Difluoroboroxymolybdenum Fischer Carbene Complexes as Precursors of Acyl Radicals: Dimerization and Trapping with 3-Buten-2-one[†]

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Summary: Pentacarbonyl acyl molybdates ***1*** *react with boron trifluoride to give difluoroboroxy Fischer carbene complexes* ***2****, which undergo loss of the metal fragment at room temperature leading to 1,2-diketones* ***3****, 1,2-hydroxyketones* ***4****, or dimers* ***5*** *via a dimerization process of acyl radicals. Decomposition of* ***2*** *in the presence of 3-buten-2-one* ***6*** *furnishes the adducts* ***7****.*

Although the reactivity of Fischer alkoxy and aminocarbene complexes has received great attention,[1] much lees effort has been directed to the chemistry of bimetallic systems in which the carbene heteroatom is bound to a second electron-deficient metal.[2] Recently, we have described the preparation of boroxy Fischer carbene complexes and their transformation into oxaborolane or oxazaborolidine derivatives *via* an intramolecular C−H insertion process.[3] On the other hand, lithium and tetramethylammonium acyl metalates were found to formally be an acetyl anion equivalent, adding to electron-deficient olefins in a Michael fashion.[4] In addition, oxidation of tetramethylammonium and lithium acyl metalate complexes with iodine is known to generate an acyl iodide or coupling products.[5] Generation of acyl radicals from chromium complexes by using manganese(III)[6] and copper(II)[7] salts as oxidants has been also recently reported. As a part of ongoing studies on the reactivity of boroxy Fischer carbene complexes, in the present communication we describe the generation of acyl radicals from difluoroboroxy carbenes, their dimerization leading to 1,2-diketones and 1,2-hydroxyketones, and trapping with 3-buten-2-one giving 1,4-dicarbonyl compounds.

Table 1. 1,2-Diketones 3, 1,2-Hydroxyketones 4, and Dimers 5 from Pentacarbonyl Acyl Molybdates 1 and Boron Trifluoride Etherate

entry	starting molybdate	R	product			yield (%)[a]
1	**1a**	Bu	**3a**	**4a**		35/30
2	**1b**	Ph	**3b**	**4b**		38/25
3	**1c**	2-Nph	**3c**	**4c**	**5c**	24/22/7[b]
4	**1d**	(*E*)-PhCH═CH			**5d**	42
5	**1e**	PhC≡C			**5e**	33

[a] Isolated yield based on $Mo(CO)_6$. [b] Bis(2-naphthyl)ketone (9%) was also obtained.

Table 2. Reaction of Pentacarbonyl Acyl Molybdates 1, Boron Trifluoride Etherate, and 3-Buten-2-one To Give 1,4-Diketones 7

starting molybdate	R	product	yield (%)[a]
1a	Bu	**7a**	56
1b	Ph	**7b**	42
1c	2-Nph	**7c**	41
1d	(*E*)-PhCH═CH	**7d**	37

[a] Isolated yield based on $Mo(CO)_6$.

The treatment of pentacarbonyl acyl molybdate intermediates **1**, obtained by reaction of molybdenum hexacarbonyl and the corresponding organolithium compound,[8] with boron trifluoride diethyl ether complex in diethyl ether at −60 °C readily led to difluoroboroxycarbene complexes **2**. Although complexes **2** are unstable, compound **2a** could be characterized by ^{13}C NMR. On warming to room temperature, compounds **2a**−**c** underwent loss of the metal fragment affording, after hydrolysis, mixtures of 1,2-diketones **3** and 1,2-hydroxyketones **4** (entries 1−3, Table 1). In the case of **2c**, a small amount of dimer **5c** (7%) and bis(2-naphthyl)ketone (9%) was also obtained (entry 3, Table 1). However, dimers **5** were the only products observed starting from carbene complexes **2d**,**e** (entries 4−5, Table 1) (Scheme 1). Moreover, when the decomposition of **2a**−**c** was carried out in the presence of benzaldehyde, formation of hydroxyketones **4** was not observed but a mixture of diketones **3** and 1,2-diphenyl-1,2-ethanediol was obtained. On the other hand, upon warming carbene complexes **2** in the presence of an excess of 3-buten-2-one **6** (2−5 equiv) to room temper-

