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Cyanoethyl Complexes of Cobalt—Their Preparation and Their Reactions with Acrylonitrile

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By the addition reaction of acrylonitrile to hydridobis(dimethyl- or diphenylglyoximato)-pyridinecobalt, only 1-cyanoethyl complexes were obtained. The 2-cyanoethyl complex was not formed from that reaction, but from the reaction of 3-bromopropionitrile with the hydride complex. NMR spectroscopy was used to confirm the structure of the complexes. The isomerization of the 2-cyanoethyl complex to the 1-cyanoethyl complex at 70°C was not observed by NMR measurements. The reaction of these complexes with acrylonitrile was carried out under a hydrogen atmosphere. It was observed that 2-methylglutaronitrile was formed from the reaction of the 1-cyanoethyl complex with acrylonitrile. The thermal decomposition and the reaction of the complexes with hydrochloric acid were also investigated.

We have already reported[1] that some systems, in which hydride complexes of cobalt or iron may presumably be formed, convert acrylonitrile to adiponitrile and 2-methylglutaronitrile as well as propionitrile. The reaction is considered to proceed through a cyanoethyl complex formed by the reaction of acrylonitrile and the hydride complex.

In the present study, we isolated 1- and 2-cyanoethylbis(DMG*[1] or DPhG*[1])pyridinecobalt through the reaction of the corresponding hydride complex with acrylonitrile or 3-bromopropionitrile.

Some cyanoethyl complexes of transition metals have been prepared[2-4] by the reaction of the corresponding transition metal hydride and acrylonitrile or by the reaction of the sodium salt of the transition metal complex with 2- or 3-halogenopropionitrile. Schrauzer reported[5] the preparation of 2-cyanoethylbis(DMG)pyridinecobalt by the addition reaction of acrylonitrile to the hydride complex which had been prepared by the reduction of chlorobis(DMG)pyridinecobalt with sodium borohydride. According to our results, however, only the 1-cyanoethyl complex could be obtained from that reaction, while the 2-cyanoethyl complex was prepared only by the reaction of 3-bromopropionitrile and the corresponding hydride

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[*1] DMG represents dimethylglyoximato, while DPhG represents diphenylglyoximato.

[1] A. Misono, Y. Uchida, K. Tamai and M. Hidai, This Bulletin, **40**, 931 (1967).

[2] J. K. P. Ariyaratne and M. L. H. Green, *J. Chem. Soc.*, **1963**, 2976.

[3] J. Kwiatek and L. K. Seyler, *J. Organometal. Chem.*, **3**, 421 (1965).

[4] K. C. Dewhirst, *Inorg. Chem.*, **5**, 319 (1966).

[5] G. N. Schrauzer, *Chem. Ber.*, **97**, 3056 (1964).

complex. In this report, the structure of the complexes will be confirmed and the reaction with acrylonitrile will be studied.

Experimental

Preparation of the Complex. *1-Cyanoethyl Complex.* $CoCl(DMG)_2Py$ (4 g) or $CoCl(DPhG)_2Py$ (6.3 g) was reduced with sodium borohydride in methanol-water at -20—-40°C, with any air rigorously excluded. The solution became dark green, and it was very sensitive to air and temperature. Upon the addition of acrylonitrile, the solution turned wine-red. The orange-yellow crystalline complex was filtered after the concentration of the reaction solution. The complex was purified by recrystallization from methanol or acetone.

Anal. 1-Cyanoethylbis(DMG)pyridinecobalt; (I), Found: C, 45.5; H, 5.53; N, 17.8; O, 16.3; Co, 14.9%. Calcd for $C_{16}H_{23}N_6O_4Co$: C, 45.6; H, 5.47; N, 19.9; O, 15.2; Co, 14.0%. 1-Cyanoethylbis(DPhG)-pyridinecobalt; (II), Found: C, 64.3; H, 4.67; N, 12.0; O, 9.32; Co, 9.70%. Calcd for $C_{36}H_{31}N_6O_4Co$: C, 64.5; H, 4.63; N, 12.5; O, 9.55; Co, 8.78%.

2-Cyanoethyl Complex. The procedure was the same as that described above except that 3-bromopropionitrile was used instead of acrylonitrile, and except that, in this case, the recrystallization was carried out using methylene chloride as the solvent.

Anal. 2-Cyanoethylbis(DMG)pyridinecobalt; (III), Found: C, 44.4; H, 5.51; N, 19.2; O, 16.2; Co, 14.7%. Calcd for $C_{16}H_{23}N_6O_4Co$: C, 45.6; H, 5.47; N, 19.9; O, 15.2; Co, 14.0%.

The reaction of hydridobis(DPhG)pyridinecobalt with 3-bromopropionitrile failed to give a cyanoethyl complex. The reaction of 3-bromopropionitrile with sodium bis(DMG)pyridinecobaltate, which had been prepared by the reduction of the corresponding chloro complex with sodium amalgam or sodium metal, did not give any type of cyanoethyl complexes.

