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New Method for the Preparation of Alkoxycarbene Complexes of Chromium, Molybdenum, and Tungsten Using Sulfonium Salts

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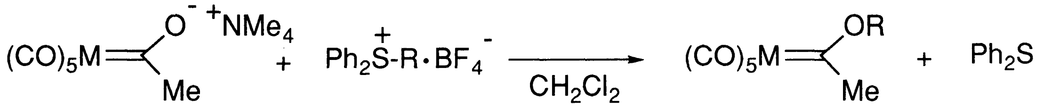
Alkylation of tetramethylammonium acylate complexes of chromium, molybdenum, and tungsten with alkyldiphenylsulfonium salts readily proceeds under mild conditions to afford alkoxycarbene complexes containing a variety of functional groups in good yields.

There is considerable current interest in Fischer-type carbene complexes, and a number of synthetically useful reactions of alkoxy- and aminocarbene complexes of chromium, molybdenum, and tungsten have been developed recently.1) Alkoxycarbene complexes have been usually prepared by alkylating pentacarbonyl(1-oxyalkylidene)-chromate(0), -molybdate(0), and -tungstate(0) with oxonium salts (Meerwein reagent).2) However, this method is limited to the preparation of alkoxycarbene complexes having simple methoxy and ethoxy groups. There are some known methods for preparing carbene complexes having functional alkyl groups;3,4) however, the methodology for the preparation of alkoxy carbene complexes of molybdenum and tungsten is still very limited.5)

It is well-known that a variety of sulfonium salts containing alkyl groups are readily available, stable, and act as good alkylating reagents for nucleophiles.6) We now report a new, general method for preparing alkoxycarbene complexes of chromium, molybdenum, and tungsten **5**, **6** and **7** using alkylation of the corresponding acylate complexes **1**, **2** and **3** with alkyldiphenylsulfonium salts **4**.

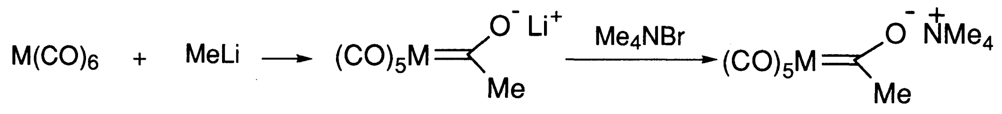


1: M = Cr
2: M = Mo
3: M = W

4

5: M = Cr
6: M = Mo
7: M = W

The tetramethylammonium acylate complexes **1**, **2** and **3** were prepared by treatment of $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ with organolithium reagents, followed by addition of $Me_4N^+Br^-$ according to the literature.2) Alkyldiphenylsulfonium salts **4a**-**g** were readily prepared by the reaction of a large excess of Ph_2S with the corresponding alkyl halides in the presence of $AgBF_4$.7)



1: M = Cr
2: M = Mo
3: M = W

$$\mathrm{Ph_2S} + \text{R-X} \xrightarrow{\mathrm{AgBF_4}} \mathrm{Ph_2\overset{+}{S}\text{-}R\cdot BF_4^-}$$

X = Br and I **4**

a: R = Me **b**: R = *i*-Pr **c**: R = $-(CH_2)_2OEt$ **d**: R = $-(CH_2)_3-CN$ **e**: R = $-(CH_2)_3-Cl$

f: R = $-(CH_2)_5CO_2Me$ **g**: R = $-(CH_2)_3OH$ **h**: R = $-(CH_2)_3CH=CH_2$ **i**: R = $-(CH_2)_2CH=CMe_2$

A typical procedure for the preparation of the chromium carbene complexes involves reaction of the acylate complex **1** (1 equiv.) with alkyldiphenylsulfonium tetrafluoroborate **4** (1 equiv.) in dichloromethane at room temperature for 12 h under an argon atmosphere. The alkoxycarbene complex **5**[8)] is purified by column chromatography on silica gel or by gel-permeation chromatography if the product and Ph_2S are difficult to separate by column chromatography.

