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NOVEL ISOMERIZATION AND SEQUENTIAL 1,2-NUCLEOPHILIC ADDITION OF ACYCLIC DIENONE-IRON TRICARBONYL COMPLEXES. HIGHLY STEREOSELECTIVE SYNTHESIS OF TERTIARY ALCOHOLS

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Abstract: 1,2-Nucleophilic addition of lithiumalkyls to the *Z*-dienone complex 2 gave the (1*RS*,2*SR*)-*Z*-dienol complex 4 exclusively, while the reaction of 2 with trialkylaluminum provided the (1*SR*,2*RS*)-*E*-dienol complex 3 *via* the isomerization to the *E*-dienone complex 1.

Acyclic and functionalized butadiene-iron tricarbonyl complexes have been proven to be valuable intermediates in organic synthesis due to the highly efficient protecting and stereodirecting properties of the $Fe(CO)_3$ moiety.[1] Concerning the 1,2-asymmetric induction using $Fe(CO)_3$ chirality, there are little studies dealing with the nucleophilic addition to the dienone complexes such as 1[2] and 2 in comparison with the dienal complexes which are known to react with organometallic reagents in a poorly stereoselective manner.[3] Although Neumann has reported that the reaction of *E*-dienone complexes 1 with lithiumalkyls resulted in an exclusive formation of (1*SR*,2*RS*)-alcohol complex 3, the reported nucleophiles and substrates are limited.[2] Then, that situation stimulated us to investigate whether *Z*-dienone complexes 2 can be employed as substrate or not. Herein we report the novel reactions of 2 which afford different product 2 or 3 depending on the organometallics employed.

The *E*- and *Z*-dienone complexes 1 and 2 were prepared by the known method.[4] Nucleophilic additions to racemic dienone complexes 1 were examined with various organometallics other than *n*-butyllithium reported by Neumann.[2] In all cases, we detected only one diastereomers (de ~100%) which were identical with the single ones observed with organolithiums. Among them, the most successful organometallic reagents are triethylaluminum and diallylcopper magnesium bromide-borontrifluoride complex to yield the diastereomeric pure (1*SR*,2*RS*)-alcohol complex 3[5] in 73 and 87% yields, respectively. From view of their mild reactivity, it is ascertained that organoaluminums and organocoppers are superior reagents to organolithiums. We next investigated the reactivity of 2 with the above mentioned organometals. The representative results are shown in Table 1, from which the unique characters of 2 compared with 1 were revealed in addition to high stereoselectivity observed in all of the entries. Namely, addition of organolithium and organocopper reagents into 2 occurred very quickly to give normal addition products 4[6] as a sole product, respectively (entry 1, 3 and 4), while similar treatment of 2 with triethylaluminum produced an unexpected product 3[5], obtained by the reaction of 1 with organometals as described above (entry 5). Furthermore in the cases of Grignard reagents (entry 2 and 6), the related reactions gave unpredictable results, that is, either 3 or 4 was obtained stereoselectively by the difference of nucleophiles (R^2) of the reagents. Such abnormal outcome may be rationalized by an initial *Z* to *E* isomerization of the starting material 2 attributed to both of the Lewis acidity and nucleophilicity of the organometallic reagents.[7,8]

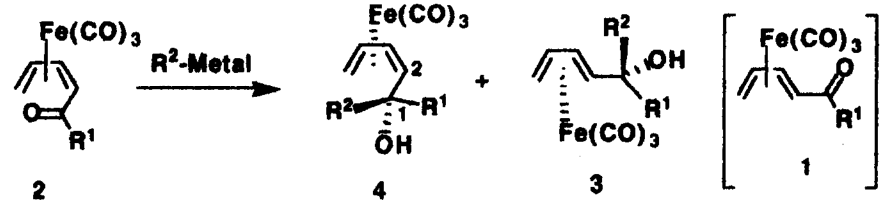

Table 1. Diastereoselective Addition of Organometallic Reagents to Z-Dienone Complex 2

entry	R^1	R^2-Metal	solvent	temperature (°C)	yield (%) (4 : 3)	d.e. (%)
1	Me	n-BuLi	THF	-78	51 : 0	100
2	Me	(allyl)MgBr	THF	-78	53 : 0	100
3	Me	(allyl)$_2$CuMgBr·BF$_3$	THF	-78	63 : 0	100
4	n-Bu	MeLi	THF	-78	96 : 0	100
5	Me	Et$_3$Al	benzene	r.t.	0 : 81	100
6	n-Bu	MeMgBr	THF	-78 → -30	0 : 89	100

In conclusion, we succeeded in synthesizing both diastereomers 3 and 4 of the tertiary alcohols with a perfect stereoselectivity by simply changing organometallic reagents (RLi *vs* R$_3$Al). This means that using chiral none-racemic Z-dienone complexes,[9] both enantiomers of tertiary alcohols can be made from the same starting materials.

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5) The stereochemistry of 3 was estimated by reference to the Franck -Neumann's report.[2]
6) The stereochemistry of 4 was deduced from the reaction mechanism (Fig. 1) and the report of hydride reduction of Z-dienone complex: Franck -Neumann, M.; Abdali, A.; Colson, P. -J.; Sedrati, M. *Synlett*, **1991**, 331.
7) Although the reaction of organometallics with Z-dienal complex have been studied by Grée,[3d] only (1*RS*,2*SR*)-addition products were given without the isomerization.

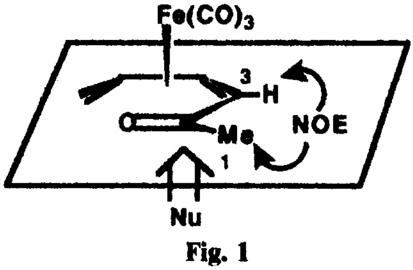

Fig. 1

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