

STUDIES OF A COBALT-PROMOTED ACRYLONITRILE COUPLING REACTION

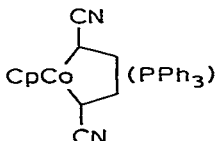
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(Received April 2nd, 1982; in revised form June 25th, 1982)

Summary

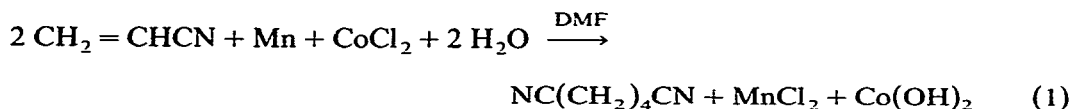
A stoichiometric cobalt-promoted acrylonitrile (AN) coupling reaction leading to adiponitrile (ADN) formation was reinvestigated. The active catalyst appears to involve cobalt(0) species. Cobalt hydride complexes are either inactive $[\text{CoH}_2(\text{PPh}_3)_3]$ or give only low yields of ADN $[\text{CoH}(\text{N}_2)(\text{PPh}_3)_3]$. Intermediate $\text{Co}(\text{AN})_2$ species can be reduced to give ADN using H_2S or using H_2 and Pt on C. Choice of ligand is a factor in determination of ADN yield, such yields decreasing in the order $(\text{CH}_3)_2\text{NCHO} \cong \text{PPh}_3 > \text{P}(\text{OPh})_3 > \text{P}(\text{CH}_3)_3 > \text{P}(\text{OC}_2\text{H}_5)_3$. Formation of stoichiometric ADN yields from $\text{Co}(\text{N}_2)(\text{PPh}_3)_3$ and AN indicate that co-promoters, such as ZnCl_2 and CoCl_2 , are not required. Different ADN/*c.t.*-1,4-dicyanobutene-1 product ratios, obtained by H_2S treatment of $\text{Co}(\text{AN})_2$ species and a known



complex, suggest that the intermediate $\text{Co}(\text{AN})_2$ species consist mainly of polymeric structures rather than monomeric metallacyclic complexes.

Introduction

A stoichiometric cobalt-promoted acrylonitrile (AN) coupling reaction has been reported [1].



* Contribution No. 2444.

The reaction was reported to occur in two stages. In the first, a dimethylformamide (DMF) solvated complex derived from two molecules of AN and one atom of cobalt was formed. In the second, the complex could be decomposed with aqueous bases or H_2S to give adiponitrile (ADN). In this paper we report the results of studies which bear on the mechanism of this coupling reaction. Contrasting reactions between AN and olefins with $\text{Co}(\text{N}_3)(\text{PPh}_3)_3$ ($\text{Ph} = \text{C}_6\text{H}_5$), $\text{CoH}(\text{N}_2)(\text{PPh}_3)_3$ and $\text{Co}(\text{H}_2)(\text{PPh}_3)_3$ are also discussed.

Experimental

All preparations and experiments were carried out under nitrogen atmosphere using a model HE432 Vacuum Atmospheres dry box. Solvents were purified by distillation or by treatment with neutral alumina. Analyses for AN and propionitrile (PN) were carried out using a $6' \times 1/8''$ Poropak QS column at 180°C . Analyses for ADN were carried out using a $8' \times 1/8''$ Tenax column at 230°C . Analyses for hexenes and hexane were carried out using a $20' \times 1/8''$ XE-60 column at 60°C . IR measurements were carried out using a Perkin-Elmer model 137 spectrophotometer.

Reaction of $\text{CoI}(\text{PPh}_3)_3$ with AN. Into a 4 ml vial containing a Teflon[®] coated stirring bar was charged 0.085 g (0.087 mmol) $\text{CoI}(\text{PPh}_3)_3$ followed by 1.60 g of a pre-mixed DMF/AN solution containing 0.016 g (0.29 mmol) AN. The green $\text{CoI}(\text{PPh}_3)_3$ complex reacted rapidly to give a dark red solution. A gradual reaction of AN was indicated by GLC analyses for unreacted AN.

t (min)	AN (wt%)
0	0.92 (calc)
9	0.80
30	0.71
116	0.65
16 (h)	0.66

After stirring 16 h, the vial was transferred to a fume hood and gently sparged with H_2S for 5 min. The resulting black slurry was allowed to stand for 1 h followed by GLC analysis for ADN. The observed wt% ADN was 0.22% (max. calc. 0.56% ADN). The ADN yield based on a maximum of 1 ADN/Co was 39%. The ADN yield based on converted AN was 79%. The analyses for AN showed no detectable PN.

