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# THE REACTION OF POTASSIUM HEXACYANODINICKELATE(I) WITH ORGANIC HALIDES IN THE PRESENCE OF CARBON MONOXIDE

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Several organo-transition metal complexes were previously prepared in aqueous solution ; i.e., $[R\text{-}Cr(H_2O)_5]^{2+}$ (1) , $[R\text{-}Co(CN)_5]^{3-}$ (R = alkyl, aryl) (2) and a series of Vitamin $B_{12}$ (alkyl cobalamine) model compounds with tetradentate ligand systems (3). Carbon monoxide (CO) insertion reactions into the carbon-metal bond of alkyl (or aryl)-transition metal complexes in aprotic solvents are well known (4). It has, however, been reported that pentacyanobenzylcobaltate $[C_6H_5CH_2\text{-}Co(CN)_5]^{3-}$ shows no immediate reaction with CO (2a) and no reports have yet appeared about such a CO insertion reaction in the complexes described above.

We now wish to report the formation of reactive organonickel intermediates by the reaction of potassium hexacyanodinickelate(I), $K_4[Ni_2(CN)_6]$ (I), with organic halides and to show a novel example of CO insertion into the carbon-metal bond of positively-charged metal complex in aqueous solution under mild conditions.

To a solution of (I) (0.035 mole) (5) in 160 ml of water and 50 ml of acetone was added dropwise 6.0 g (0.035 mole) of benzyl bromide in 20 ml of acetone at 0° with efficient stirring*. The blood red color of solution changed gradually (~30 min.) to pale yellow. When the reaction temperature was raised up to about 20°, a rapid decomposition took place to give finally a yellow-green suspension. After filtration of Ni(II) cyanide and ordinary treatment of the organic part, bibenzyl 2.83 g (89.0 %), benzaldehyde 0.02 g (0.6 %), and benzyl alcohol 0.08 g (2.0 %) were obtained, but benzyl cyanide was not detected.

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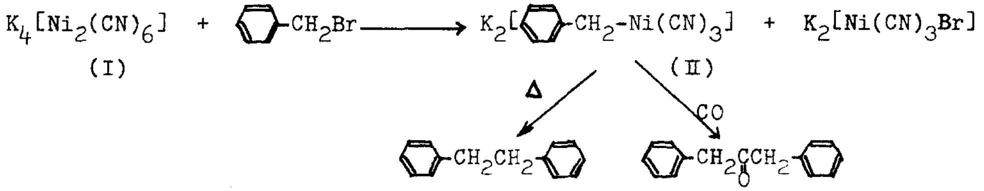
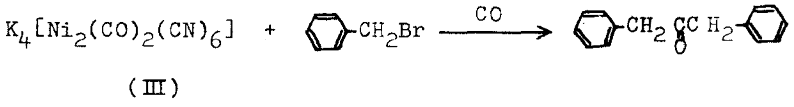
[*] All the reactions were carried out under a nitrogen atmosphere.

When 2 moles of benzyl bromide were used per mole of (I), just 1 mole of the halide reacted to give bibenzyl (96.4 % based on (I) used) and the excess of the halide was recovered. The yellow intermediate described above is stable at 0° for several hours. Our attempts to isolate it from reaction mixture were unsuccessful thus far because of its thermal unstability. But it is reasonable to assume the formation of tricyanobenzylnickelate, (II) , as an intermediate by analogy with the corresponding cobalt complex, pentacyanobenzylcobaltate (2a). Hereupon, the organonickel complex, (II) , is coordinatively unsaturated and so is expected to be reactive towards CO. Indeed, bubbling of CO into the yellow solution at 0° for 3 hr. gave dibenzyl ketone (34 %) as well as bibenzyl (59 %).



It is well known that (I) is also coordinatively unsaturated and its aqueous solutions absorb two molecules of CO to give the yellow salt, $K_4[Ni_2(CO)_2(CN)_6]$ (III) (6). The yield of dibenzyl ketone increased remarkably when (III) was used as a starting material. To the yellow aqueous solution containing 0.035 mole of (III) was added an excess of benzyl bromide 12.0 g (0.070 mole) at 5°, and stirring was continued for 12 hr. with gentle bubbling of CO at 5~20°. Upon work-up, dibenzyl ketone 3.32 g (90.4 % based on (III)) was isolated, accompanied by a small amount of bibenzyl (0.10 g, 3.1 %) and benzaldehyde (0.01 g, 0.3 %).

These results show a good contrast to the inactiveness of the saturated complex, pentacyanobenzylcobaltate, towards CO.



Alkyl- and aryl halides seem to be less reactive towards (I) or (III) under these conditions : n-butyl iodide gave di-n-butyl ketone in 4 % yield and iodo benzene was unaffected.

However, the reaction of cinnamyl bromide with (I) is intriguing. Treatment of an excess of cinnamyl bromide with (I) at room temperature produced cinnamyl cyanide (83 %) as a main product and a small amount of coupling product, *trans*, *trans*-1,6-diphenyl-1,5-hexadiene. It is interesting to note the difference of reactivity between (I) and pentacyanocobaltate ; *i.e.*, the latter reacts with allylic halides to form π-allyl complexes, which afford propene derivatives instead of allyl cyanide by abstraction of hydrogen atom from solvent or on acidification (*7*). During the course of our study, Corey and Hegedus reported the replacement of the bromine atom of *trans*-1-bromo-2- phenylethylene by cyano group using (I) (*8*).

Our studies of this reaction are continuing from a mechanistic as well as synthetic approach.

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