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Preliminary communication

A new nickel-catalyzed synthesis of aromatic nitriles

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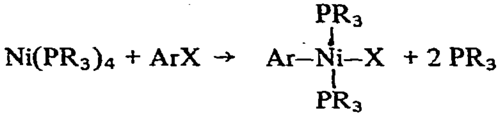
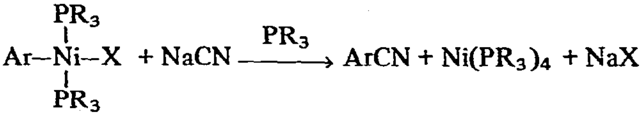
The oxidative addition of nickel(0) complexes to aromatic halides provides a simple route to arylnickel compounds[1] (II). Several groups have prepared and characterized these compounds obtained by reacting nickel(0) complexes with phosphines (I) (Eqn. 1).



$$\mathrm{Ni(PR_3)_4} + \mathrm{ArX} \rightarrow \mathrm{Ar{-}}\overset{\mathrm{PR_3}}{\underset{\mathrm{PR_3}}{\mathrm{Ni}}}\mathrm{{-}X} + 2\,\mathrm{PR_3} \tag{1}$$

(I) (II)

We have observed that complex II reacts with NaCN in various solvents at 50–80° to give aromatic nitriles* (Eqn. 2).



$$\mathrm{Ar{-}}\overset{\mathrm{PR_3}}{\underset{\mathrm{PR_3}}{\mathrm{Ni}}}\mathrm{{-}X} + \mathrm{NaCN} \xrightarrow{\mathrm{PR_3}} \mathrm{ArCN} + \mathrm{Ni(PR_3)_4} + \mathrm{NaX} \tag{2}$$

$(\mathrm{R} = \mathrm{C_6H_5},\ \mathrm{C_6H_{11}};\ \mathrm{X} = \mathrm{Cl, Br, I})$

The reaction is a several step process probably involving metathetical replacement of halogen by the cyano group, followed by reductive elimination. Thus nickel returns to the zero valence state ready for further oxidative addition and initiation of a new cycle. The result is a catalytic process by which aromatic halides are transformed into the corresponding nitriles in the presence of tetrakis(triphenylphosphine)nickel[2] (Eqn. 3):

$$\mathrm{ArX} + \mathrm{NaCN} \xrightarrow[\mathrm{EtOH;\ 50\text{–}60^\circ C}]{\mathrm{Ni[P(C_6H_5)_3]_4}} \mathrm{ArCN} + \mathrm{NaX} \tag{3}$$

$(\mathrm{X} = \mathrm{Cl, Br, I})$

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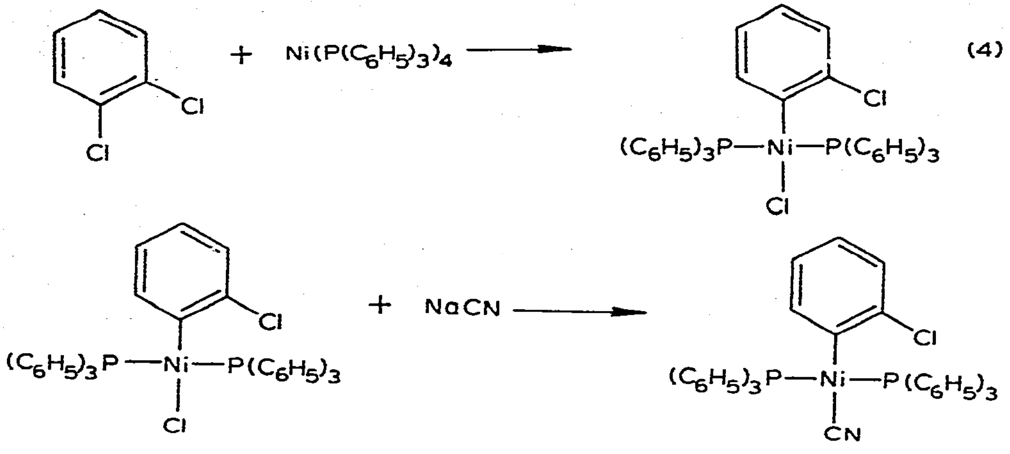
[*] Recently the oxidative addition of benzonitrile to $\mathrm{Ni[P(C_6H_5)_3]_4}$ has been reported[1f].

The reaction is general for *meta*- and *para*-substituted aryl halides[2]* and for triarylphosphine complexes are far more effective catalysts than trialkylphosphine complexes. *o*-Substituted aromatic halides (such as *o*-bromotoluene, *o*-dichlorobenzene, *o*-chlorobenzonitrile) do not yield cyanation products and only react by oxidative addition and the metathetical replacement of the halogen by the cyano group. For example *o*-dichlorobenzene gives the complex III** (Eqns. 4 and 5):



(4)

(III)

Complex III does not give *o*-chlorobenzonitrile even in boiling ethanol in the presence of triphenylphosphine. However when a diphosphine $(C_6H_5)_2P(C_6H_5)_2$ is added to the ethanolic solution, *o*-chlorobenzonitrile (yield 70%) is formed during 16 h at 55°.

This result indicates that the diphosphine replaces the triphenylphosphine and then facilitates the formation of nitrile, the aryl and the CN groups being mutually *cis****.

Further work is in progress.

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*Yields are ca. 90% based upon ArHal introduced. For PhBr, 120 moles of PhCN are obtained per mole of $(Ph_3P)_4Ni$.

**Satisfactory elemental analyses were obtained for all new compounds.

***See ref. 3. These authors were not aware of the occurrence of an oxidative addition in the reaction of benzonitrile with dipyridyldiethylnickel, probably because the reverse reaction of formation of benzonitrile is strongly favored by the chelating ligand, which forces the aryl and the cyanogroup to occupy mutually *cis* positions in the complex.