Reaction of $\text{Co}(\text{N}_2)(\text{PPh}_3)_3$ with 1-hexene. A 4 ml serum-capped vial was charged with 0.5 ml of a 0.3 M $\text{Co}(\text{N}_2)(\text{PPh}_3)_3$ solution in toluene followed by 0.020 ml 1-hexene. After 2 h a GLC analysis showed the presence of a mixture of linear hexene isomers with no detectable hexane.

Reaction of propylene with ortho-deuterated $\text{Co}(\text{N}_2)(\text{PPh}_3)_3$ [$\text{Co}(\text{N}_2)(\text{P-d}_6)_3$]. A 10 ml stainless steel tube was charged with 0.1 g (0.11 mmol) $\text{Co}(\text{N}_2)(\text{P-d}_6)_3$ dissolved in 2 ml benzene. The tube was cooled in dry ice and charged with 0.5 g (11.9 mmol) propylene. The tube was agitated for 16 h at room temperature. The liquid phase of the reaction product was analyzed by GLC mass spectroscopy for propylene and hexenes (Discussion section).

Preparation and characterization of $\text{Co}(\text{N}_2)(\text{PPh}_3)_3$. $\text{Co}(\text{N}_2)(\text{PPh}_3)_3$, free of $\text{CoH}(\text{N}_2)(\text{PPh}_3)_3$, was prepared according to the procedure of Speier and Marko.

Experimentally determined $\text{N}\equiv\text{N}$ stretching frequencies (2093, THF and 2085 cm^{-1} , Nujol) duplicated published values [2]. The magnetic susceptibility parameter, χ_g , (1.6×10^{-6}) agreed well with the published value (1.7×10^{-6}) [3].

Results

Effect of cobalt complex on ADN yield. Several cobalt complexes were examined in place of $\text{CoCl}_2 + \text{Mn}$ and gave varying ADN yields (Table 1). High ADN yields can be obtained in solvents other than DMF provided excess PPh_3 is present and provided AN is added after $\text{Co}(\text{N}_2)(\text{PPh}_3)_3$ is pre-dissolved in solvent to dilute it. Treatment of $\text{Co}(\text{N}_2)(\text{PPh}_3)_3$ with neat AN results in rapid exothermic polymerization of AN. Typical yields to ADN using $\text{Co}(\text{N}_2)(\text{PPh}_3)_3$ were 90–100% (DMF), 90–100% (THF), 35–50% (PhCN), and 40–90% (benzene). Solutions of $\text{Co}(\text{N}_2)(\text{PPh}_3)_3$ in DMF or dimethylacetamide were shown to be only moderately stable over a period of days [4].

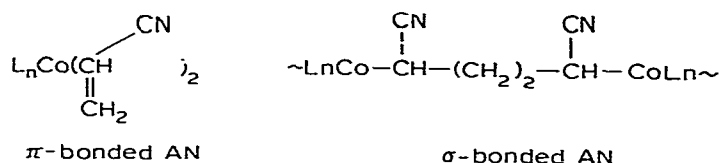
IR and NMR spectra and structure of the $\text{Co}(\text{AN})_2$ complex. The reddish-brown intermediate complex obtained from $\text{CoI}(\text{PPh}_3)_3/\text{AN}/\text{DMF}$ (Experimental section) gave an elemental analysis indicating the stoichiometry $\text{Co}/\text{AN}/\text{DMF}/\text{PPh}_3/\text{I}$ equal to 1/2/1/0.3/0.3. Calculated $\text{Co}/\text{C}/\text{H}/\text{N}/\text{P}/\text{I}$ ratios were 1/14.8/17.8/3.0/0.3/0.3. Observed ratios were 1/13.2/18.7/2.9/0.32/0.31. The infrared spectrum of this $\text{Co}(\text{AN})_2$ complex is characterized by a strong broad adsorption at $\sim 2200 \text{ cm}^{-1}$ in Nujol or in reaction product solutions. This absorption does not allow a differentiation to be made between σ - or π -bonding of the coordinated AN. For example, representative $\text{C}\equiv\text{N}$ stretching frequencies for AN π -bonded to low valent metals are 2194 cm^{-1} $\text{AN} \cdot \text{Ni}[\text{P}(\text{O}-o\text{-tolyl})_3]_2$, 2195 cm^{-1} $\text{AN} \cdot \text{Pt}(\text{PPh}_3)_2$ and 2227 cm^{-1} $\text{AN} \cdot \text{Fe}(\text{CO})_4$ [5]. The $\text{C}\equiv\text{N}$ stretching frequency for σ -bonded AN in $\text{Cp}(\text{CO})_2\text{FeCH}(\text{CH}_3)\text{CN}$ is 2210 cm^{-1} [6].

