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Regiochemistry of molybdenum-catalyzed O–H insertions of vinylcarbenoids

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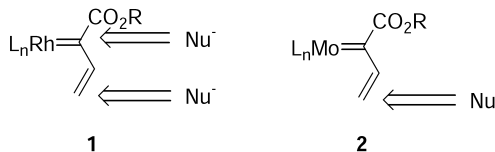
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Abstract

Molybdenum-catalyzed decomposition of vinyl diazoacetates generates vinylcarbenoids that preferentially react with alcohols at the vinylogous position of the vinylcarbenoid rather than at the carbenoid site. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: carbenes and carbenoids; diazo compounds; O–H insertion; molybdenum; rhodium.

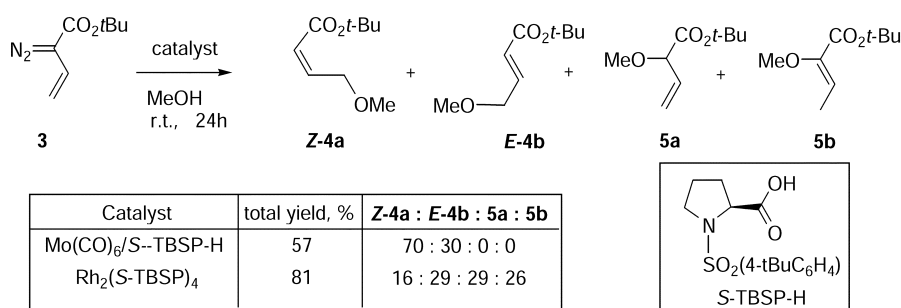
In recent years numerous examples of the synthetic utility of rhodium-stabilized vinylcarbenoids have been reported.^{1,2} An intriguing aspect of this chemistry is that the vinylcarbenoid can display electrophilic reactivity at either the carbenoid site or the vinyl terminus, as illustrated in structure **1**.³ So far, this effect has only been observed when the vinylcarbenoid lacks functionality at the vinyl terminus. In such systems, enhancement of vinylogous reactivity can be achieved by using electron withdrawing ligands on the dirhodium, by using a slightly polar solvent such as CH₂Cl₂ instead of hydrocarbons, or by increasing the size of the ester group on the vinyl diazoacetate. In this paper, we describe that by using a molybdenum catalyst⁴ instead of rhodium-based catalysts, considerable enhancement of the vinylogous reactivity can be achieved, as illustrated in structure **2**.



The impetus for this study arose from the fact that electron-withdrawing ligands around rhodium tended to enhance the vinylogous reactivity of the vinylcarbenoid.³ It was therefore, reasoned that dimolybdenum complexes may further enhance vinylogous reactivity because these complexes

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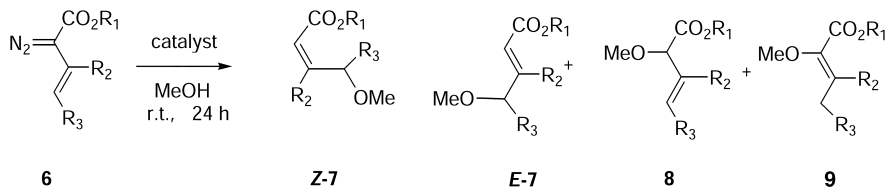
contain quadruple metal–metal bonds with several low-energy empty antibonding orbitals⁵ and would be expected to be highly electron withdrawing. As the plan of this study was to compare the effect of the molybdenum versus rhodium, attempts were made to prepare a molybdenum complex analogous to the chiral catalyst $\text{Rh}_2(\text{S-TBSP})_4$ ^{2e,6} by heating $\text{Mo}(\text{CO})_6$ with *S*-TBSP-H in THF for 3 days.⁷ Even though the resulting yellow-green solution decomposes quickly on exposure to air, the mixture can be transferred by syringe into a reaction flask and is effective at vinyldiazoacetate decomposition. A comparison study of the reaction of the vinyldiazoacetate **3** with methanol revealed that the $\text{Mo}(\text{CO})_6/\text{S-TBSP-H}$ catalyst was much more effective than $\text{Rh}_2(\text{S-TBSP})_4$ at enhancing vinylogous reactivity. The $\text{Mo}(\text{CO})_6/\text{S-TBSP-H}$ catalyzed reaction of **3** with methanol gave exclusive formation of the 4-methoxybutenoates as a mixture of double bond regioisomers **Z-4a** and **E-4b**, while the $\text{Rh}_2(\text{S-TBSP})_4$ catalyzed reaction of **3** with methanol gave a mixture of **Z-4a**, **E-4b** and the 2-methoxybutenoates **5a**, **5b**. An interesting feature of the $\text{Mo}(\text{CO})_6/\text{S-TBSP-H}$ catalyzed reaction of **3** was the preferential formation of **Z-4a**, which was not the case in the $\text{Rh}_2(\text{S-TBSP})_4$ -catalyzed reaction.



