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Preliminary communication

Preparation of a new nickel(0) complex, nickel(dipyridyl)(benzonitrile), an active polymerization catalyst of acrylonitrile

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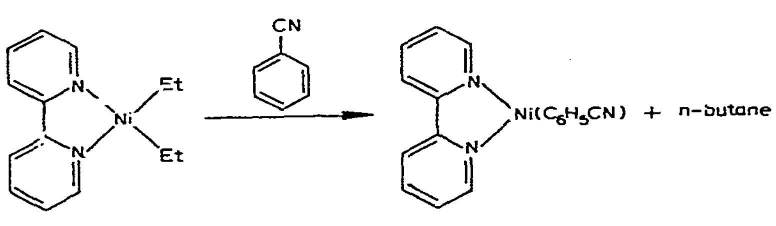
Previously we reported the reaction of diethyl(dipyridyl)nickel (I) with chlorobenzene which led to the formation of a phenyl-nickel complex[1]. In continuation of our work, compound I was treated with benzonitrile in which the dissociation energy of the phenyl-CN bond is much greater than that of phenyl-Cl. The reaction proceeded differently without breaking the phenyl-CN bond and led to the formation of a new nickel(0) complex, Ni(dipy)(C_6H_5CN) (II), which becomes an active polymerization catalyst of acrylonitrile.

We report herein the preparation and characterization of compound II and its catalytic activity of polymerization.

After dissolving compound I (5g, 18.3 mmol) in benzonitrile (300 ml) under nitrogen atmosphere, the green solution was heated to 65° and stirred for 2 hours. The green solution gradually changed to orange. This color change is accompanied by evolution of n-butane (7.3 mmol). In order to bring the reaction to completion, the solution was stirred for another 1 hour at 65° under nitrogen atmosphere. The reaction mixture was cooled to room temperature and allowed to stand overnight. The orange precipitate formed was filtered and washed with n-hexane and dried. An orange crystalline powder II (4.6 g) was obtained. m.p. 165–167° (dec.) (Anal.: Found: C, 64.71; H, 4.19; N, 13.60. Calcd.: C, 64.50; H, 4.10; N, 13.30%). The infrared spectrum of the orange complex II showed a sharp ν(C≡N) absorption band at 2105 cm^{-1} which is at about 150 cm^{-1} lower frequency than that of free benzonitrile. Compound II is stable to air and soluble in benzonitrile and dimethylformamide, but is insoluble in benzene and toluene.



(I)

(II)

Treatment of compound II (77.4 mg) with acetylacetone (2.95 g) at room temperature afforded almost stoichiometric quantities of benzonitrile (23 mg), determined by gas-chromatographic technique. After treatment with dilute nitric acid, no benzene was observed and 76% of benzonitrile from II was recovered.

Compound I has been reported as a polymerization catalyst of acrylonitrile[2], but compound II offered some advantages of easy handling and simple operation required for polymerization. Upon mixing 20 ml of acrylonitrile with 140 mg of II in a beaker under air, acrylonitrile polymerized explosively and 6 g of polyacrylonitrile was obtained after 3 minutes. At polymerization temperatures controlled within 20–35°, 182 mg of II and 40 ml of acrylonitrile afforded 11 g of polymer after 15 minutes. The molecular weight of polyacrylonitrile thus obtained was about $8 \cdot 10^4$. Methacrylonitrile was also polymerized by II in air, but in this case a long induction period was observed.

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