TABLE I

YIELDS TO ADIPONITRILE FOR REACTION OF ACRYLONITRILE WITH COBALT COMPLEXES^a

Co Complex	ADN/Co
$\text{CoCl}_2 + \text{Zn}(\text{Mn})$	1.02
$\text{CoI}(\text{PPh}_3)_3$ [12]	0.39, 0.48, 0.34 ^b
$\text{CoI}(\text{PPh}_3)_3 + \text{Zn}$	1.11
$\text{CoH}(\text{N}_2)(\text{PPh}_3)_3$ [13]	0.36 (+0.41 mol $\text{CH}_3\text{CH}_2\text{CN}$)
$\text{Co}(\text{N}_2)(\text{PPh}_3)_3$	0.94
$\text{CoH}(\text{PPh}_3)_3$	0
$\text{Co}[\text{P}(\text{CH}_3)_3]_4$ [14]	trace
$\text{CoH}[\text{P}(\text{OPh})_3]_3 \cdot \text{CH}_3\text{CN}$ [15]	trace
$\text{CoH}[\text{P}(\text{OPh})_3]_4$ [15]	0
$\text{CoCl}[\text{OPh}_3]_3$ [16]	0.10
$\text{CoCl}[(\text{OC}_2\text{H}_5)_3]_3$ [17]	0
$\text{CoP}(\text{OPh}_3)_3$ [18]	trace

^a Reactions carried out in DMF solvent at 25°C with H_2S workup as shown in Experimental for the reaction of $\text{CoI}(\text{PPh}_3)_3$ with AN and using 2.5 to 8 mol AN/mol Co. ^b Duplicate experiments showing range of variability.



A C–H stretching frequency for the $\text{Co}(\text{AN})_2$ complex at $\sim 2900 \text{ cm}^{-1}$ (KBr) is also consistent with either saturated $\sim \text{CH}_2 \sim$ groups from coupled AN or with the C–H from AN π -bonded to Co. For example, the aliphatic C–H stretching frequency for AN $\cdot \text{Ni}[\text{P}(\text{O}-o\text{-tolyl})_3]_2$ was found to be $\sim 2900 \text{ cm}^{-1}$ (KBr). The highly insoluble nature of the reddish-brown $\text{Co}(\text{AN})_2$ complex, precipitated from DMF by addition of hydrocarbon solvents or by removal of solvent for reactions carried out in THF, tends to suggest a polymeric structure(s) rather than a monomolecular species.

Attempts to obtain well resolved ^{13}C or ^1H NMR spectra were not successful due to low solubilities of several samples of $\text{Co}(\text{AN})_2$ complexes. Typical spectra contained, in addition to aromatic absorption of PPh_3 groups, only broad complex multiplets. In contrast, the ^1H NMR spectrum of a monoacrylonitrile complex, $\text{CpCo}(\text{AN})\text{PPh}_3$ (1), formed by rapid room temperature reaction of AN with $\text{CpCo}(\text{PPh}_3)_2$, gave well resolved 1/1/2 olefinic ^1H NMR resonances at δ 2.7, 1.5 and 1.1 ppm, in close analogy to the known complex $\text{Ni}[\text{P}(\text{O}-o\text{-tolyl})]\text{AN}$ whose olefinic ^1H NMR resonances occur at δ 2.9, 1.3 and 1.2 ppm [7].