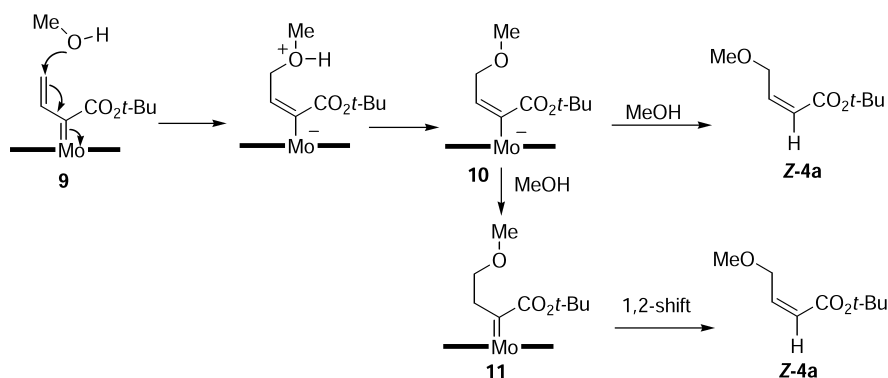
The reaction was then extended to three representative vinyldiazoacetates **6a–c** as illustrated in Table 1. $\text{Rh}_2(\text{S-TBSP})_4$ -catalyzed decomposition of **6a** in the presence of methanol resulted in exclusive O–H insertion at the carbenoid center. In contrast, the reaction with $\text{Mo}(\text{CO})_6/\text{S-TBSP-H}$ resulted in a mixture of products derived from reactions at both the carbenoid and the vinyl terminus positions. Once again, the *Z*-isomer predominated. A control experiment was carried out to verify that excess $\text{Mo}(\text{CO})_6$ was not the cause of the catalysis for the molybdenum reactions. Only traces of the O–H insertion products were formed under these conditions. In the cases of **6b** and **6c** the $\text{Mo}(\text{CO})_6/\text{S-TBSP-H}$ -catalyzed reaction resulted in the predominant formation of O–H insertion products derived from attack at the vinyl terminus, while the $\text{Rh}_2(\text{S-TBSP})_4$ -catalyzed reaction resulted in the formation of a mixture of O–H insertion products. The $\text{Mo}(\text{CO})_6/\text{S-TBSP-H}$ -catalyzed reactions of **6b** and **6c** preferentially formed the *Z*-isomer of the O–H insertion products. In no instance, however, was any appreciable asymmetric induction (> 15% ee) obtained in these reactions.

One of the most interesting aspects of these vinyl terminus O–H insertions is the high *Z* selectivity that is observed in these reactions. Two explanations are possible for the high *Z* selectivity and these are summarized in Scheme 1. The vinylcarbenoid **9** may have a preferred conformation of the vinyl group in order to limit ligand steric influence. The resulting vinylmolybdenum ion **10** is configurationally stable and on protonation–deprotonation generates the *Z* product **4**. Alternatively, the vinyl molybdenum ion is protonated to form a new molybdenum carbenoid complex **11**, which then undergoes a 1,2-hydride shift to form **Z-4a**. The preferential formation of *Z*-alkenes from a 1,2-hydride shift on a metal–carbenoid complex is well-established.⁸

Table 1
Reaction of vinyl diazoacetates with methanol

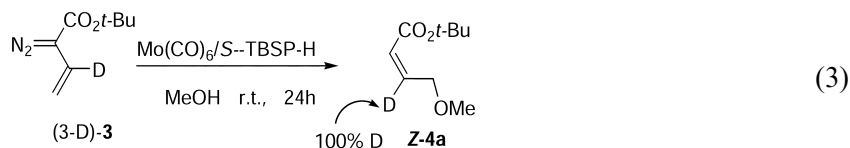
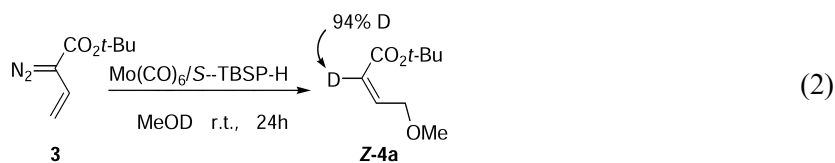


	Catalyst	total yield, %	Z-7 : E-7 : 8 : 9
 6a	Mo(CO) ₆ /S-TBSP-H	93	34 : 17 : 40 : 9
	Rh ₂ (S-TBSP) ₄	86	0 : 0 : 89 : 11
	Mo(CO) ₆	7	25 : 40 : 35 : 0
 6b	Mo(CO) ₆ /S-TBSP-H	51	63 : 28 : 9 : 0
	Rh ₂ (S-TBSP) ₄	75	5 : 25 : 22 : 48
 6c	Mo(CO) ₆ /S-TBSP-H	58	76 : 24 : 0 : 0
	Rh ₂ (S-TBSP) ₄	55	29 : 40 : 27 : 4



Scheme 1.

In order to distinguish between the pathways in Scheme 1, two test reactions were devised. In the first, reaction of **3** was carried out in the presence of CH₃OD (Eq. (2)). This resulted in the predominant formation of vinyl ether **Z-4a** in which 94% deuterium incorporation had occurred at the C-2 position. The second test was the reaction of (3-D)-**3** with methanol (Eq. (3)). This resulted again in the predominant formation of **Z-4a** with 100% deuterium remaining at the C-3 position. These results indicate that the most likely mechanism for the formation of **4a** is by the direct protonation of a geometrically defined vinylmolybdenum ion because if a 1,2-hydride shift was involved, scrambling of the deuterium label between C-2 and C-3 would have been expected.



Acknowledgements

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