

[4+2] Cyclization reactions of chiral C β -substituted Fischer alkenyl carbene complexes: efficient synthesis of enantiopure cyclohexenone and norbornene derivatives

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Abstract—Chiral alkenyl carbene complexes of tungsten(0) **1** and **2**, readily available from the chiral pool, undergo the [4+2] cycloaddition with the Danishefsky diene to provide enantiopure 4-alkenyl-2-cyclohexenone adducts **5** and **7** with high stereoselectivity after treatment of the primary cycloadducts **4** and **6** with TBAF. Cyclopentadiene also cycloadds to carbenes **1** and **2** affording the expected norbornene metal carbene complexes **10** and **12** with remarkable diastereo and face selectivity. Oxidative removal of the metal pentacarbonyl fragment leads to the ester derivatives **11** and **13**. The X-ray structure analysis of two cycloadducts derived from carbenes **1** and **2** has been performed. © 2007 Elsevier Ltd. All rights reserved.

1. Introduction

Due to the high electron-accepting power of the pentacarbonylmetal unit, Fischer-type α,β -unsaturated carbene complexes have demonstrated to be excellent partners for different cycloaddition reactions.¹ In particular, the [4+2] cycloaddition of alkenyl carbene complexes toward electron-rich dienes,² which emerged two decades ago,³ reveals some advantages over that based on electron-poor, non-metal dienophiles: (i) the reaction occurs under much milder reaction conditions and, therefore, higher selectivity is attained and (ii) the versatile metal carbene functionality is maintained unaltered in the cycloadduct allowing to undertake further elaboration.⁴

On the other hand, the asymmetric version of this process has not been so widely developed.⁵ The most relevant contribution has been delivered by Wulff et al. who found that chiral aminoalkenyl carbene complexes of chromium(0) exhibited very high exo- and facial diastereoselectivity toward 1-methoxy-3-trimethylsilyloxy-1,3-butadiene (Danishefsky's diene).⁶ In contrast, chiral alkoxyalkenyl carbene complexes, e.g., carbene complexes derived from (–)-menthol, have been shown to induce modest selectivity.^{5,7} In a different approach, the cycloaddition reaction of cyclopentadiene and

2,3-dimethyl-1,3-butadiene with methoxyalkenyl carbenes having a monosaccharide unit (arabinose and galactopyranose) attached to the C- β carbon has been reported to take place with moderate selectivity.⁸ In this context, we have focused recently on the potential of tungsten alkenyl carbenes **1** and **2** containing a chiral group—1,3-dioxolane (**1**) and 1,3-dioxane (**2**)—that are readily available from the chiral pool⁹ and, importantly, very promising for further elaboration. This type of chiral carbene complexes has been shown to exhibit high selectivity in Michael–Mukaiyama addition¹⁰ and cyclopropanation (Michael type addition/cyclization)¹¹ reactions with 2-trimethylsilyloxy and 2-methoxyfuran, respectively (Fig. 1).

On the basis of these findings, we have explored the behavior of carbenes **1** and **2** in the Diels–Alder cycloaddition. We report herein that they undergo the [4+2] cycloaddition reaction with 1-methoxy-3-trimethylsilyloxy-1,3-butadiene and cyclopentadiene with good chemical yield and high selectivity. The transformation of the cycloadducts into metal-free derivatives is also undertaken.

2. Results and discussion

First we found that enantiopure tungsten carbene complexes **1** and **2** are highly reactive toward the Danishefsky's diene **3** at low temperature (Scheme 1).¹² Thus, the reaction of the methoxycarbene **1a** (R=Me) with **3** (5 equiv) in toluene

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