Deuterium and trimethylsilylation labeling experiments. The $\text{Co}(\text{AN})_2$ complex was worked up using Me_3SiCl as well as various reducing agents containing deuterium to try to determine the number of Co–C bonds hydrogenolyzed to give ADN. The *ortho*-deuterated complex $\text{Co}(\text{N}_2)(\text{P}-d_6)_3$, prepared using *ortho*-deuterated PPh_3 , was treated with AN to test for the intervention of *ortho*-metallated intermediates [8]. The product following H_2S workup was shown by GLC-mass spectroscopy to contain 98–99% ADN- d_0 with < 1–2% ADN- d_1 . These results do not support the

TABLE 2

EXTENT OF DEUTERATION OF ADN PRODUCT FROM TREATMENT OF $\text{Co}(\text{AN})_2$ COMPLEXES WITH VARIOUS REDUCING AGENTS AT 25°C

Cobalt complex	Reductive agent	ADN/Co	Product ADN			
			No. D/ADN	Isomer distribution		
				d_0	d_1	d_2
$\text{CoI}(\text{PPh}_3)_3/\text{DMF}$	D_2/Pt	0.37	0.62	48	42	10
$\text{CoCl}_2/\text{Zn}/\text{DMF}^a$	D_2S	0.39	1.36	11	42	47
$\text{CoCl}_2/\text{Zn}/\text{DMF}^a$	D_2/Pt	0.38	0.39	65	31	4
$\text{Co}(\text{N}_2)(\text{P}-d_6)_3/\text{THF}^b$	D_2S	0.50	0.28	73	26	1
$\text{Co}(\text{N}_2)(\text{P}-d_6)_3/\text{THF}^b$	D_2/Pt	0.33	0.34	72	22	6
$\text{Co}(\text{N}_2)(\text{PPh}_3)_3/\text{THF}$	$\text{DCl}/\text{D}_2\text{O}$	0.29	1.09	0	92	5

^a Same product mixture from reaction of $\text{CoCl}_2/\text{Zn}/\text{DMF}$ used. ^b Same product mixture from reaction of $\text{Co}(\text{H}_2)(\text{P}-d_6)_3/\text{THF}$ used.

involvement of *ortho*-metallated species in the AN coupling step. The possibility that hydrogen could be abstracted from solvent was also checked by using DMF-*d*₇. No significant abstraction was observed with Co(N₂)(PPh₃)₃ (> 99% ADN-*d*₀, < 0.5% ADN-*d*₁) and a limited amount was obtained with CoI(PPh₃)₃ (89% ADN-*d*₀, 10% ADN-*d*₁, 1% ADN-*d*₂).

Several ADN workups were carried out using D₂S, DCl/D₂O, D₂/Pt, and D₂/Pd to try to determine whether one or two Co–C bonds in the Co(AN)₂ complex could be cleaved to give ADN-*d*₁ or ADN-*d*₂, respectively (Table 2). Deviation of the D/ADN values from 1.0 or 2.0 indicated that exchange of deuterium with sources of hydrogen possibly occurred prior to hydrogenolysis of the Co(AN)₂ complex. Isotopic exchange between deuterium and hydrogen was shown to occur. Mass spectral analysis of the vapor from reaction of CoCl₂/Zn/AN/DMF, following reduction of the Co(AN)₂ complex solution with D₂, gave a completely equilibrated hydrogen product vapor:

	D ₂	HD	H ₂	Fraction deuterated
Found	59.3	34.6	6.1	0.765
Calcd.	58.6	35.9	5.5	

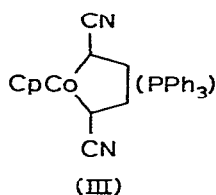
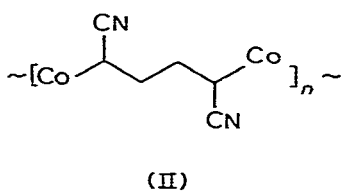
The calculated values are theoretical for a hydrogen mixture containing 76.5% D, 23.5% H. Since hydrogen abstraction was shown not to take place with DMF solvent or the *ortho*-hydrogens of PPh₃ ligands, it is most likely that AN undergoes hydrogen exchange.

Although loss of isotopic purity in deuteration experiments precluded their use as a probe for the number of Co–C bonds cleaved in ADN formation, Me₃SiCl was successfully used. Treatment of a solution obtained by reaction of CoI(PPh₃)₃ with AN in DMF gave rise to only one silicon-containing compound eluting in the range of ADN by GLC-mass spectroscopy. A peak with a *m/e* = 252, consistent with NCCH(SiMe₃)CH₂CH₂CH(SiMe₃)CN, was observed. No peak with a *m/e* = 180 for NC(CH₂)₃CH(SiMe₃)CN was observed, indicating that two Co–C bonds in the Co(AN)₂ complex were cleaved to give ADN.

