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STUDIES OF A COBALT-PROMOTED ACRYLONITRILE COUPLING REACTION

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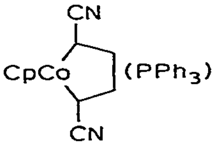
Summary

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 [$CoH_2(PPh_3)_3$] or give only low yields of ADN [$CoH(N_2)(PPh_3)_3$]. Intermediate $Co(AN)_2$ 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 $(CH_3)_2NCHO \cong PPh_3 > P(OPh)_3 > P(CH_3)_3 > P(OC_2H_5)_3$. Formation of stoichiometric ADN yields from $Co(N_2)(PPh_3)_3$ 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 $Co(AN)_2$ species and a known



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

Introduction

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

$$2\,CH_2{=}CHCN + Mn + CoCl_2 + 2\,H_2O \xrightarrow{DMF} NC(CH_2)_4CN + MnCl_2 + Co(OH)_2 \qquad (1)$$

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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 $Co(N_3)(PPh_3)_3$ ($Ph = C_6H_5$), $CoH(N_2)(PPh_3)_3$ and $Co(H_2)(PPh_3)_3$ 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′ × 1/8″ Poropak QS column at 180°C. Analyses for ADN were carried out using a 8′ × 1/8″ Tenax column at 230°C. Analyses for hexenes and hexane were carried out using a 20′ × 1/8″ XE-60 column at 60°C. IR measurements were carried out using a Perkin–Elmer model 137 spectrophotometer.

Reaction of $CoI(PPh_3)_3$ with AN. Into a 4 ml vial containing a Teflon® coated stirring bar was charged 0.085 g (0.087 mmol) $CoI(PPh_3)_3$ followed by 1.60 g of a pre-mixed DMF/AN solution containing 0.016 g (0.29 mmol) AN. The green $CoI(PPh_3)_3$ 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 $Co(N_2)(PPh_3)_3$ with 1-hexene. A 4 ml serum-capped vial was charged with 0.5 ml of a 0.3 *M* $Co(N_2)(PPh_3)_3$ 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 $Co(N_2)(PPh_3)_3$ [$Co(N_2)(P\text{-}d_6)_3$]. A 10 ml stainless steel tube was charged with 0.1 g (0.11 mmol) $Co(N_2)(P\text{-}d_6)_3$ 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 $Co(N_2)(PPh_3)_3$. $Co(N_2)(PPh_3)_3$, free of $CoH(N_2)(PPh_3)_3$, was prepared according to the procedure of Speier and Marko.

Experimentally determined N≡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 $CoCl_2$ + 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 $Co(N_2)(PPh_3)_3$ is pre-dissolved in solvent to dilute it. Treatment of $Co(N_2)(PPh_3)_3$ with neat AN results in rapid exothermic polymerization of AN. Typical yields to ADN using $Co(N_2)(PPh_3)_3$ were 90–100% (DMF), 90–100% (THF), 35–50% (PhCN), and 40–90% (benzene). Solutions of $Co(N_2)(PPh_3)_3$ in DMF or dimethylacetamide were shown to be only moderately stable over a period of days [4].

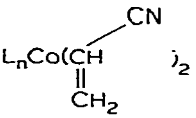
IR and NMR spectra and structure of the Co(AN)₂ complex. The reddish-brown intermediate complex obtained from $CoI(PPh_3)_3$/AN/DMF (Experimental section) gave an elemental analysis indicating the stoichiometry Co/AN/DMF/PPh_3/I equal to 1/2/1/0.3/0.3. Calculated Co/C/H/N/P/I ratios were 1/14.8/17.8/3.0/0.3/0.3. Observed ratios were 1/13.2/18.7/2.9/0.32/0.31. The infrared spectrum of this $Co(AN)_2$ complex is characterized by a strong broad adsorption at ~ 2200 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 C≡N stretching frequencies for AN π-bonded to low valent metals are 2194 cm^{-1} AN · Ni[P(O-*o*-tolyl)$_3$]$_2$, 2195 cm^{-1} AN · $Pt(PPh_3)_2$ and 2227 cm^{-1} AN · $Fe(CO)_4$ [5]. The C≡N stretching frequency for σ-bonded AN in $Cp(CO)_2FeCH(CH_3)CN$ is 2210 cm^{-1} [6].

