CHEMISTRY LETTERS, pp. 1707-1710, 1982.

C-CN BOND CLEAVAGE UNDER MILD CONDITIONS PROMOTED BY ELECTRON-RICH COBALT COMPLEXES

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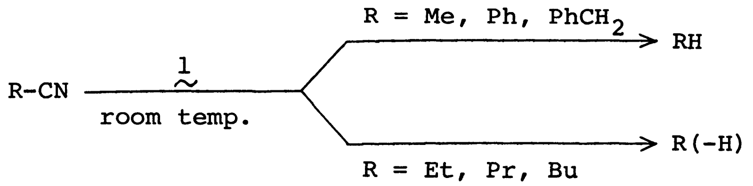
Electron-rich cobaltate dinitrogen complex, $[Co(PPh_3)_3N_2]Li(Et_2O)_3$ **1**, reacts with alkyl and aryl nitrile compounds causing the cleavage of C-CN bond under mild conditions to release hydrocarbons. Catalytic activity of the cobalt complex to isomerize allyl cyanide to crotononitrile is also noted.

Finding of means for selective cleavage of a covalent bond in organic compounds should provide new methods in organic synthesis. The discovery of a carbon-halogen bond cleavage caused by oxidative addition of organic halogen compounds to low valent transition metal opened up new pathways to various applications in organic synthesis.[1)] The carbon-oxygen bond cleavage promoted by transition metal complexes is also finding some applications in organic synthesis recently.[2)] In contrast, examples of C-CN bond cleavage by transition metal complexes are still limited.[3)] For a transition metal complex to cause the particular bond cleavage by an oxidative addition mechanism there are several conditions to be met. (a) The complex should be coordinatively unsaturated before or during the reaction. (b) The complex should be electron-rich to cause the nucleophilic attack on the substrate. (c) The energetics should be favorable for the oxidative addition to proceed.

We recently prepared N_2-containing cobalt complexes having triphenylphosphine ligands $[Co(PPh_3)_3N_2]ML_n$ (M = Li, Na, 1/2Mg; L = Et_2O, THF).[4)] These are electron-rich complexes having dinitrogen ligand which is readily liberated from the complexes to provide a coordination site for other substrates. In fact these cobaltate complexes have proved to be reactive for causing the C-O bond in carboxylic esters and capable to cause the cleavage of even C-CN bond in nitriles under mild conditions. In this paper we describe some typical examples of the C-CN bond cleavage reactions. The present system provides a rare example for C-CN bond cleavage in organic nitriles.

The anionic cobalt N_2 complex $[Co(PPh_3)_3N_2]Li(Et_2O)_3$ **1** soomthly reacts with nitriles at room temperature with C-CN bond cleavage. The ligating dinitrogen is readily liberated quantitatively followed by slow release of hydrocarbons over several hours. Nitriles without β-hydrogen afford saturated hydrocarbons and those with β-hydrogens predominantly give olefins.



(1)

The results are summarized in Table I which shows that C-CN bond cleavage took place for all the nitriles examined. The reactions occur under milder conditions than those in the reactions of nitriles with $Ni(cyclo\text{-}C_6H_{11})_2$.[3a] The presence of a cyanide ion in the reaction system was confirmed by formation of a gray precipitate of AgCN upon treatment of the reaction residue with silver nitrate after removal of the volatile matters. The cyanide ion may be present in the form of cobalt cyanide or lithium cyanide.