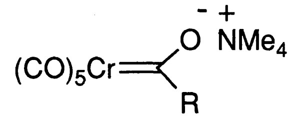
As shown in Table 1, alkylation of **1**, **2**, and **3** with methyl- or isopropyldiphenylsulfonium tetrafluoroborates **4a** or **4b** produces the alkoxycarbene complexes **5a-b**, **6a-b** and **7a-b** in good yields. A variety of functional groups can be introduced into the alkoxy part of the carbene complex using this method. Thus, the reactions of **1**, **2**, and **3** with diphenylsulfonium tetrafluoroborates **4c-f** containing ether, nitrile, ester and halide groups afford the corresponding alkoxycarbene complexes **5c-f**, **6c-f**, and **7c-f** in moderate to high yields. Most of the carbene complexes of chromium and tungsten having functional groups are rather stable compounds and can be stored at -20 °C without decomposition. However, the complexes containing ether and ester groups (i.e., **5c**, **5f**, and **7f**) decomposed gradually at -20 °C. The alkoxycarbene complexes of molybdenum can be easily prepared using this method, although the yields of the complexes **5a-g** are decreased compared with those of chromium and tungsten. Most of the molybdenum complexes decomposed gradually at -20 °C, and **5f** and **5h** were stable only in solutions of non-polar aprotic solvents.

As has been reported previously, acyloxycarbene complexes having an α-hydrogen on the alkylidene chain are unstable at room temperature and decompose to give enol esters.[9)] In contrast, the acylate complexes **1-3** are stable under the reaction conditions and can be converted into the alkoxycarbene complexes **5a-f**, **6a-f**, and **7a-f** without any detectable side reactions. It is worth noting that the alkoxycarbene complexes **5-7g** which contain a hydroxy substituent can be prepared by using the reaction of **1-3** with **4g**. The complexes **5g** and **7g** are stable at room temperature under a nitrogen atmosphere. The method reported here can be successfully applied for the preparation of the known alkoxycarbene complexes **5h** and **5i** in 87 and 55% yields, which are useful precursors for the synthesis of terpenoids.[4)]

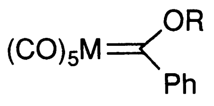
Alkoxyphenylcarbene complexes of chromium, molybdenum, and tungsten have been synthesized starting from the acylate complexes **8**, **10**, and **11**. Thus, the reaction of **8** with **4a-i** gives the alkoxycarbene complexes of chromium **13a-h** in moderate to high yields, and the carbene complexes **14h** and **15h** can be prepared from **10** and **11** in 52 and 99% yields, respectively. In a similar manner, the reactions of **9** and **12** with **4** having functional groups lead to the formation of the corresponding alkoxybutylcarbene complexes **16** and **17**.

Table 1. Reaction of Tetramethylammonium Acylate Complexes **1**, **2**, and **3** with Sulfonium Salt **4**

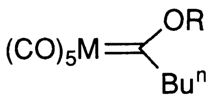
Acylate complex	Sulfonium salt	Product	Isolated yield/ %	Acylate complex	Sulfonium salt	Product	Isolated yield/ %
1	**4a**	**5a**	84	**1**	**4e**	**5e**	88
2	**4a**	**6a**	67	**2**	**4e**	**5e**	67
3	**4a**	**7a**	93	**3**	**4e**	**7e**	90
1	**4b**	**5b**	92	**1**	**4f**	**5f**	93
2	**4b**	**6b**	74	**2**	**4f**	**6f**	65
3	**4b**	**7b**	95	**3**	**4f**	**7f**	85
1	**4c**	**5c**	68	**1**	**4g**	**5g**	41
2	**4c**	**6c**	57	**2**	**4g**	**6g**	6
3	**4c**	**7c**	85	**3**	**4g**	**7g**	48
1	**4d**	**5d**	84				
2	**4d**	**6d**	42				
3	**4d**	**7d**	69				



8: R = Ph, M = Cr
9: R = Bu^n, M = Cr
10: R = Ph, M = Mo
11: R = Ph, M = W
12: R = Bu^n, M = W