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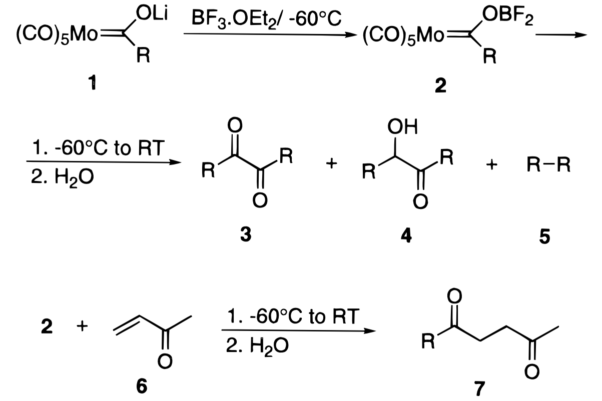
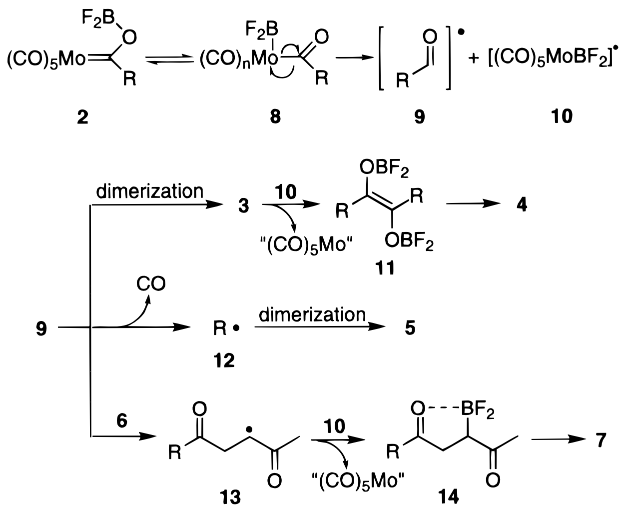
Scheme 1



Scheme 2



ature, the corresponding formal Michael addition products **7** were isolated together with variable amounts of dimerization products **3** and **4**. Use of a larger excess of **6** (10 equiv) did not result in the formation of the 2:1 adducts by introduction of a new molecule of alkene.[4a]

The formation of the products described above is considered to proceed *via* the pathway shown in Scheme 2. We could consider an equilibrium between the difluoroboroxy Fischer carbene complexes **2** and the acylmolybdenum complexes **8**, presumably favored by an interaction between the boron and the molybdenum,[3] which by the homolytic scission of the carbon−molybdenum bond leads to the acyl radicals **9** and the radical species **10**. The acyl radical can undergo a dimerization process to afford the 1,2-diketones **3**. The formation of 1,2-hydroxyketones **4** can be understood by considering the reaction of **3** and the radical species **10** by a double electron transfer with release of $Mo(CO)_5$, giving the endiol derivatives **11**. Hydrolysis of these intermediates would afford the 1,2-hydroxyketones **4**. This electron transfer is avoided in the presence of benzaldehyde, which could act as a trapping agent of the unpaired electron of radical species **10**, thus generating the corresponding radical anion. The dimerization of this radical anion would give rise to 1,2-diphenyl-1,2-ethanediol after protonation. On the other hand, the acyl radicals **9** could suffer a decarbonylation reaction[9] affording radicals **12**, which by dimerization would generate dimers **5**. Finally, when the reaction is carried out in the presence of 3-buten-2-one, direct addition of acyl radicals **9** to the alkene would lead to radical intermediates **13**.[10] Further electron transfer from **10** to intermediates **13** produces loss of $Mo(CO)_5$ with formation of boroenolates **14**. Hydrolysis of **14** leads to the formal 1:1 Michael-addition products **7**. The lack of formation of the 2:1 adducts, when a large excess of electron-deficient olefins is used, can be due to the stabilizing interaction between the boron atom and the oxygen of the carbonyl group in **14**, which prevents the reaction with a second molecule of the alkene.

In conclusion, we have described, for the first time, a simple method to generate acyl radicals from difluroboroxy Fischer carbene complexes in very mild reaction conditions and in the absence of an oxidant. These acyl radicals undergo dimerization to give 1,2-diketones or dimerization followed by reduction to afford 1,2-hydroxyketones. Finally, the acyl radicals can be trapped with electron-poor olefins leading to 1,4-dicarbonyl compounds. Further studies with other boroxy Fischer carbene complexes as acyl radical precursors and their behavior in multicomponent reactions are currently underway in our laboratories.

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Supporting Information Available: Text giving the synthetic procedures and listings of spectral data for **3**−**5** and **7** (3 pages). Ordering information is given on any current masthead page.

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