

## Reduction of Diaryldiselenides by System of $\text{Cp}_2\text{TiCl}_2/\text{Bu}^i\text{MgBr}/\text{THF}$ and Its Application in Synthesis of Unsymmetrical Diaryl Selenides

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**Abstract:** Reduction of diaryldiselenides by the system of  $\text{Cp}_2\text{TiCl}_2/\text{Bu}^i\text{MgBr}/\text{THF}$  gave the nucleophilic arylselenium complex. They reacted with diaryl iodonium salts to afford unsymmetrical diaryl selenides in high yields.

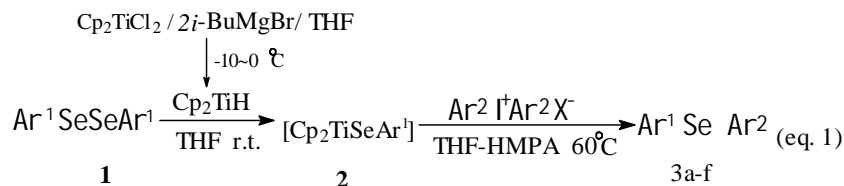
**Keyword:** Diaryl selenides, reduction, titanocene dichloride, isobutylmagnesium bromide, arylselenium complex of titanocene, diaryl iodonium salts, unsymmetrical diaryl selenides.

In organic selenium chemistry, diaryldiselenides are important intermediate due to their stability against air and water. When they are reduced, the nucleophilic selenoates can be obtained. There have been several methods for the reduction of diselenides such as *via*  $\text{NaBH}_4$ <sup>1</sup>,  $\text{SmI}_2$ <sup>2</sup>, the reduction system of Se,  $\text{H}_2\text{O}$  and  $\text{CO}^3$ , hydrazine-sodium methanolate<sup>4</sup> and  $\text{Sm}/\text{HgCl}_2$ <sup>5</sup>. In this paper, we report the reduction system of  $\text{Cp}_2\text{TiCl}_2/\text{Bu}^i\text{MgBr}/\text{THF}$  and its application in synthesis of unsymmetrical diaryl selenides.

Titanocene hydride  $[\text{Cp}_2\text{TiH}]^6$  was derived from the reaction of  $\text{Cp}_2\text{TiCl}_2$  with  $\text{Bu}^i\text{MgBr}$ . It is a very strong reductant. This led us to investigate the reaction cleavage of Se-Se bond by the system of  $\text{Cp}_2\text{TiCl}_2/\text{Bu}^i\text{MgBr}$ . The results showed that in THF the system of  $\text{Cp}_2\text{TiCl}_2$  and  $\text{Bu}^i\text{MgBr}$  reduced diaryldiselenides readily and gave deep blue arylselenium complexes of titanocene  $[\text{Cp}_2\text{TiSeAr}]$ , which were assumed to be reactive species.

We have studied the reaction of the species with haloarenes or *p*-chloro nitrobenzene, But the reaction did not occur in THF-HMPA at 60°C. Considering that diaryliodonium salts are stronger electrophilic arylating agents, This led us to investigate the reaction of the species with diaryliodonium salts. As we expected, diaryliodonium salts could react smoothly to give the unsymmetrical diaryl selenides in high yields (eq. 1). The results were summarized in **Table 1**.

Unsymmetrical aryl selenides are important intermediate for conversion into optically active selenoxides<sup>7</sup>. Their preparation has been reported in some papers<sup>8,9,10</sup>. Reduction diaryldiselenides with system of  $\text{Cp}_2\text{TiCl}_2/2i\text{-BuMgBr}/\text{THF}$  provides a new efficient path for the preparation of unsymmetrical diarylselenides.



The reaction were carried out as follows: (THF was distilled from sodium benzophenone, commercial HMPA was dried over 4A molecular sieves, the reaction was carried out under pure nitrogen). The suspension of  $\text{Cp}_2\text{TiCl}_2$  (0.25g, 1.0mmol) in 6 ml THF reacted with  $\text{Bu}^i\text{MgBr}$  (1.0M×2.0mL) in THF at  $-10-0^\circ\text{C}$  to give the brown-blackish titanocene hydride. Diaryldiselenide (0.5mmol) was added to above reaction mixture. The reaction mixture became in deep blue color. It indicated that  $[\text{Cp}_2\text{TiSeAr}]$  formed. Then to the solution diaryliodonium salts (1.0mmol) and HMPA (2.0ml) were added. The reaction mixture was stirred at r.t. for 2 h., then for 2 h at  $60^\circ\text{C}$ . Finally the mixture turned to brownish. After work-up, the products were purified by preparative TLC on silica gel using light petroleum ether as eluent (30:1).

**Table 1:** Melting points and yields of unsymmetrical diarylselenides.

Product	Ar <sup>1</sup>	Ar <sup>2</sup>	m.p.(Lit)	yield(%)
<b>3a<sup>11</sup></b>	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	Ph	oil	78
<b>3b<sup>11</sup></b>	<i>m</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	Ph	oil	70
<b>3c<sup>11</sup></b>	<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	Ph	oil	73
<b>3d<sup>11</sup></b>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	Ph	oil	69
<b>3e<sup>9</sup></b>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	71-72(72-73)	75
<b>3f<sup>9</sup></b>	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub>	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	77-79(80-81)	75

The structures of **3a-3f** were confirmed by <sup>1</sup>HNMR and IR

## References

1. N. Ohira, Y. Aso, T. Otsubo, F. Ogaya, *Chem. Lett.*, **1984**, 853.
2. S. I. Fkuzawa, et al., *Heteratom Chem.*, **1990**, 6, 49.
3. O. AKiya, N.Yuttaya, K. Nobuaki, M. Shinji, *Tetrahedron Lett.*, **1987**, 3271.
4. L. Henriksen, S.H. Nicolai, *J. Chem. Soc. Perkin Tran. 1*, **1999**, 1915.
5. L. Wang, Y. M. Zhang, *Heteroatom Chemistry*, **1999**, 203.
6. G.Yuan, S. Fumie, *J.Chem.Soc., Chem. Commun.*, **1995**, 659.
7. T. S. Shimizu, S. Noboru, T. Hideo, M. Nobu, *J.Org.Chem.*, **1996**, 61, 6013.
8. P.G.Gassman, A.Miura, T.Miura, *J. Org. Chem.*, **1982**, 47, 951.
9. H. J. Cristau, B. Chabaud, R. Labaudiniere, H. Christol, *Organometallics*, **1985**, 4, 657.
10. M. J. Evera, L. E. Christiaens, M.J. Renso, *J.Org.Chem.*, **1986**, 51, 5196.
11. Z. D. Liu, H. Zeng, Z. C. Chen, *Synth. Commun.*, **1994**, 24, 475.

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