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NOVEL OXIRANE FORMATION VIA 1-METALLA-2-OXACYCLOBUTANES

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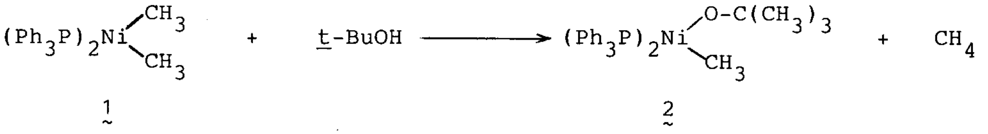
Summary: 1-Metalla-2-oxacyclobutane complex, which was formed by intramolecular γ-hydrogen elimination of alkoxy(alkyl)metal complex of Ni or Pd, yields mainly oxirane, while its Ti complex affords olefins resulting from C-O bond cleavage.

Preparation as well as the chemistry of metallacycle compounds have been under active investigation, especially because of the importance as the reactive intermediates for olefin cyclooligomerization, polymerization, and metathesis reactions.[1,2] In this paper, we report the generation and thermal reaction of previously unknown 1-metalla-2-oxacyclobutane complexes of Ti, Ni and Pd.

Bis(triphenylphosphine)-t-butoxy(methyl)nickel (2) was prepared by the treatment of bis(triphenylphosphine)dimethylnickel (1) with slightly excess amount of t-butyl alcohol. The reaction was carried out in toluene below -35 °C over a period of 10 days by monitoring the amount of methane evolved on gas chromatogrophy (glc)(eq. 1). After evolution of methane ceased, the solvent was evaporated under reduced pressure at -30 °C, and the resulted yellow brown crystals were purified by column chromatography on florisil below -30 °C under argon, giving the complex 2 in 43% yield.[3] The complex 2 can also be prepared from the reaction of bis(triphenylphosphine)nickel dibromide with 1.2 mole equiv. of CH_3MgI in THF at -40 °C followed by treatment of the resulting yellow orange product with potassium t-butoxide (1.5 mole equiv.) below -30 °C for two weeks (eq. 2).[4]

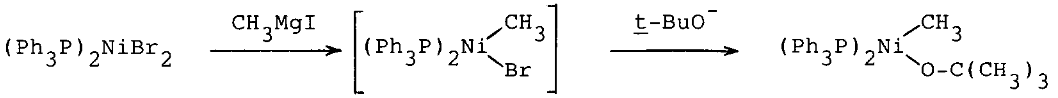
The complex 2 completely decomposed in toluene at 50 °C (12 h) affording 2,2-dimethyloxirane in 45% yield accompanied by methane (81%/Ni), ethane (8%),



$$(Ph_3P)_2Ni(CH_3)_2 \;\; + \;\; t\text{-BuOH} \longrightarrow (Ph_3P)_2Ni(O\text{-}C(CH_3)_3)(CH_3) \;\; + \;\; CH_4 \qquad (1)$$

1 2

2-methylpropene (21%), and 2-methyl-2-butene (16%). Trideuteriomethylnickel complex 3 with ortho-deuterated triphenylphosphine was prepared and pyrolyzed in



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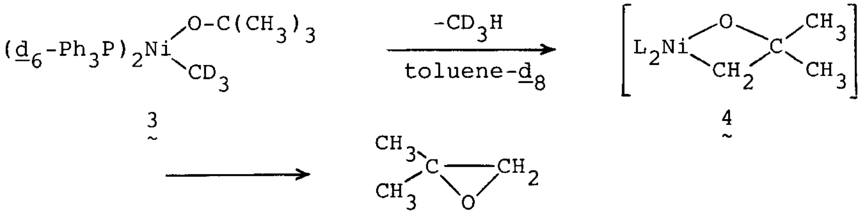
(2)

