mmol) in CH_2Cl_2 (5 mL) was stirred at room temperature for 24 h under Ar. The product was separated by gel permeation chromatography, and a mixture of **12a** (67%), diphenyl sulfide (66%), and 4,4′-dimethoxydiphenyl sulfide (25%) was obtained (see Scheme 7).

(c) Similarly, a mixture of ammonium acylate complex **7e** (0.5 mmol), methyldiphenylsulfonium tetrafluoroborate **11** (1.5 mmol), and methyl(4,4′-dinitrodiphenyl)sulfonium tetrafluoroborate **42** (1.5 mmol) in CH_2Cl_2 (5 mL) was stirred at room temperature for 24 h under Ar, and a mixture of **32** (87%), diphenyl sulfide (13%), and 4,4′-dinitrodiphenyl sulfide (82%) was obtained (see Scheme 7).

(d) Similarly, a mixture of ammonium acylate complex **7e** (0.5 mmol), methyldiphenylsulfonium tetrafluoroborate **11** (1.5 mmol), and methyl(4,4′-dimethoxydiphenyl)sulfonium tetrafluoroborate **43** (1.5 mmol) in CH_2Cl_2 (5 mL) under Ar was stirred at room temperature for 24 h, and a mixture of **32** (85%), diphenyl sulfide (74%), and 4,4′-dimethoxydiphenyl sulfide (19%) was obtained (see Scheme 7).

According to the results described above, we calculated the relative reactivities of sulfonium salts **11**, **42**, and **43** based on the yields of the resulting diaryl sulfides, since the yields of the methylation of the acylate ion from **7** are almost equal to those of the diaryl sulfides. The results are as follows: toward ammonium acylate complexe **7a** (M = Cr), 4-$NO_2C_6H_4$ (6.9):C_6H_5 (1.0):4-$MeOC_6H_4$ (0.38); toward ammonium acylate complex **7e** (M = W), 4-$NO_2C_6H_4$ (6.3):C_6H_5 (1.0):4-$MeOC_6H_4$ (0.26).

Acknowledgment. Financial support by a Grant-in-Aid (No. 06227257) for Scientific Research on Priority Areas from the Ministry of Education, Science, Culture, and Sports, Japan is gratefully acknowledged. We thank Dr. Masato Yoshida for helpful discussions, and Mr. Yuhki Yamaguchi and Mr. Takeshi Aizawa for helping the preparation of **42** and **43**.

Supporting Information Available: Characterization data for all new compounds (^{1}H and/or ^{13}C NMR spectra and IR data of sulfonium salts **10** and carbene complexes **12**−**39**). This material is available free of charge via the Internet at http://pubs.acs.org.

JO991549N