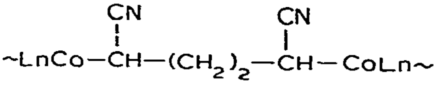
TABLE 1

YIELDS TO ADIPONITRILE FOR REACTION OF ACRYLONITRILE WITH COBALT COMPLEXES[a]

Co Complex	ADN/Co
$CoCl_2$ + Zn(Mn)	1.02
$CoI(PPh_3)_3$ [12]	0.39, 0.48, 0.34[b]
$CoI(PPh_3)_3$ + Zn	1.11
$CoH(N_2)(PPh_3)_3$ [13]	0.36 (+0.41 mol CH_3CH_2CN)
$Co(N_2)(PPh_3)_3$	0.94
$CoH(PPh_3)_3$	0
$Co[P(CH_3)_3]_4$ [14]	trace
$CoH[P(OPh)_3]_3 \cdot CH_3CN$ [15]	trace
$CoH[P(OPh_3]_4$ [15]	0
$CoCl[(OPh)_3]_3$ [16]	0.10
$CoCl[(OC_2H_5)_3]_3$ [17]	0
$CoP(OPh_3]_3$ [18]	trace

[a] Reactions carried out in DMF solvent at 25°C with H_2S workup as shown in Experimental for the reaction of $CoI(PPh_3)_3$ with AN and using 2.5 to 8 mol AN/mol Co. [b] Duplicate experiments showing range of variability.


π-bonded AN


σ-bonded AN

A C–H stretching frequency for the $Co(AN)_2$ complex at ~ 2900 cm^{-1} (KBr) is also consistent with either saturated ~ CH_2 ~ 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 · Ni[P(O-*o*-tolyl$)_3]_2$ was found to be ~ 2900 cm^{-1} (KBr). The highly insoluble nature of the reddish-brown $Co(AN)_2$ 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 ^{1}H NMR spectra were not successful due to low solubilities of several samples of $Co(AN)_2$ complexes. Typical spectra contained, in addition to aromatic absorption of PPh_3 groups, only broad complex multiplets. In contrast, the ^{1}H NMR spectrum of a monoacrylonitrile complex, $CpCo(AN)PPh_3$ (I), formed by rapid room temperature reaction of AN with $CpCo(PPh_3)_2$, gave well resolved 1/1/2 olefinic ^{1}H NMR resonances at δ 2.7, 1.5 and 1.1 ppm, in close analogy to the known complex Ni[P(O-*o*-tolyl)]AN whose olefinic ^{1}H NMR resonances occur at δ 2.9, 1.3 and 1.2 ppm [7].

Deuterium and trimethylsilylation labeling experiments. The $Co(AN)_2$ 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 $Co(N_2)(P\text{-}d_6)_3$, 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 $Co(AN)_2$ 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
$CoI(PPh_3)_3$/DMF	D_2/Pt	0.37	0.62	48	42	10
$CoCl_2$/Zn/DMF [a]	D_2S	0.39	1.36	11	42	47
$CoCl_2$/Zn/DMF [a]	D_2/Pt	0.38	0.39	65	31	4
$Co(N_2)(P\text{-}d_6)_3$/THF [b]	D_2S	0.50	0.28	73	26	1
$Co(N_2)(P\text{-}d_6)_3$/THF [b]	D_2/Pt	0.33	0.34	72	22	6
$Co(N_2)(PPh_3)_3$/THF	DCl/D_2O	0.29	1.09	0	92	5

[a] Same product mixture from reaction of $CoCl_2$/Zn/DMF used. [b] Same product mixture from reaction of $Co(H_2)(P\text{-}d_6)_3$/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 $Co(N_2)(PPh_3)_3$ (> 99% ADN-d_0, < 0.5% ADN-d_1) and a limited amount was obtained with $CoI(PPh_3)_3$ (89% ADN-d_0, 10% ADN-d_1, 1% ADN-d_2).

