

Preliminary communication

Preparation of a phenyl–nickel complex, phenyl(dipyridyl)nickel chloride, an olefin dimerization catalyst

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Diethyl(dipyridyl)nickel (I), isolated from a mixed catalyst system composed of nickel acetylacetonate, diethylethoxyaluminium and dipyridyl, catalyzes the cyclo-trimerization of butadiene without a cocatalyst¹, but is inactive for α -olefin dimerization.

On treatment with organoaluminium halides, however, I exhibits the catalytic activity for olefin dimerization which is remarkably enhanced when chlorobenzene is used as solvent^{*}. Olefin dimerizations catalyzed by mixed systems containing nickel and organo-aluminium compounds have been extensively studied²⁻⁵ and in some cases rate acceleration in chlorobenzene solvent has been noted²⁻⁵. The striking enhancement of the catalytic activity in our system^{*} by chlorobenzene suggested a profound change in the nature of the catalyst and hence the study of the reaction of I with chlorobenzene was undertaken.

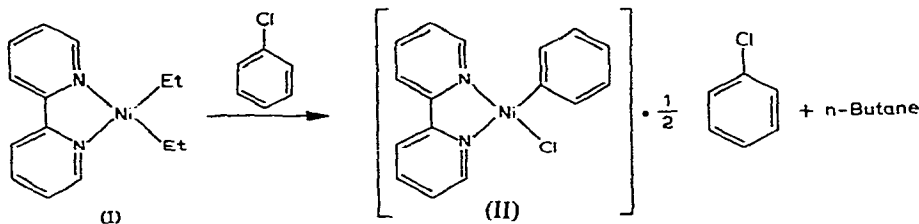
The reaction led to the formation of a phenyl–nickel complex, $C_6H_5(dipy)NiCl \cdot \frac{1}{2}C_6H_5Cl$ (II), which generates a highly active dimerization catalyst for α -olefins in combination with alkylaluminium halides. The complex II bears an analogy to compounds of the type $NiX(aryl) \cdot 2PR_3$ prepared by Chatt and Shaw⁶ and studied recently by Miller and coworkers⁷. However, the reported method of preparation is satisfactory only for *ortho*-substituted arylnickel compounds and the preparation of the unsubstituted phenyl analog remains equivocal because of the instability of the phenylnickel derivatives.

We report herein the preparation and the characterization of compound II which possesses a nickel–phenyl bond stabilized by dipyridyl and which can be isolated in the crystalline state.

Upon dissolving compound I in chlorobenzene at room temperature under a nitrogen atmosphere, the green solution gradually changes to red. This color change is accompanied by evolution of n-butane together with small amounts of ethane and ethylene. In order to bring the reaction to completion, the solution was stirred for several hours at room temperature under nitrogen. After cooling the reaction mixture to -10° , the red precipitate formed was filtered and dried and the red powder thus obtained was recrystallized from chlorobenzene at 65° . The reddish brown crystalline II was obtained in 60% yield. m.p. (dec.) $75.5-75.7^\circ$ (*Anal.*: Found: C, 59.48; H, 4.05; N, 7.26; Cl, 14.39. Calcd.:

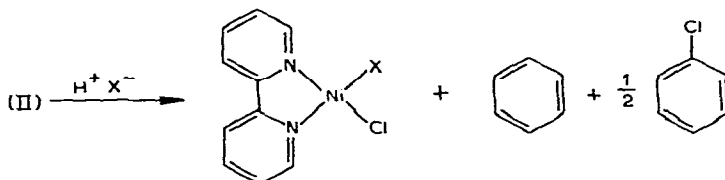
^{*}Details of the dimerization catalyst will be published separately.

C, 59.40; H, 4.04; N, 7.30; Cl, 13.87%). The inorganic chlorine content was determined by Fajans method. (Found: 10.3. Calcd.: 10.7%).



Compound II is soluble in chlorobenzene, tetrahydrofuran, acetone and toluene, but is stable only in chlorobenzene, solutions in other solvents decomposing gradually to give unidentified precipitates even at room temperature.

Treatment of compound II with dilute nitric acid afforded stoichiometric quantities of benzene and chlorobenzene according to the following equation:



The reaction of compound II with methyl iodide gave toluene and chlorobenzene. On treatment with ethanol, compound II afforded benzene and chlorobenzene.

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