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MOLYBDENUM CARBENE COMPLEXES: CYCLOPROPANATION OF ELECTRON-POOR OLEFINS

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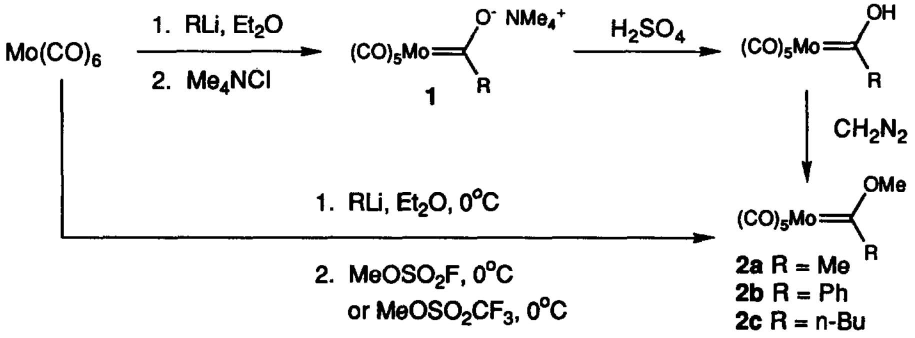
Summary: Fischer carbene complexes of molybdenum have been prepared and found to readily cyclopropanate electron-poor olefins in good yield.

Since their initial preparation in the 1960's, Fischer carbene complexes of chromium and tungsten have been found to undergo a variety of synthetically useful transformations.[1] In contrast, the analogous Fischer carbene complexes of molybdenum have been relatively unexplored.[2] Herein we report our initial observations on the synthesis and reactivity of alkylmethoxycarbene complexes of molybdenum.

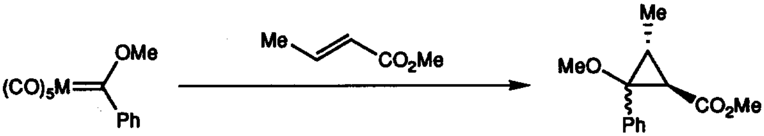
In 1967, Fischer and Maasböl reported the synthesis of the first molybdenum carbene complexes.[2a] Their method of preparation involved the addition of methyl- or phenyllithium to $Mo(CO)_6$ and isolation of the addition product as the tetramethylammonium salt **1**. Acidification and treatment with diazomethane gave molybdenum carbene complexes **2a** and **2b**.



We have applied a simpler and more direct one-pot procedure that leads to the desired molybdenum carbene complexes in reasonable yield. Addition of n-BuLi to $Mo(CO)_6$ followed by direct methylation via addition of FSO_2OMe or CF_3SO_2OMe produced molybdenum carbene complex **2c** in 54% or 56% yield, respectively.[3] This procedure was found to be simpler and more reproducible than methods previously reported for the preparation of molybdenum carbene complexes[2] and methods for the preparation of chromium and tungsten Fischer carbene complexes.[4]

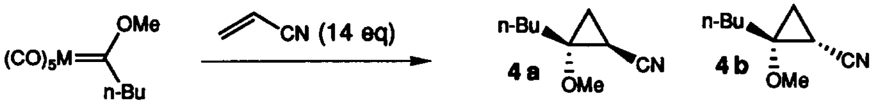
Molybdenum complexes **2a** and **2b** have been observed to rapidly decompose.[2a,d] Indeed, we have found that carbene **2a** is not sufficiently stable to readily survive purification. However, the analogous n-butylmethoxymolybdenum carbene complex **2c** was found to be considerably more stable than methylmethoxycarbene complex **2a**. We have prepared several other alkylmethoxycarbene complexes of molybdenum and found that the majority of them are relatively stable. Carbene complex **2c** can be handled in the same fashion as the analogous chromium carbene complex.

Fischer and Dötz have described the preparation of substituted cyclopropanes by treatment of molybdenum, chromium and tungsten arylmethoxycarbene complexes **3a**, **3b** and **3c** with electron-rich and electron-poor olefins.[2b,c,5] They reported several examples of cyclopropanations using chromium and tungsten complexes but only two examples of cyclopropanations with molybdenum carbene complex **3c**. Since then, there have been several reports of cyclopropane formation using chromium and tungsten carbene complexes.[6] The absence of additional examples of the utilization of molybdenum carbene complexes in this type of transformation is presumably due to the relative instability of the molybdenum based system. Because of our interest in using Fischer carbene complexes to prepare polycarbocyclic arrays,[7] we sought to determine whether this cyclopropanation process was viable with alkylmethoxymolybdenum carbene complexes.