Several ADN workups were carried out using D_2S, DCl/D_2O, D_2/Pt, and D_2/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 $CoCl_2/Zn/AN/DMF$, following reduction of the $Co(AN)_2$ complex solution with D_2, 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	

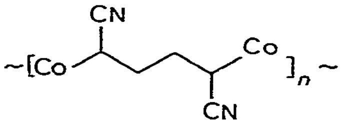
The calculated values are theoretical for a hydrogen mixture containing 76.5% D, 23.5% H. Since hydrogen abstraction was shown not to take place with DMF solvent or the *ortho*-hydrogens of PPh_3 ligands, it is most likely that AN undergoes hydrogen exchange.

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, Me_3SiCl was successfully used. Treatment of a solution obtained by reaction of $CoI(PPh_3)_3$ 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 $NCCH(SiMe_3)CH_2CH_2CH(SiMe_3)CN$, was observed. No peak with a $m/e = 180$ for $NC(CH_2)_3CH(SiMe_3)CN$ was observed, indicating that two Co–C bonds in the $Co(AN)_2$ complex were cleaved to give ADN.

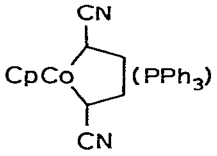
Discussion

Characterization of $Co(AN)_2$ complexes. Achievement of a stoichiometric yield of ADN with the $Co(N_2)(PPh_3)_3$ complex indicates that a cobalt(0) species may be required for the AN coupling step (Table 1). The cobalt dihydride complex, $CoH_2(PPh_3)_3$, was not active. Reaction of AN with $CoH(N_2)(PPh_3)_3$ gave hydrogenation of AN to PN accompanied by a low yield of ADN, perhaps via disproportionation of $CoH(N_2)(PPh_3)_3$ 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 $ZnCl_2$ or $CoCl_2$. Reduction of the $Co(AN)_2$ complexes to give ADN can also be done using H_2 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).



(II)



(III)

The contrast between the reactivities of $CpCo(PPh_3)_2$ and $CoI(PPh_3)_3$ is striking. $CoI(PPh_3)_3$ reacts rapidly with excess AN at room temperature to give a $Co(AN)_2$ complex which gives, upon H_2S treatment, ~ 0.4 mol ADN/Co. Room temperature treatment of $CpCo(PPh_3)_2$, on the other hand, gives $CpCo(AN)PPh_3$ 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 ~ 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 $Co(AN)_2$ complexes indicates that most of the Co is not in the form of metallacyclic structures.

Contrasting reactivities of AN and olefins with $Co(N_2)(PPh_3)_3$ *and* $CoH_2(PPh_3)_3$. Olefins are rapidly isomerized with $Co(N_2)(PPh_3)_3$ and hydrogenated with $CoH_2(PPh_3)_3$ [2]. Coupling of olefins also occurs with $Co(N_2)(PPh_3)_3$ [11]. Significant deuteration of products and starting material was found in the case of propylene dimerization using *ortho*-deuterated $Co(N_2)(PPh_3)_3$ $[Co(N_2)(P\text{-}d_6)_3]$ (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 $Co(N_2)(P\text{-}d_6)_3$ 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 $Co(N_2)(PPh_3)_3$ with H_2 afforded $CoH_2(PPh_3)_3$ 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 $CoH_2(PPh_3)_3$, appears to undergo neither hydrogenation to PN nor coupling to complexes which afford ADN on treatment with H_2S.

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