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REACTIONS OF ALLYL PHENYL AND DIALLYL ETHERS WITH Ni(cod)$_2$ IN THE PRESENCE OF PHOSPHINE LIGANDS WITH AND WITHOUT C-O BOND CLEAVAGE. PREPARATION OF Ni(η^3-C_3H_5)(OC_6H_5)(PPh_3) BY THE OXIDATIVE ADDITION OF ALLYL PHENYL ETHER TO NICKEL AND PREPARATION OF Ni(π-DIALLYL ETHER)(PR_3)

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The reaction of allyl phenyl ether with a mixture of bis(1,5-cyclooctadiene)nickel and PPh_3 leads to the oxidative addition of the ether involving the PhO-C bond cleavage to afford Ni(η^3-C_3H_5)(OC_6H_5)(PPh_3) $\underset{\sim}{1}$. Similar reactions of diallyl ether with Ni(cod)$_2$ in the presence of PR_3 (R = C_6H_5, cyclo-C_6H_{11}) give uncleaved π-type complexes formulated as Ni(π-allyl ether)(PR_3).

Oxidative addition of substrates to transition metal is one of the most important elemental reactions in homogeneous catalysis.[1)] Allyl phenyl ether has been often employed as an allylating reagent in the transition metal catalyzed allylation of organic compounds[2,3)] and intermediacy of allyl transition metal species which are formed by the oxidative addition of the ether has been postulated. However, isolation of such an intermediate species has no precedent. As part of our program of studies on the oxidative addition of organic compounds having C-O bonds,[4)] we have investigated reactions of allyl phenyl and diallyl ethers with mixtures of bis(1,5-cyclooctadiene)-nickel, Ni(cod)$_2$, and phosphine ligands, and found out that the C-O bond in allyl phenyl ether is easily cleaved in the reaction to give an oxidative addition product.

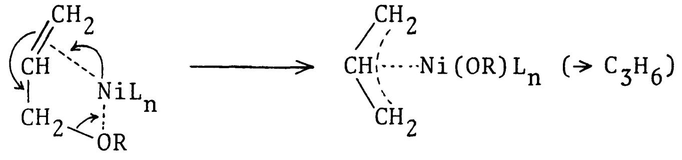
When a THF (2 ml) solution of Ni(cod)$_2$ (370 mg, 1.4 mmol), PPh_3 (390 mg, 1.5 mmol), and allyl phenyl ether (0.8 ml, 5.9 mmol) was stirred for 4 h at 30°C, a deep red homogeneous solution was obtained. After completion of the reaction by stirring the solution further for 1 hr at 50°C, the solution was cooled to -78°C to yield reddish brown crystals (500 mg, yield = 81 %), whose recrystallization from toluene gave 390 mg (yield = 63 %) of a known π-allyl(phenoxo)nickel complex Ni(η^3-C_3H_5)(OC_6H_5)(PPh_3) $\underset{\sim}{1}$,[5)]

$$\mathrm{Ni(cod)_2 + PPh_3 + CH_2{=}CH{-}CH_2OC_6H_5 \longrightarrow \underset{\underset{\sim}{1}}{Ni(\eta^3\text{-}C_3H_5)(OC_6H_5)(PPh_3)}} \quad (1)$$

Eisch and Im carried out similar reactions between allyl phenyl ether and Ni(cod)$_2$ or Ni(PPh_3)$_4$.[3)] They added HCl to the reaction product without isolation and obtained 80-100 % of phenol and propylene. We think that similar compounds to $\underset{\sim}{1}$ were formed also in their reactions. Cleavage of the C-O bond of allyl ethers by rhodium compounds at higher temperatures has been also reported.[6)]

In contrast to the reaction of allyl phenyl ether a similar reaction of diallyl ether with Ni(cod)$_2$ in the presence of PPh_3 gave a π-type complex of uncleaved diallyl ether, Ni(π-diallyl ether)(PPh_3) 2; Anal.: Found: C, 68.4; H, 6.1. Calcd.: C, 68.8; H, 6.0. Quantitative liberation of diallyl ether on iodolysis of 2 excludes the possibility of the occurrence of the C-O bond cleavage in the reaction of diallyl ether with the Ni(0)-complex. An analogue of 2, Ni(π-allyl ether)(PCy_3) 3, was also prepared by employing PCy_3(tricyclohexylphosphine) as the ligand: Anal.: Found: C, 65.2; H, 10.2; Calcd.: C, 65.9; H, 9.9. IR and ^{1}H-, ^{31}P-, and ^{13}C-NMR spectra of complexes 2 and 3 agree with the structures. Although Pt and Rh complexes of diallyl ether are known,7) preparation of a Ni complex of diallyl ether has no precedent.

Heating of a benzene solution of 3 at 150°C in a sealed tube led to the liberation of a considerable amount of C_3H_6, indicating the occurrence of the C-O bond cleavage of nickel at the higher temperature. Similar treatment of complex 2 did not lead to the C-O bond cleavage but it caused liberation of diallyl ether and formation of a mirror of nickel. That the C-O bond cleavage of diallyl ether proceeds only in the Ni complex with more basic ligand (PCy_3) agrees with our previous observation that the rate of the acyl-O bond cleavage of carboxylic esters by Ni(0)-complexes increases with increase in the basicity of the ligand attached to Ni.4) The C-O bond cleavage of allyl phenyl ether at room temperature and that of diallyl ether at the elevated temperature most probably proceeds through a rearrangement of the bonds in the ethers on Ni (Scheme). In the case of diallyl ether the source of hydrogen to give C_3H_6 has not been clarified. It is reported that the C-O bond of diallyl ether is cleaved on interaction with platinum hydride complexes, although in this case the C-O bond cleavage is considered to proceed not through the oxidative addition of the ester to Pt but through the insertion of the C=C double bond into the Pt-H bond.8)



Scheme

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