REACTIONS OF ORGANIC HALIDES WITH A TRIGONAL PYRAMIDAL NICKEL(0) COMPLEX

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Summary

The nickel(0) complex [Ni(np$_3$)], np$_3$ = tris(2-diphenylphosphinoethyl)-amine, which has a trigonal pyramidal geometry in the solid state, readily reacts in solution with organic halides (CH$_3$I, C$_2$H$_5$Cl, C$_3$H$_7$Cl, C$_6$H$_5$Cl, C$_6$H$_5$Br, C$_6$H$_5$I and C$_6$H$_5$CH$_2$Cl) to give nickel(I) species with formula [NiX(np$_3$)], (X = Cl, Br, I). Benzene, biphenyl, *o*-, *m*-, *p*-chlorobiphenyl are the other products from the reaction between the title complex and chlorobenzene.

Introduction

The reaction of organic halides with d^{10} transition-metal(0) complexes can be regarded as one of the basic transformations in organometallic chemistry, in the light of its important role in the conversion of organic substrates to reactive intermediates in many metal-catalyzed processes [1]. Such reactions have been carried out with tetracoordinate metal complexes having four phosphorus atoms as donors, either in mono-phosphines [2] or di-phosphines [3]: these complexes react with organic halides to give either nickel(II) compounds by oxidative addition, or nickel(I) species. The basic interactions between metal complexes and organo-halogen compounds have been considered, and the apparently diverse mechanisms leading to either nickel(I) or nickel(II) species have been reconciled [4]. Nickel(I) species, which can be formed in addition to nickel(II) complexes, are obtained in higher yield from aromatic bromides or iodides.

It has been recently reported that oxidation of [(dipy)Ni(PPh$_3$)$_2$], having mixed donor atoms, by alkyl and aryl bromides or iodides quantitatively affords the nickel(I) complexes [(dipy)Ni(PPh$_3$)X] (X = Br, I) [5].

We now describe the reaction between [Ni(np$_3$)] (np$_3$ = tris(2-diphenyl-phosphinoethyl)amine and alkyl or aryl halides, as part of our research on the

reactivity of this unusual nickel(0) complex in which the tripod tetradentate ligand constrains the metal in a trigonal pyramidal geometry.

Experimental

All reactions were carried out under dry, oxygen-free argon using standard inert-atmosphere techniques. Organic halides, benzene and tetrahydrofuran were reagent grade, and were dried by distillation from suitable agents [6] under an inert atmosphere. The complex [Ni(np$_3$)] was prepared as reported previously [7].

Gas-chromatographic analyses were performed on a Perkin—Elmer Sigma 2 instrument equipped with 2 m Chromosorb columns. ^{31}P{^{1}H} spectra were run in C_6D_6 solution on a Varian CFT 20 operating at 32.19 MHz. ^{31}P positive chemical shifts are reported downfield relative to H_3PO_4 at 0.0 ppm. Visible spectra and magnetic data were obtained as reported previously [8].

Reactions of the complex

A stoichiometric amount of a 0.06 M benzene or tetrahydrofuran solution of the organic halide (CH_3I, C_2H_5Cl, C_3H_7Cl, C_6H_5Cl, C_6H_5Br, C_6H_5I, $C_6H_5CH_2Cl$) was slowly added to a stirred solution of [Ni(np$_3$)] (ca. 140 mg, 0.2 mmol) in the same solvent (10 ml). The temperature of the sealed reaction vessel was kept constant by use of a water-bath ultrathermostat. The reaction was apparent by the ready discharge of the red color upon addition of the organic halide. The light green microcrystalline compounds which separated were filtered off, washed with ethanol then light petroleum, and dried in vacuo: they were identified as [NiX(np$_3$)] (X = Cl, Br, I) [9] from elemental analyses, visible spectra and magnetic measurements. The yield of the nickel(I) complex was determined by weighing.

GLC analyses on the reaction mixture derived from [Ni(np$_3$)] and chlorobenzene were carried out as follows. Chlorobenzene (10 ml) was added to [Ni(np$_3$)] (ca. 140 mg) in a Schlenk flask. The mixture was stirred for 15 min at constant temperature. After removal of the nickel(I) complex, the filtrate was concentrated to 3—4 ml, then analyzed by gas-chromatography. Biphenyl, o-, m- and p-chlorobiphenyl came of the column in that order, and were identified by comparison of their retention times with those of pure samples. Benzene was also detected in the distilled fraction.

Results and discussion

The [Ni(np$_3$)] complex reacts with a stoichiometric amount of alkyl or aryl halide (CH_3I, C_2H_5Br, C_3H_7Cl, C_6H_5Cl, C_6H_5Br, C_6H_5I, $C_6H_5CH_2Cl$) in tetrahydrofuran or benzene to form nickel(I) complexes of formula [NiX(np$_3$)], which have a trigonal bipyramidal geometry with the three phosphorus atoms in equatorial positions and the nitrogen atom and the halide ion in axial positions [9]. The [NiX(np$_3$)] complexes were isolated from all the reactions in good yield (70—75%). The reaction takes place at room temperature with alkyl halides, bromo- and iodo-benzene; the oxidation involving chlorobenzene occurs less readily at room temperature but is immediate at ca. 50°C.