Discussion

Characterization of Co(AN)₂ complexes. Achievement of a stoichiometric yield of ADN with the Co(N₂)(PPh₃)₃ complex indicates that a cobalt(0) species may be required for the AN coupling step (Table 1). The cobalt dihydride complex, CoH₂(PPh₃)₃, was not active. Reaction of AN with CoH(N₂)(PPh₃)₃ gave hydrogenation of AN to PN accompanied by a low yield of ADN, perhaps via disproportionation of CoH(N₂)(PPh₃)₃ to give small amounts of cobalt(0) species. The results in Table 1 show that formation of the intermediate Co(AN)₂ complexes does not require additional promoters such as ZnCl₂ or CoCl₂. Reduction of the Co(AN)₂ complexes to give ADN can also be done using H₂ and Pt on C (Table 2).

Although IR and NMR measurements could not distinguish between monomeric Co-containing metallacycles or oligomeric structures (II), a recent report [9] of a well characterized complex III suggests that the Co(AN)₂ complexes may contain some metallacyclic structures (II).



The contrast between the reactivities of $\text{CpCo}(\text{PPh}_3)_2$ and $\text{CoI}(\text{PPh}_3)_3$ is striking. $\text{CoI}(\text{PPh}_3)_3$ reacts rapidly with excess AN at room temperature to give a $\text{Co}(\text{AN})_2$ complex which gives, upon H_2S treatment, ~ 0.4 mol ADN/Co. Room temperature treatment of $\text{CpCo}(\text{PPh}_3)_2$, on the other hand, gives $\text{CpCo}(\text{AN})\text{PPh}_3$ which in turn reacts with excess AN to give III only upon prolonged heating at 100°C [9]. A sample of III, when treated with H_2S at room temperature, gave only $\sim 5\%$ ADN plus about equal amounts of *c,t*-1,4-dicyanobutene-1 [10]. The low ADN yield perhaps reflects added stability from the Cp group. Formation of only traces of *c,t*-1,4-dicyanobutene-1 with the $\text{Co}(\text{AN})_2$ complexes indicates that most of the Co is not in the form of metallacyclic structures.

Contrasting reactivities of AN and olefins with $\text{Co}(\text{N}_2)(\text{PPh}_3)_3$ and $\text{CoH}_2(\text{PPh}_3)_3$. Olefins are rapidly isomerized with $\text{Co}(\text{N}_2)(\text{PPh}_3)_3$ and hydrogenated with $\text{CoH}_2(\text{PPh}_3)_3$ [2]. Coupling of olefins also occurs with $\text{Co}(\text{N}_2)(\text{PPh}_3)_3$ [11]. Significant deuteration of products and starting material was found in the case of propylene dimerization using *ortho*-deuterated $\text{Co}(\text{N}_2)(\text{PPh}_3)_3$ [$\text{Co}(\text{N}_2)(\text{P-}d_6)_3$] (Experimental Section).

Propylene			Hexenes		
d_0	d_1	d_2	d_0	d_1	d_2
93.3	5.2	1.5	78.6	11.6	9.8

Since the ADN from AN coupling with $\text{Co}(\text{N}_2)(\text{P-}d_6)_3$ gave only minor amounts of ADN- d_1 and no ADN- d_2 , it is likely that *ortho*-metallated intermediates are involved in propylene dimerization but not in AN dimerization. Treatment of $\text{Co}(\text{N}_2)(\text{PPh}_3)_3$ with H_2 afforded $\text{CoH}_2(\text{PPh}_3)_3$ which stoichiometrically converted 1-hexene to hexane, in agreement with published results for 1-heptene hydrogenation [2]. It was also found that AN, unlike propylene when treated with $\text{CoH}_2(\text{PPh}_3)_3$, appears to undergo neither hydrogenation to PN nor coupling to complexes which afford ADN on treatment with H_2S .

Acknowledgements

The authors wish to thank Drs. D.R. Coulson, R.J. McKinney and T.H. Tulip for helpful discussions and F.G. Kitson for mass spectral analyses.

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carbonyl complexes. Loss of the $\text{N}\equiv\text{N}$ stretching frequency at 2093 cm^{-1} can be followed along with growth of a CO stretching frequency at $\sim 1904\text{ cm}^{-1}$.

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