Dimerization of Ethylene Catalyzed by σ-Arylnickel(II) Compounds

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(Received July 31, 1970)

In a previous paper,[1] it was reported that an isotopic exchange between C_2H_4 and C_2D_4 is effectively catalyzed by bis(triphenylphosphine)nickel(II) halide in an aprotic solvent in the presence of molecular hydrogen without accompaning any hydrogenation or dimerization. The complex shows some catalytic activity for the ethylene dimerization when it is used together with boron trifluoride etherate. During the course of study dealing with the effect of ligand coordinated to nickel(II) atom, it has been found that the activity of the nickel(II) complex for the ethylene dimerization is highly increased by substituting one of the halogen ligands by a σ-aryl ligand such as 1-naphthyl, *o*-tolyl, *etc.* This communication reports a highly selective dimerization of ethylene catalyzed by bis(triphenylphosphine)σ-aryl nickel(II) bromide[2] in the presence of boron trifluoride etherate in benzene or methylene chloride.

Ethylene dimerization with this catalyst system took place almost quantitatively(95%) without any induction period at room temperature under atmospheric pressure. Only a trace amount of hexene was detected in the product. Co-dimerization of ethylene with propylene occurred to some extent, but no dimer of propylene was detected under these mild reaction conditions. Butadiene as well as triphenylphosphine strongly inhibited the ethylene dimerization. 1-Naphthyl ligand and triphenylphosphine seem to remain in the nickel complex during the reaction, because only small amounts of decomposed products of the complex such as naphthalene, 1,1′-dinaphthyl and triphenylphosphine were detected in the solution after the reaction. Bis(triphenylphosphine) *o*-tolyl nickel(II) bromide is more effective than the corresponding 1-naphthyl complex. The treatment of bis(triphenylphosphine) 1-naphthyl nickel(II) bromide with sodium tetraphenylborate ($1\text{-}C_{10}H_7Ni(P\phi_3)_2Br + NaB\phi_4 + s \rightarrow [1\text{-}C_{10}H_7Ni(P\phi_3)_2(s)]^+[B\phi_4]^- + NaBr$, $\phi = C_6H_5$, s=solvent)[3] results in a considerable decrease in catalytic activity for ethylene dimerization. This suggests that halogen ligand is important for the catalytic activity.

The experimental procedure is illustrated by the following ethylene dimerization. To a solution of bis(triphenylphosphine) 1-naphthyl nickel(II) bromide (1 mmol, 0.79 g) in dry methylene chloride (20 m*l*) under nitrogen in a 50 m*l*-flask was added boron trifluoride etherate (1 mmol, 0.125 g). The nitrogen gas in the flask had been evacuated before ethylene gas (64.5 m*l* at STP) was introduced at the temperature of liquid nitrogen. The flask was warmed up to 0°C and kept at that temperature for 1 hr with vigorous stirring. Subsequently all volatile materials (C_2H_4, C_4H_8 and solvent) were transferred into another 50 m*l*-flask by means of a liquid nitrogen trap. Their amounts were determined by gas chromatography. From the residual materials only trace amounts of naphthalene, 1,1′-dinaphthyl and triphenylphosphine were extracted by *n*-hexane. The results are shown in Table 1.

Table 1. Dimerization of ethylene catalyzed by σ-aryl nickel(II) compounds

Catalyst (mmol)		Olefin introduced (m*l* STP) and solvent(m*l*)	Reaction time and temperature	Products (m*l* STP)
$(1\text{-}C_{10}H_7)Ni(P\phi_3)_2Br$,	1.0	C_2H_4(64.5)	1 hr	C_4H_8(30.8)
$BF_3 \cdot O(C_2H_5)_2$,	1.0	CH_2Cl_2(20)	0 °C	C_2H_4(2.5)
(*o*-tolyl)$Ni(P\phi_3)_2Br$,	0.1	C_2H_4(99.1)	5 min	C_4H_8(44.0)
$BF_3 \cdot O(C_2H_5)_2$,	1.0	CH_2Cl_2(5.0)	0 °C	C_6H_{12}(0.90)
				C_2H_4(6.2)
$(1\text{-}C_{10}H_7)Ni(P\phi_3)_2Br$	1.0	C_2H_4(59.7)	15 hr	C_4H_8(26.3)
$BF_3 \cdot O(C_2H_5)_2$,	5.0	C_3H_6(60.4)	34°C	C_5H_{10}(7.0)
		C_6H_6(50)*		C_2H_4(tr.)
				C_3H_6(48.1)

* The reaction was carried out in a 100 m*l*-flask.

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