3a M = Cr
3b M = W
3c M = Mo

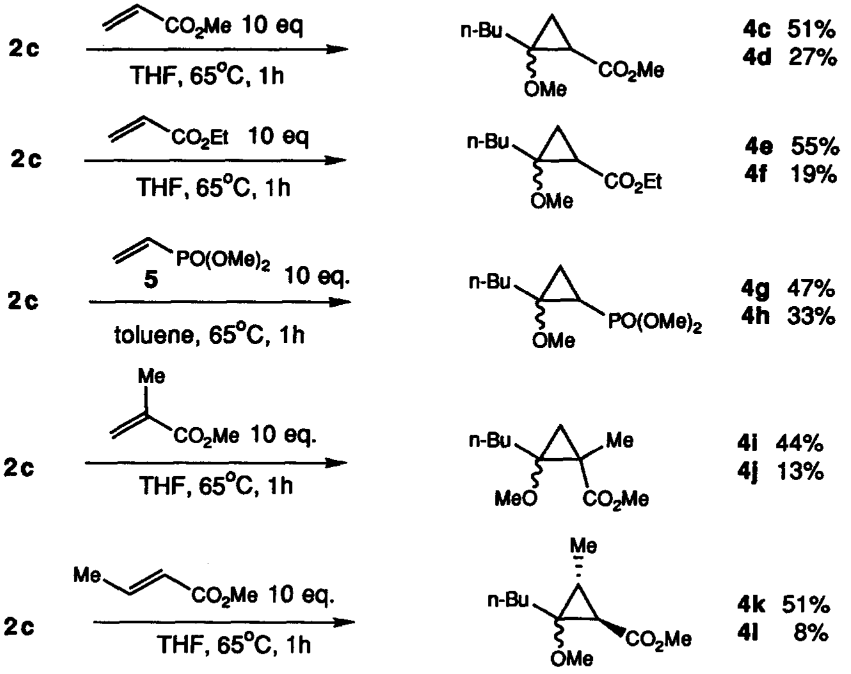
Mild thermolysis of n-butylmethoxymolybdenum carbene complex **2c** in the presence of a variety of electron poor olefins was found to produce substituted cyclopropanes **4a-l** in good yield. The conditions necessary to effect cyclopropanation with **2c** were found to be considerably milder than those necessary for the corresponding chromium and tungsten complexes (see table). In the molybdenum case, cyclopropanation occurs slowly even at room temperature. At 65°C in THF, the process is complete in 1h or less. Cyclopropanation of vinyl phosphonate **5** was done in toluene because of the low solubility of **5** in THF. As with the chromium and tungsten carbene complexes, mixtures of cyclopropane isomers were produced. These were readily separable by silica gel chromatography. By comparison to previous studies,[2b,c,5] the major cyclopropane isomer appears to



Conditions	4a	4b	Recovered Carbene
M = Mo; THF, RT, 62h	35%	27%	5%
M = Mo; THF, 65°C, 1h	32%	23%	0%
M = Cr; toluene, 80°C, 2.5h	26%	24%	0%
M = W; toluene, 110°C, 5h	39%	30%	5%

have the methoxy substituent anti to the electron withdrawing group. Cyclopropanation of methyl methacrylate gave **4i** and **4j** and varying amounts of a cyclopropane hydrolysis product.

Studies of the application of molybdenum carbene complexes to the synthesis of more complex organic frameworks are currently in progress.



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Representative Experimental Procedures:

Synthesis of molybdenum carbene complex **2c**. To a suspension of $Mo(CO)_6$ (530 mg, 2.0 mmol) in Et_2O (10 mL) at 0°C was added n-BuLi (1.6 M in hexane, 1.25 mL, 2.0 mmol). After stirring until all of the solid $Mo(CO)_6$ had disappeared (solution turns reddish-orange), methyl triflate (0.45 mL, 4.0 mmol) was slowly added. After an additional 5 min at 0°C, the reaction mixture was treated with saturated $NaHCO_3$ soln. and extracted with hexanes. The combined organics were dried ($MgSO_4$) and purified by silica gel chromatography to give 379 mg of **2c** (56%).

Representative example of formation of cyclopropane from **2c**.[8] Methyl acrylate (1.20 mL, 13.1 mmol) was added to a solution of **2c** (442 mg, 1.31 mmol) in THF (15 mL) and warmed to 65°C for 1 h. Concentration *in vacuo* and purification by silica gel chromatography gave 124 mg (51%) of **4a** and 67 mg (27%) of **4b**.

