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Novel Catalytic Metathesis of Substituted Olefins Promoted by Rhenium(I) Enolate Complexes

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Rhenium(I) enolate complexes $Re(NCCHCO_2Et)[NC(EtO_2C)C{=}CHPh](PMe_2Ph)_4$ and $Re(NCCHCO_2Et)(NCCH_2CO_2Et)(PMe_2Ph)_4$ are found to catalyze unique olefin metathesis reaction of tetracyanoethylene with ethyl α-cyanocinnamate to give 1,1-dicyano-2-phenylethylene and ethyl 2,3,3-tricyanopropenoate at room temperature.

Olefin metathesis reactions catalyzed by transition metals are regarded as one of the recent topics in relation to transition metal carbene chemistry, catalytic higher olefin production process, and stereospecific ring opening polymerization of cyclic olefins.[1, 2] However, the limitation of the reactions severely discourages wide applications as versatile synthetic tools in organic synthesis: the reactions are usually applicable only to the olefins having no functional groups at α- or even allylic positions.[3,4] Recently we have communicated the synthesis of novel rhenium enolate complexes $Re(NCCHCO_2Et)[NC(EtO_2C)C{=}CHPh](PMe_2Ph)_4$ (**1**) and $Re(NCCHCO_2Et)(NCCH_2CO_2Et)(PMe_2Ph)_4$ (**2**) as active intermediates in catalytic aldol and Michael reactions.[5] In the course of our continuing investigations concerning the rhenium enolate complexes, we have found a novel metathesis reaction of olefins having electron withdrawing substituents at α-position catalyzed by rhenium(I) enolate complexes **1** and **2**.

Treatment of **1** with four-fold excess of tetracyanoethylene (TCNE) in THF at room temperature gave 1,1-dicyano-2-phenylethylene (12% / Re) and ethyl 2,3,3-tricyanopropenoate (10% / Re) in addition to ethyl α-cyanocinnamate (52% / Re) at room temperature. Formation of the former two products results from olefin metathesis of the coordinated ethyl α-cyanocinnamate with TCNE, though the yields are relatively low. When the reaction of TCNE and ethyl α-cyanocinnamate was carried out in the presence of ca. 1 mol% of **1**, the catalytic olefin metathesis reaction smoothly proceeded under ambient conditions as shown in Table 1. Interestingly turnover frequency of the catalytic olefin metathesis reaction dramatically increased to give 1,1-dicyano-2-phenylethylene and ethyl 2,3,3-tricyanopropenoate in 4410 and 1950% yields per Re, respectively, when the polar solvent such as dimethylsulfoxide was employed as a reaction media. Complex **2** also catalyzed the same olefin metathesis reaction: 1,1-dicyano-2-phenylethylene (267%) and 2,3,3-tricyanopropenoate (943%) were obtained, in the presence of catalytic amount of **2** (0.7 mol%) in THF at room temperature. Since complex **1** can be prepared from the reaction of **2** with ethyl α-cyanocinnamate, the reactions catalyzed by **1** and **2** are essentially the same.

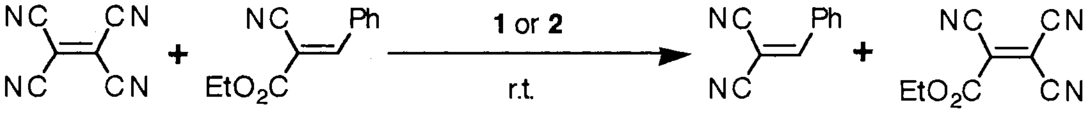

Table 1. Catalytic metathesis reaction of tetracyanoethylene with ethyl α-cyanocinnamate promoted by rhenium(1) enolate complex **1**

Solvent	1,1-Dicyano-2-phenylethylene	Ethyl 2,3,3-tricyanopropenoate
	% / Re	% / Re
C_6H_6	156	80
Et_2O	336	183
THF	114	42
CH_2Cl_2	310	150
DMSO	4110	1950

Reaction conditions: **1** / TCNE / ethyl α-cyanocinnamate, 0.0145 / 2.20 / 2.20 mmol; solvent, 2.0 ml; temperature, r.t.; reaction time, 99 h.

Although alkyl 2,3,3-tricyanopropenoate is known to be derived from the conventional reaction of tetracyanoethylene with alkyl cyanocinnamate in the presence of Lewis acid or base *via* retro-Michael type reaction,(6) the present reaction is considered as an olefin metathesis reaction by the following reasons. Both olefin metathesis products were obtained in these reaction,(7) whereas no reaction took place in the absence of rhenium complexes **1** or **2**. In addition, neither water nor dimethylphenylphosphine catalyzed the olefin metathesis reaction.

The present result is the first example of catalytic olefin metathesis of olefins containing functional groups at α-position and provides new possibility of olefin metathesis chemistry. Further scope and limitations of this unique reaction and the mechanistic investigations are now in progress.

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References

1) K. J. Ivin, "Olefin Metathesis," Academic Press, London (1983), pp 149.

2) J. C. Mol, "Olefin Metathesis and Polymerization Catalysts," ed by Y. Ìmanoglu, B. Zümeroglu-Karan, and A. J. Amass, Kluwer Academic Publishers, Dordrecht (1990), pp 115.

3) R. Toreki, G. A. Vaughan, R. R. Schrock, and W. M. Davis, *J. Am. Chem. Soc.*, **115**, 127 (1993).

4) G. C. Fu and R. H. Grubbs, *J. Am. Chem. Soc.*, **115**, 3800 (1993).

5) M. Hirano, Y. Ito, M. Hirai, A. Fukuoka, and S. Komiya, *Chem. Lett.*, **1993**, 2057.

6) T. Gotoh, A. B. Padias, and H. K. Hall, Jr., *J. Am. Chem. Soc.*, **108**, 4920 (1986).

7) The reason for the unequal in the apparent yields of two metathesis products in these reactions remains unresolved.

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