



Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/lcyc20>

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Published online: 22 Aug 2006.

To cite this article: Puhong Liao, You Huang & Yongmin Zhang (1997) Reductive Coupling of Aldimines Mediated with Samarium Catalyzed by Cp_2TiCl_2 , Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 27:9, 1483-1486, DOI: [10.1080/00397919708006083](https://doi.org/10.1080/00397919708006083)

To link to this article: <http://dx.doi.org/10.1080/00397919708006083>

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REDUCTIVE COUPLING OF ALDIMINES MEDIATED WITH SAMARIUM CATALYZED BY Cp_2TiCl_2

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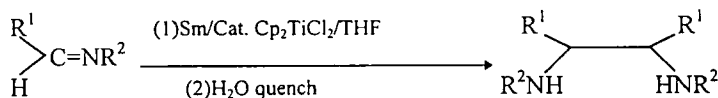
ABSTRACT: Reductive coupling of aldimines into vicinal diamines mediated with samarium catalyzed by Cp_2TiCl_2 proceeds in refluxing THF with good yields.

Despite the frequent occurrence of vicinal diamine units in natural products and medicinal agents¹, only a few methods are available for the preparation of vicinal diamines². Apparently, the reductive coupling of imines is a straightforward route to vicinal diamines. Recently, a few reagents have been employed for the formation of vicinal diamines, namely aluminium^{3a}, ytterbium^{3b}, indium^{3c}, titanium^{3d}, and SmI_2 ^{3e}. These reports encouraged us to explore the reactions with our recently reported $\text{Cp}_2\text{TiCl}_2/\text{Sm}$ system, which is a good reagent of reduction and coupling⁴.

Accidentally, we found that the coupling reaction of aldimines could be carried out in refluxing THF with metallic samarium (1mmol) and a catalytic amount of Cp_2TiCl_2 (0.1-0.2mmol) (Scheme 1). The reaction times and product yields are listed in Table 1.

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Scheme 1

**Table 1:** Reductive Coupling of Aldimines to Vicinal Diamines^a

product	R ¹	R ²	Ratio of moles ^b	Reaction ^c Time(h)	Yield(%) ^d (dl:meso) ^e
1 ^[9]	C ₆ H ₅	C ₆ H ₅	2:1:0.1	4	88(70:30)
2 ^[10]	p-ClC ₆ H ₄	C ₆ H ₅	2:1:0.2	5	80(75:25)
3 ^[10]	p-CH ₃ C ₆ H ₄	C ₆ H ₅	2:1:0.2	5	84(80:20)
4 ^[3e]	C ₆ H ₅	C ₆ H ₅ CH ₂	2:1:0.2	6	75(85:15)
5 ^[10]	p-CH ₃ OC ₆ H ₄	C ₆ H ₅	2:1:0.1	4	82(80:20)
6 ^[11]	C ₆ H ₅	p-BrC ₆ H ₄	1:1:0.2	6	73(90:10)
7 ^[8]	p-(CH ₃) ₂ NC ₆ H ₄	C ₆ H ₅	1:1:0.2	9	67(80:20)
8 ^[12]	C ₆ H ₅	n-C ₄ H ₉	1:1:0.2	9	57(60:40)
9 ^[3e]	C ₆ H ₅	c-C ₆ H ₁₁	1:1:0.2	9	55(85:15)

a. Carried out in the manner as described in the text unless otherwise noted; b. Ratio of moles of aldimine:samarium:Cp₂TiCl₂; c. The reaction time was monitored by TLC until most of imines was consumed; d. Isolated yields, the products were confirmed with IR and ¹H NMR;

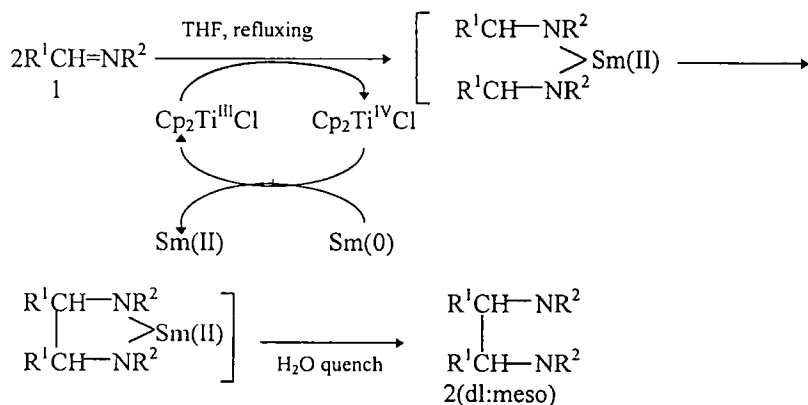
e. Ratio of dl:meso is calculated from ¹H NMR.

The coupling reaction of aldimines can not be carried out without Cp₂TiCl₂ under the same conditions. Moreover, we have investigated the Cp₂TiCl₂/Sm system and obtained evidence of Cp₂Ti^{III}Cl in the system⁵. Meanwhile, we have observed that Cp₂Ti^{III}Cl which is prepared according to lit.[6] also mediated the reducing and coupling of aldimines. According to above experiment and referring to Kham⁸, a possible mechanism is proposed (Scheme 2).

Experimental:

Starting materials - The aldimines were prepared from the freshly distilled

Scheme 2



aldehyde and aniline according to a published procedure⁷. Tetrahydrofuran was preparative TLC on silica gel (hexane:Et₂O=10:1)

Acknowledgement: We thank the National Natural Science Foundation of China and the Open Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy Sciences for financial support.

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5. Preparation of Cp_2TiCl by reduction of Cp_2TiCl_2 with Sm. 0.15g(2mmol)Sm and 0.5g (2mmol) Cp_2TiCl_2 were mixed in a Schlenk type apparatus under a nitrogen atmosphere, then 10ml THF was added by syringe. After refluxing 0.5 h, a deep blue solution was obtained. The solvent was evaporated under reducing pressure. Benzene(5ml) was added and this benzene solution was preserved under a nitrogen atmosphere in the Schlenk flask, then a deep blue solid was gradually precipitated out. Recrystallization from hot benzene, gave deep blue crystals. Mass spectrum was recorded on a HP 5989A type apparatus. MS m/z(rel. intensity) 213(M^+ ,100), 178(96), 148(62), 83(10), 65(7).
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(Received in the UK 17th September 1996)