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Catalytic Enantioselective Conjugate Addition of Diethylzinc using Ni^{II} -DAIB complexes.

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Key Words: enantioselective catalysis, conjugate addition, diethylzinc, enones.

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Abstract : The conjugate addition of diethylzinc to chalcone, catalyzed by a Ni^{II} complex of the chiral amino-alcohol (-)-DAIB, resulted in the formation of (R)-1,3-diphenyl-penta-1-one with enantiomeric excess up to 85%.

Although there are numerous reports on catalytic asymmetric 1,2-additions¹, only a limited number of catalytic enantioselective 1,4-addition reactions of organometallic reagents are known. Excellent selectivities have however been reached in the synthesis of β -substituted ketones using stoichiometric or excess amounts of chiral organocopper reagents². Realizing these facts the design of an efficient chiral catalyst for this important carbon-carbon formation is a challenging goal. Enantioselective additions of *Grignard reagents* to cyclohexenone using catalytic amounts of a chiral copper complex (ee 14-78%)³ or various chiral zincates (ee $\leq 33\%$)⁴ have been demonstrated. Furthermore it has been shown that the use of *dialkylzinc reagents* and Ni^{II} complexes, based on norephedrine⁵ or a substituted bipyridine⁶, as chiral catalysts resulted in modest to high enantioselectivities (up to 90%).

As a result of our studies on the conjugate addition of organozinc reagents **7** we now report a Ni^{II} -(-)-dimethylaminoisoborneol (DAIB) catalyst for high regio- and enantio-selective diethylzinc additions to enones.

The reaction of diethylzinc with chalcone in CH₃CN using a Ni-catalyst (7 mol%), in situ prepared from Nickel acetylacetonate (Ni(acac)₂) and (-)-DAIB (1:2.4 ratio), afforded R-(-)-1,3-diphenylpentan-1-one (**3**) in 94% isolated yield and 59% ee⁸ (scheme, Table).

Table: Enantioselective 1,4-addition using Ni(II)-(-)-DAIB complex and an achiral additive

entry	achiral additive ^a	Y(%) ^b	ee(%) ^c	configuration ^d
1	---	94	59	R
2	2,4,6-trimethylpyridine	83	65	R
3	2,2'-bipyridine	75	85	R
4	morpholine	88	56	R
5	piperidine	77	70	R

a) ratio; 1 : 2 : Ni(acac)₂ : (-)-DAIB : additive 1:1.1:0.07:0.17:0.07; b) isolated yield of **3**;

c) determined by HPLC; d) based on reported elution order⁶ of (R)- and (S)-**3**.

The addition of achiral amine ligands led to a substantial improvement of the enantioselectivity although yields are slightly lower. Thus addition of 2,2'-bipyridine (1 eq. with respect to Ni^{II}) raised the enantiomeric excess to 85% (75% yield of **3**). Although less effective some monodentate ligands also improve the selectivity (entries 2,5). The promoting effect on the stereoselectivity of additional achiral ligands (*achiral ligand control*) is in excellent agreement with recent results described by Soai⁵ and coworkers. It should be emphasized that in contrast to the observation of low enantioselectivities in previous studies using bidentate aminoalcohols⁵ the (-)-DAIB derived Ni-catalyst gives already a remarkable enantiomeric excess of 59% without additional achiral ligands. Preliminary investigations with the well characterized⁹ pentacoordinated chiral Ni^{II}-complex **4** showed high activity (84% yield) but poor selectivity (ee 10%) so far in the formation of **3**.

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- The ee was determined by HPLC analysis: chiral column: CHIRACEL OD; 0.25% iPrOH in hexane, flow rate 1.0 ml/min, UV detector (254 nm), ret. times: (S) 16.3 min, (R) 19.0 min.
- The crystal and molecular structure as determined by X-ray analysis will be reported elsewhere.