toluene-d_8 at 50 °C (eq. 3). Methane, collected as non-condensable gas (86%/Ni) at liquid N_2 temperature, was analysed by mass spectroscopy. It was composed of methane-d_3 (93%) and methane-d_4 (7%). 2,2-Dimethyloxirane, recovered from the reaction mixture, contained no deuterium as proved by ^{1}H-NMR and mass spectroscopy. This result apparently suggests that the intramolecular γ-hydrogen elimination[5] of 3 takes place affording unstable metallacycle intermediate 4 and methane. Reductive elimination of the ligand from 4 results in the formation of 2,2-dimethyloxirane as the major reaction pathway as shown in eq. 3.[6] The formation of 2-methyl-propene is attributable to the metathesis type cleavage of carbon-oxygen bond in 4. It is not clear so far the origin of 2-methyl-2-butene.



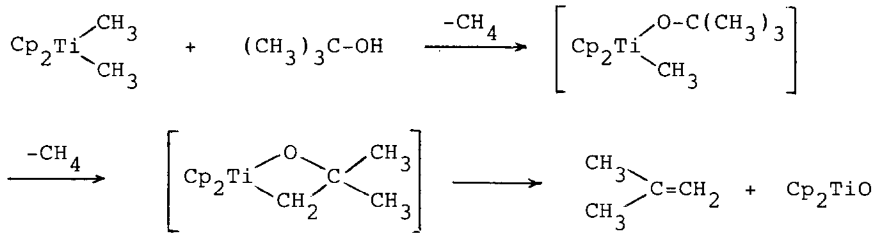
L= d_6-Ph$_3$P

(3)

Bis(triphenylphosphine)-*t*-butoxy(methyl)palladium (5) was also prepared by analogous method described in eq. 1. In a toluene solution, 5 slowly decomposes by raising the temperature from -30 °C to 50 °C to give 2,2-dimethyloxirane in 68% yield (glc), releasing methane (94%), 2-methylpropene (7%), and 2-methyl-2-butene (4%).

By contrast, the reaction of titanium complex proceeded with completely different mode giving 2-methylpropene as the major product with trace amount of oxirane. A toluene solution of dimethyltitanocene with stoichiometric amount of *t*-butanol was allowed to react initially at -30 °C and then, the reaction temperature was slowly raised up to 50 °C. 2-Methylpropene (92% yield per Ti), methane (189%) and a trace amount of ethylene were obtained in addition to yellow precipitate of Cp_2TiO. During the reaction, apparently 2-oxa-1-titanacyclobutane complex 6 also forms and yields 2-methylpropene rather than taking reductive elimination pathway as shown in eq. 4. The compound 6 has been also proposed to be an active intermediate for the methylene transfer reaction of titanium methylene complex with ketone or carboxylic acid derivatives, resulting in the formation of the methylenated products.[7]

In summary, it has been found that 1-metalla-2-oxacyclobutanes can be



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(4)

derived from *t*-butoxymetal complexes by γ-hydrogen elimination. Reductive elimination giving oxiranes is the most favorable reaction mode for Ni or Pd compounds, while the Ti complex suffers from carbon-oxygen bond cleavage to give the corresponding olefins and titanium oxides.[8] It should be added that the above findings suggest that metallaoxacyclobutanes are formed as reactive intermediates in certain metal-catalysed olefin epoxidation reactions and furthermore they are playing important roles in determining the reaction course and even the stereospecificity of the reactions.[9,10]

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(3) ^{1}H-NMR (toluene-d_8, -30 °C): δ 0.31 ppm (Ni-CH_3, 3H); 1.54 (s, -OC(CH_3)$_3$, 9H); 7.50 (m, (C_6H_5)$_3$P, 30H).

(4) No apparent disproportionation reaction was observed at this temperature.

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(8) The reaction of **1** with stoichiometric amount of iso-propyl alcohol resulted to yield acetone (68%/Ni) and 2-methyloxirane (2%). The formation of acetone is presumed to account for β-hydrogen elimination of iso-propyl(methyl)nickel intermediate prior to the formation of 1-nickela-2-oxacyclobutane complex.

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