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8. All new compounds were characterized by ^{1}H NMR, ^{13}C NMR, IR, LRMS, and HRMS or analysis. ^{1}H NMR data (300 MHz, CDCl$_3$) for representative compounds is as follows. **2c**: δ 4.68 (s, 3H), δ 3.24 (t, J=7.6 Hz, 2H), δ 1.51-1.43 (m, 2H), δ 1.34 (sextet, J=7.2 Hz, 2H), δ 0.90 (t, J=7.2 Hz, 3H). **4a**: δ 3.26 (s, 3H), δ 2.02-1.98 (m, 1H), δ 1.62-1.36 (m, 7H), δ 1.07 (t, J=6.0 Hz, 1H), δ 0.94 (t, J=7.2 Hz, 3H). **4b**: δ 3.41 (s, 3H), δ 1.81-1.77 (m, 1H), δ 1.46-1.27 (m, 7H), δ 1.09 (dd, J=9.3, 5.7 Hz, 1H), δ 0.90 (t, J=7.0 Hz, 3H). **4c**: δ 3.67 (s, 3H), δ 3.25 (s, 3H), δ 1.88-1.74 (m, 2H), δ 1.70-1.67 (m, 1H), δ 1.46-1.26 (m, 5H), δ 1.18 (t, J=6.1 Hz, 1H), δ 0.89 (t, J=7.1 Hz, 3H). **4d**: δ 3.69 (s, 3H), δ 3.24 (s, 3H), δ 1.69-1.63 (m, 3H), δ 1.52-1.32 (m, 5H), δ 0.97-0.93 (m, 1H), δ 0.90 (t, J=7.1 Hz, 3H). **4e**: δ 4.10 (q, J=7.1 Hz, 2H), δ 3.23 (s, 3H), δ 1.85-1.67 (m, 3H), δ 1.45-1.27 (m, 5H), δ 1.23 (t, J=7.1 Hz, 3H), δ 1.14 (t, J=6.2 Hz, 1H), δ 0.87 (t, J=7.0 Hz, 3H). **4f**: δ 4.18-4.09 (m, 2H), δ 3.22 (s, 3H), δ 1.76-1.70 (m, 1H), δ 1.61-1.60 (m, 2H), δ 1.44-1.32 (m, 5H), δ 1.24 (t, J=7.0 Hz, 3H), δ 0.93-0.91 (m, 1H), δ 0.88 (t, J=7.0 Hz, 3H). **4g**: δ 3.70 (d, J=3.4 Hz, 3H), δ 3.67 (d, J=3.3 Hz, 3H), δ 3.20 (s, 3H), δ 2.04-1.99 (m, 1H), δ 1.64-1.24 (m, 6H), δ 1.11-0.96 (m, 2H), δ 0.87 (t, J=7.1 Hz, 3H). **4h**: δ 3.69 (d, J=2.3 Hz, 3H), δ 3.66 (d, J=2.0 Hz, 3H), δ 3.28 (s, 3H), δ 1.81-1.76 (m, 1H), δ 1.45-1.22 (m, 6H), δ 0.95-0.86 (m, 2H), δ 0.86 (t, J=7.0 Hz, 3H). **4i**: δ 3.69 (s, 3H), δ 3.18 (s, 3H), δ 1.78 (d, J=5.8 Hz, 1H), δ 1.68-1.35 (m, 6H), δ 1.31 (s, 3H), δ 0.92 (t, J=7.2 Hz, 3H), δ 0.47 (d, J=5.8 Hz, 1H). **4j**: δ 3.67 (s, 3H), δ 3.28 (s, 3H), δ 1.75-1.61 (m, 1H), δ 1.43-1.25 (m, 9H), δ 0.89 (t, J=7.0 Hz, 3H), δ 0.81 (d, J=5.9 Hz, 1H). **4k**: δ 3.64 (s, 3H), δ 3.17 (s, 3H), δ 1.90 (pentet, J=6.5 Hz, 1H), δ 1.75-1.65 (m, 1H), δ 1.46-1.29 (m, 5H), δ 1.23 (d, J=6.5 Hz, 1H), δ 1.07 (d, J=6.5 Hz, 3H), δ 0.89 (t, J=7.1 Hz, 3H). **4l**: δ 3.66 (s, 3H), δ 3.30 (s, 3H), δ 1.92-1.83 (m, 1H), δ 1.64-1.24 (m, 6H), δ 1.43 (d, J=6.6 Hz, 1H), δ 1.18 (d, J=6.2 Hz, 3H), δ 0.90 (t, J=7.0 Hz, 3H).

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