

Asymmetric Carbon Dioxide Insertion into a π -Allyltitanium(III) Complex

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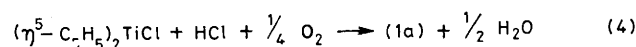
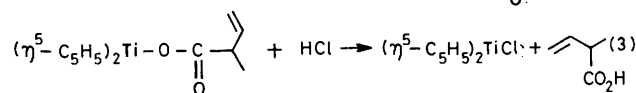
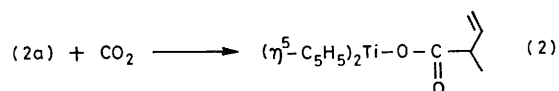
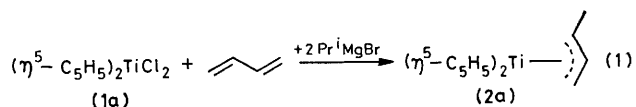
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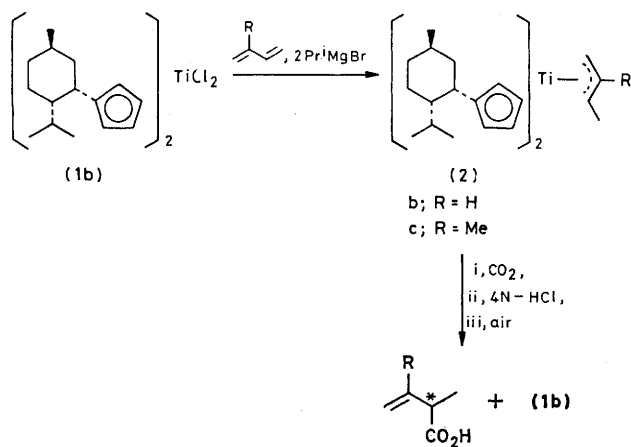
Summary A π -allyltitanium complex with a chiral cyclopentadienyl ligand reacts with carbon dioxide under mild conditions to form a carbon-carbon bond, thus providing the first demonstration of asymmetric carbon dioxide fixation.

In connection with the current interest in carbon dioxide fixation by transition metal complexes¹ and in asymmetric carbon-carbon bond formation utilizing transition metal organometallics² we report the first demonstration of asymmetric carbon dioxide fixation by an organometallic complex.

π -Allyl-nickel³ and -palladium⁴ complexes have been shown to react with carbon dioxide to afford the corresponding carboxylate complexes. These findings have attracted special attention because nickel or palladium complexes catalyse the addition of carbon dioxide to butadiene.⁵ We have now found that the π -allyltitanium complex $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\eta^3\text{-C}_4\text{H}_7)$ (**2a**), prepared or formed *in situ* by reaction of $(\eta^5\text{-C}_5\text{H}_5)_2\text{TiCl}_2$ (**1a**) and isopropylmagnesium bromide in the presence of butadiene (equation

1),⁶ reacted with carbon dioxide at ordinary pressure at room temperature in ether and gave 2-methyl-3-butenic acid and (**1a**) in 85 and 87% yields, respectively, by hydrolysis of the reaction mixture with 4N-HCl, followed by oxidation with air. These results strongly suggested that the reaction proceeded *via* the pathway shown in equations 2, 3, and 4.⁷





SCHEME

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With this result in hand we applied the reaction to the asymmetric fixation of carbon dioxide using a π -allyl-titanium complex containing a chiral cyclopentadienyl ligand. The chiral titanium complex (**2b**), prepared *in situ* from (**1b**),⁸ butadiene, and isopropylmagnesium bromide (2 h at room temperature in ether) reacted with carbon dioxide to give 2-methyl-3-butenic acid with $[\alpha]_D^{25} + 7.23^\circ$ (neat) in 70% yield while reproducing 84% of (**1b**) (Scheme, where an asterisk indicates the chiral centre). The configuration and optical purity of the acid were determined to be (*S*) and 18.9% e.e., respectively, by hydrogenation of the acid to the saturated acid for which a maximum rotation has been reported.⁹ Similarly, (**2c**), prepared *in situ* from (**1b**), isopropylmagnesium bromide, and isoprene, reacted with carbon dioxide to afford (*R*)-(-)-2,3-dimethyl-3-butenic acid with $[\alpha]_D^{25} - 7.32^\circ$ (neat) (11.3% optical purity, determined by converting it into the saturated acid¹⁰) in 86% yield and reproduced 80% of (**1b**).

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