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Unexpected Formation of 1,3-Diols from Unsaturated Chromium Fischer Carbene Complexes and Borane

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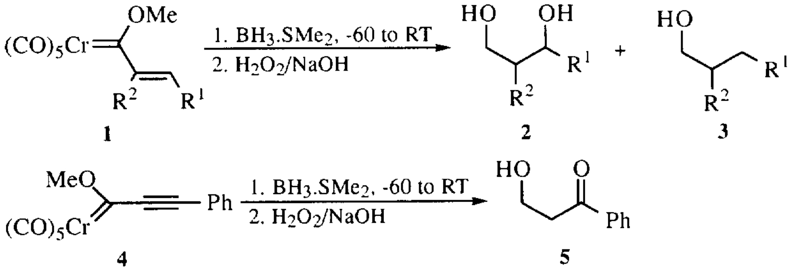
Abstract: α,β-unsaturated Fischer carbene complexes of chromium **1** react with borane-dimethyl sulfide complex to give, after oxidation with hydrogen peroxide and sodium hydroxide, 1,3-diols **2** and variable amounts of alcohols **3**. The same procedure applied to alkynyl chromium carbene complex **4** leads to 3-hydroxyketone **5**. © 1997 Elsevier Science Ltd.

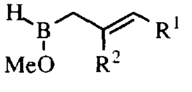
Reaction at the metal center in Fischer carbene complexes have been extensively studied.[1] However, only a few examples have been described in which the addition of hydrides such as Bu_3SnH,[2] R_3SiH,[3] borohydrides,[4] or $LiAlH_4$[5] to heteroatom stabilized carbene complexes were involved. In the present communication we describe the reaction of α,β-unsaturated methoxy chromium carbene complexes with borane-dimethyl sulfide complex and further oxidation to give 1,3-diols and 3-hydroxyketones.

The treatment of α,β-unsaturated chromium carbene complexes **1** in THF[6] with 1 to 2 equivalents of a solution of borane in dimethyl sulfide at temperatures ranging between -60 and 20°C (16 to 18 h) and subsequent oxidation with alkaline hydrogen peroxide in water led to 1,3-diols **2** and variable amounts of alcohols **3**. This behaviour is in marked contrast with that of methyl cynamate, which leads to 3-phenyl-1,2-propanediol by treatment with borane at room temperature for 14 days and further oxidation. On the other hand, when the reaction was carried out with the alkynyl chromium carbene complex **4** under the same reaction conditions, 3-hydroxy-1-phenyl-1-propanone **5** was obtained (Scheme 1 and Table). The outcome of the latter reaction depends on the stoichiometry carbene-borane and on the reaction time. So, when an excess of borane was used for a longer reaction time a mixture of hydroxyketone **5** and diol **2a** was obtained after oxidation.



Scheme 1

The formation of products **2** can be understood by assuming first a double transfer of hydride from borane to the carbene carbon atom of carbene complexes **1**, probably favoured by an interaction between the boron atom of borane and the chromium of carbene complex,[7] giving the allylic borane **6** after loss of the metal fragment. In fact, we have found that the reaction of pentacarbonyl methoxy(phenyl)methylen chromium with borane affords, after oxidation, benzyl alcohol in 90% yield. Further inter or intramolecular hydroboration of the resulting allylborane 6[8] would produce 1,3-propanediylbis(borane) or boracyclobutane derivatives **7** and **8** respectively, which after oxidation would lead to 1,3-diols **2**. A partial hydrolysis of the boron-secondary carbon bond before the oxidation would furnish the alcohols **3**. Similarly, reduction of the chromium-carbon double bond of carbene complex **4** followed by hydroboration of the carbon-carbon triple bond would lead to a 1,3-propenediylbis(borane) derivative **9**, which after oxidation would lead to **5**. The formation of **2a** in this reaction can be explained by considering a new hydroboration of the bis(borane) **9** intermediate and partial hydrolysis before the oxidation.



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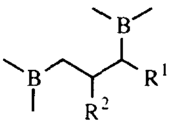

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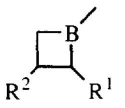

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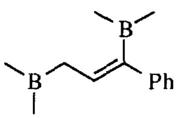

9

In conclusion, we have described a straightforward transformation of α,β-unsaturated Fischer carbene complexes into 1,3-diols or 3-hydroxyketones by using hydroboration-oxidation tandem reaction. Further studies on the mechanism and synthetic applications are underway in our laboratories.

Table. Reaction of carbene complexes **1** and **4** with borane-dimethyl sulfide complex followed by oxidation to give 1,3-diols **2**, alcohols **3**, and 3-hydroxy-1-propanone **5**[a].

Starting carbene	R^1	R^2	Product		Yield (%)[b]
1a	Ph	H	**2a**	**3a**	50/10[b]
1b	1-Naph	H	**2b**	-	45
1c	Bu	H	**2c**	**3c**	35/15[c]
1d	H	Ph	**2d**	**3d**	40/18[c]
4			**5**		48[d]

[a] 1 to 2 equiv. of $BH_3.SMe_2$ was added at -60°C to a 0.05 M THF solution of the corresponding carbene complex **1** or **4**. The mixture was allowed to warm to RT (16-18 h) and 5 ml of 3N NaOH solution and 1 ml of H_2O_2 were added. After usual workup **2** and **3** or **5** were obtained. [b] Based on the starting carbene **1** or **4**. [c] The first yield corresponds to product **2** and the second to **3**. [d] When an excess of borane is used and for 48 h **5** (32%) and **2a** (21%) are obtained.

Acknowledgements

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