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# Phosphorus, Sulfur, and Silicon and the Related Elements

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# 1,2-Addition of Diphosphine Monoxide to a Double Bond of a Titanocene Carbene Complex

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## 1,2-ADDITION OF DIPHOSPHINE MONOXIDE TO A DOUBLE BOND OF A TITANOCENE CARBENE COMPLEX

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A titanocene carbene complex reacted with diphosphine monoxide to give  $R_2PCH_2PR_2$ .

A titanocene carbene complex exhibits various reactivities. For example, it eliminates an oxygen atom from a carbonyl compound because of strong affinity of titanium for oxygen, or it undergoes 1,2-addition of E-H bond (E=Si, Ge, Sn). Since disphosphine monoxides 1a and 1b in Scheme 1 have both P=O bond and scissile P-P bond, its reaction with titanocene carbene is of interest. The results are shown below. 2a and **2b** are obtained when the reaction mixture is heated to 50°C in benzene or toluene. It is proposed that the P-P bond cleavage takes place through a rearrangement shown in a bracket in the scheme. And when 2a is heated up to 80°C, titanocene oxide is eliminated from 2a to give a bisphosphine compound **3a**.

$$\begin{array}{c} \mathsf{Cp}_2\mathsf{Ti}\text{=}\mathsf{CH}_2 \\ + \\ \mathsf{O} \\ \mathsf{R}_2\mathsf{P}\text{-}\mathsf{P}^\mathsf{n}\mathsf{R'}_2 \\ \mathsf{1a} \ \mathsf{R}\text{-}\mathsf{Ph} \ \mathsf{R'}\text{=}^\mathsf{n}\mathsf{Bu} \end{array} \\ \begin{array}{c} \mathsf{Cp}_2\mathsf{Ti} \\ \mathsf{O}\text{-}\mathsf{PR}_2 \\ \mathsf{R}_2 \end{array} \\ \begin{array}{c} \mathsf{Cp}_2\mathsf{Ti} \\ \mathsf{O}\text{-}\mathsf{PR}_2 \\ \mathsf{R}_2 \end{array} \\ \begin{array}{c} \mathsf{Cp}_2\mathsf{Ti}\text{-}\mathsf{O} \\ \mathsf{R}_2 \\ \mathsf{R}_2 \end{array} \\ \begin{array}{c} \mathsf{R}^\mathsf{2a}, \, \mathsf{2b} \\ \mathsf{Cp}_2\mathsf{Ti}\text{=}\mathsf{O} \\ \mathsf{R}_2 \\ \mathsf{R}_2 \end{array}$$

#### SCHEME 1

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## **REFERENCES**

- D. L. Hughes, J. F. Payack, D. Cai, T. R. Verhoeven, and P. J. Reider, Organometallics, 15, 663 (1996).
- [2] Y. Hanzawa, N. Kuwase, and T. Taguchi, Tetrahedron Lett., 39, 583 (1998).