The organic products resulting from the reaction of chlorobenzene with [Ni(np₃)] were identified by gas-chromatographic analysis: they consisted mainly of biphenyl, *o*-, *m*- and *p*-chlorobiphenyl (ca. 70% total yield based on the nickel(0) complex). The relative GLC peak areas are in the ratios 0.5/1/0.3/0.5, respectively. These products are consistent with radical pathways [10] which can be accounted for in terms of the following homolytic reaction scheme:

$$[Ni(np_3)] + PhCl \longrightarrow [Ni(np_3)ClPh] \longrightarrow [Ni(np_3)Cl] + C_6H_5{\cdot}$$
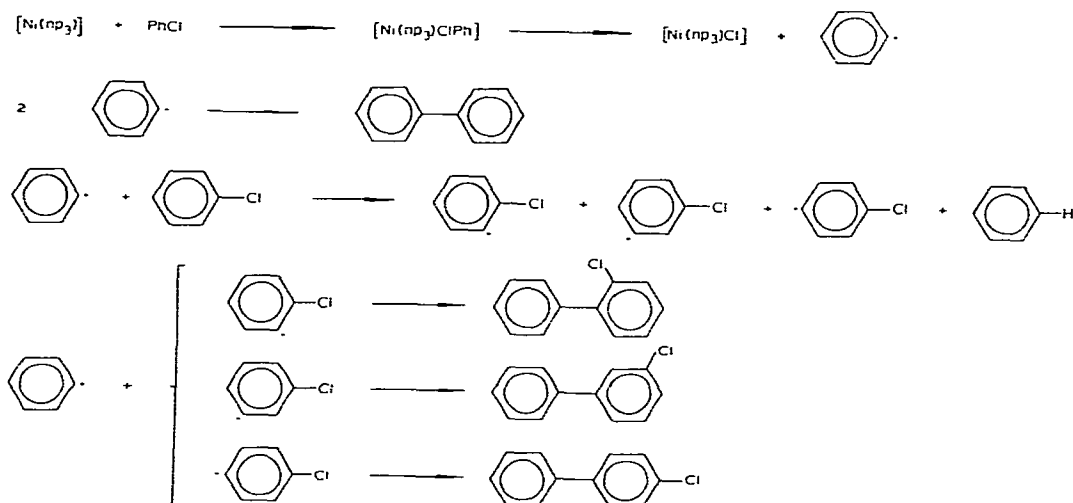
The type of products obtained by reaction of [Ni(np₃)] with chlorobenzene indicate a substantially different behaviour from either the tetrakisphosphine d^{10} metal complexes or the nickel(0) complexes with mixed ligands [5] towards the same reagents: such complexes react with organic halides to afford a mixture of nickel(II) and nickel(I) species, the latter being formed only when bromo- and iodo-benzene (but not chlorobenzene) are employed. The different reactivity of [Ni(np₃)] compared with [Ni(PR₃)₄] and [(dipy)Ni(PR₃)₂] must be ascribed to the different geometric features. The [M(PR₃)₄] complexes have a pseudotetrahedral geometry in the solid state, but stepwise dissociation takes place in solution. The [Ni(np₃)] complex, on the other hand, has been found by X-ray analysis to exhibit a trigonal pyramidal geometry in which the three phosphorus atoms of the ligand occupy equatorial positions and the nitrogen atom is at the apex [7]. In benzene solution, the $^{31}P\{^1H\}$ NMR spectrum of this complex shows a singlet at 23.24 ppm: this pattern does not change with temperature from −60 to +50°C. The large deshielding (coordination chemical shift 42.80 ppm) found for this complex with respect to the coordination chemical shifts of tetrakisphosphinemetal(0) complexes [11] suggests that a ring contribution is present, indicating that no coordination change occurs on going from solid state to solution [12]. Indirect but convincing evidence that the same coordination number is maintained in solution derives from the fact that even in pure chlorobenzene the yield of nickel(I) complex is high (ca. 75—80%), and that quaternization of the donor atoms, which takes place readily with organic halides both with the free ligand and the free donors of a partially coordinated ligand, does not occur to any significant extent [13].

The trigonal pyramidal geometry, forced on the metal by the rigid framework of the ligand, leaves a free coordination site opposite to the nitrogen atom, allowing the metal to react with the organic halide. This eighteen-electron configuration of the metal enhances its electron-transfer properties so that the 1-equivalent process [4] involving halogen atom transfer can take place even with chlorobenzene.

The lack of dissociation of the phosphine groups, furthermore, appears to be a determining factor in the formation of nickel(I) species.

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