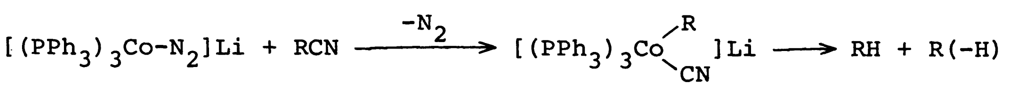
Table I. R-CN Bond Cleavage of Nitriles on the Reactions with $[Co(PPh_3)_3N_2]Li(Et_2O)_3$ **1**[a]

R	Products (mol/Co)
CH_3	CH_4 (0.52)
C_2H_5	C_2H_4 (0.65), C_2H_6 (0.01)
n-C_3H_7	C_3H_6 (0.48)
i-C_3H_7	C_3H_6 (0.41)
n-C_4H_9	*trans*-C_4H_8 (0.58), *cis*-C_4H_8 (0.19) 1-C_4H_8 (0.02), *n*-C_4H_{10} (0.01)
i-C_4H_9	*i*-C_4H_8 (0.78), *i*-C_4H_{10} (0.03)
C_6H_5	C_6H_6 (0.27)
o-$CH_3C_6H_4$	$C_6H_5CH_3$ (0.16)
$C_6H_5CH_2$	$C_6H_5CH_3$ (0.47)

a) Neat, at room temperature.

b) *Cis* and *trans* mixture, 99% yield per allyl cyanide.

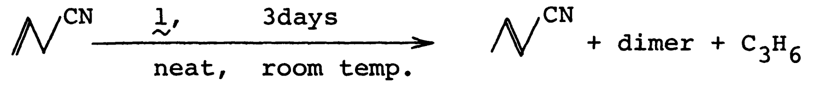
The reaction probably proceeds by oxidative addition mechanism involving the C-CN bond cleavage.



$$[(PPh_3)_3Co\text{-}N_2]Li + RCN \xrightarrow{-N_2} [(PPh_3)_3Co\overset{R}{\underset{CN}{\ }}]Li \longrightarrow RH + R(-H) \qquad (2)$$

The alkyl-cobalt bond thus formed may be cleaved via β-hydrogen elimination to liberate an olefin, when the R group has β-hydrogen, or via hydrogen abstraction to yield RH. For confirming the source of hydrogen, methane formed on the reaction of **1** with CD_3CN was examined by mass spectrometry to reveal that CD_3H and CD_4 were produced in a 2.8 : 1 ratio. The result suggests ortho-hydrogens in the triphenylphosphine ligands may be involved in the formation of methane$^{5)}$ in addition to the direct hydrogen abstraction from the acetonitrile. Predominant formation of alkanes or olefins depending on the presence or absence of the β-hydrogen in nitriles excludes a radical decomposition pathway of the alkylcobalt intermediate as less likely.$^{6)}$ Formation of *trans*- and *cis*-2-butenes in the reaction of *n*-C_4H_9CN with **1** suggests that a cobalt hydride formed by β-hydrogen elimination of the alkylcobalt intermediate serve as an isomerization catalyst.

The isomerization involving the hydrogen transfer was also observed in the reaction of allyl cyanide with **1**. In this reaction only 0.01 mmol/Co of propylene was formed and the allyl cyanide was catalytically converted into *trans*- and *cis*-crotononitrile (99%/ allyl cyanide) and dimeric products of crotononitrile.



(3)

The isomerization of allyl cyanide to crotononitrile is also catalyzed by cobalt hydrido complex $CoH(N_2)(PPh_3)_3$, although the dimerization of allyl cyanide in this case was negligible and no propylene was produced.

Among the cobalt complexes examined for the C-CN bond cleavage of acetonitrile the activity was found to be highest for the lithium cobaltate complex **1** with formation of 0.52 mol of methane per cobalt. The analogous magnesium containing complex $[Co(PPh_3)_3N_2]_2Mg(thf)_4$$^{4)}$ was less reactive to form methane (0.27 mol/Co), while the cobalt hydride complex $CoH(N_2)(PPh_3)_3$ formed a simple adduct $CoH(CH_3CN)$-$(PPh_3)_3$$^{7)}$ without cleavage of the C-CN bond. Replacement of the ligating dinitrogen with the more electron-withdrawing CO ligand causes the decrease in the electron density of cobalt. Thus $[Co(CO)(PPh_3)_3]Li(thf)_3$ [8] caused no C-CN bond cleavage of acetonitrile.

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(Received August 27, 1982)