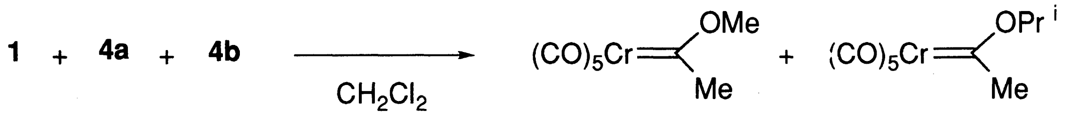


13: M = Cr
14: M = Mo
15: M = W



16: M = Cr
17: M = W

An interesting feature of alkylation using sulfonium salts is the difference in the reactivity of primary and secondary carbons attached to sulfur atom. Thus, the competitive alkylation of **1** (1 mmol) in the presence of methyldiphenylsulfonium tetrafluoroborate **4a** (5 mmol) and isopropyldiphenylsulfonium tetrafluoroborate **4b** (5 mmol) affords **5a** and **5b** in the ratio of 1 : 9. These results show an unusual reactivity of the secondary carbon adjacent to the sulfonium group and are consistent with the observation that nucleophiles such as carboxylates and phenolates react with *sec*-butyl carbons faster than the methyl carbons of sulfonium groups via S-O sulfurane as an intermediate.[10]



5a (1 : 9) **5b**

In summary, our method permits a simple, efficient synthesis of the functionalized alkoxycarbene complexes, and in principle should provide access to a variety of interesting starting materials for the intra- and intermolecular cyclization of carbene complexes.

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8) All new compounds reported in this communication were thoroughly characterized by spectral and HRMS data. Selected data for alkoxycarbene complexes are as follows: **5c**, orange oil, ^{1}H NMR ($CDCl_3$) δ 1.25 (br s, 3 H), 2.99 (s, 3 H), 3.62 (br s, 2H), 3.95 (br s, 2 H), 5.02 (br s, 2 H); ^{13}C NMR ($CDCl_3$) δ 15.1, 49.6, 67.2, 68.4, 80.1, 216.5, 223.5, 359.5; IR (neat) 2060, 1920 cm^{-1}; MS *m/z* 308 (M^+); HRMS Found: 308.0046. Calcd for $C_{11}H_{12}O_7Cr$: 307.9988; **5d**, yellow cryst., mp 40.8-42.0 °C, ^{1}H NMR ($CDCl_3$) δ 2.37 (br s, 2 H), 2.64 (br s, 2 H), 2.99 (s, 3 H), 4.96 (br s, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.4, 25.5, 49.2, 76.0, 118.5, 216.3, 223.4, 360.6; IR (KBr) 2256, 2061, 1921 cm^{-1}; MS *m/z* 303 (M^+); HRMS Found: 302.9753. Calcd for $C_{11}H_9O_6NCr$: 302.9835; **5e**, orange oil, ^{1}H NMR ($CDCl_3$) δ 2.45 (br s, 2 H), 2.97 (s, 3 H), 3.77 (br s, 2 H), 5.03 (br s, 2 H); ^{13}C NMR ($CDCl_3$) δ 32.0, 40.7, 49.3, 76.1, 126.4, 223.4, 359.5; IR (neat) 2059, 1922 cm^{-1}; MS *m/z* 312, 314 (M^+); HRMS Found: 311.9425. Calcd for $C_{10}H_9O_6{}^{35}ClCr$: 311.9492; **5f**, orange oil, ^{1}H NMR ($CDCl_3$) δ 1.57 (br s, 2 H), 1.75 (br s, 2 H), 2.02 (br s, 2 H), 2.38 (br s, 2 H), 2.94 (s, 3H), 3.68 (s, 3 H), 4.92 (br s, 2 H); ^{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; IR (neat) 2063, 1917, 1739 cm^{-1}; MS *m/z* 364 (M^+); HRMS Found: 364.0205. Calcd for $C_{14}H_{16}O_8Cr$: 364.0250.
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