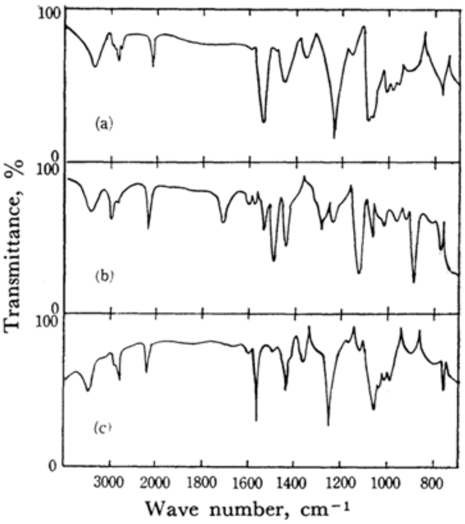


Fig. 1. Infrared spectra of complexes.

(a) (1-cyanoethyl)$Co(DMG)_2Py$
(b) (1-cyanoethyl)$Co(DPhG)_2Py$
(c) (2-cyanoethyl)$Co(DMG)_2Pyr$

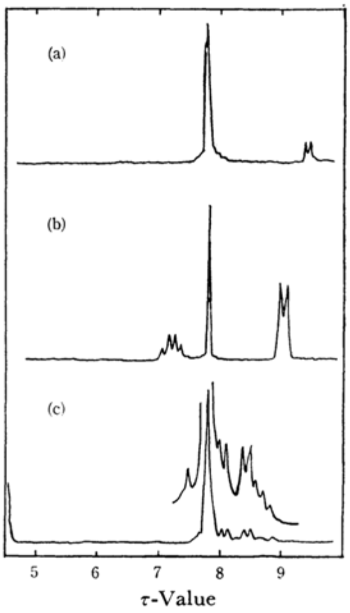


Fig. 2. NMR spectra of complexes.

(a) (1-cyanoethyl)$Co(DMG)_2Py$
(b) (1-cyanoethyl)$Co(DPhG)_2Py$
(c) (2-cyanoethyl)$Co(DMG)_2Py$

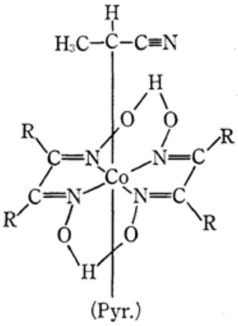
Measurements. The infrared spectra of the complexes, taken by the KBr disk method, are shown in Fig. 1. The NMR spectra, recorded at room temperature in a chloroform or methylene chloride solution, are shown in Fig. 2.

Reactions. Upon heating the complexes *in vacuo*, both I and II decomposed at about 180°C, giving acrylonitrile, propionitril, and pyridine in a ratio 0.5 : 0.5 ; 1.0 in the case of I, and 0.8 : 0.2 : 1.0 in the case of II. III decomposed at about 200°C to give acrylonitrile, propionitrile, and pyridine in a ratio of 0.97 : 0.03 : 1.0. The reaction of I with hydrochloric acid was carried out in a Schlenk tube under a reflux of methanol; propionitrile was then formed. The reaction of these complexes with acrylonitrile was carried out in a 100 m*l* autoclave at 110°C for 4 hr under hydrogen gas pressure (80 atm), using methanol as the solvent. In the reactions described above, the products were identified by comparing the gas chromatographic retention times with those of authentic samples.

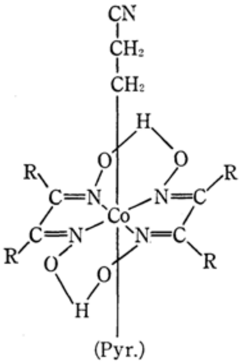
Results and Discussion

The characteristic absorption of ν_{-CN} at about 2200 cm^{-1} in infrared spectra, and the results of the thermal decomposition experiments, the elemental analysis, and the reaction with hydrochloric acid indicate that each complex has a cyanoethyl group directly bound to the metal. In the NMR spectrum of II, a doublet at 9.0 τ and a quartet at 7.2 τ appeared in an intensity ratio of 3 : 1. These are assignable to the methyl and methyne protons in the 1-cyanoethyl group. I shows a doublet at 9.4 τ and a singlet at 7.8 τ in a ratio of 3 : 13. The singlet is assigned to four identical methyl protons in DMG, and the doublet to the methyl protons in the 1-cyanoethyl group. In this case, the quartet for the methyne proton is considered to overlap the peak at 7.8 τ. No bands assignable to the methylene protons in the 2-cyanoethyl group were observed in either I or II. In the case of III, we could observe complex bands in the region of 7.8—8.8 τ, besides a singlet of methyl protons in DMG at 7.8 τ.

The addition reaction of acrylonitrile with hydride complexes forms two different cyanoethyl complexes, *i. e.,* 1- and 2-cyanoethyl complexes, according to the direction of the addition. The direction is due to the electronic nature of the hydrogen attached directly to the metal and to the steric effects of other ligands. The experimental results described above indicate that both I and II have a 1-cyanoethyl group, while III has a 2-cyanoethyl group. The isomerization of the 2-cyanoethyl complex to the 1-cyanoethyl complex in chloroform at 70°C for 13 hr was not observed by NMR measurements. The results of the elemental analysis, the thermal decomposition, and the infrared and NMR measurements of the complex recrystallized from acetone indicate that there was one mole of acetone per two moles of the complex (Fig. 2-b).



(I) ; $R=CH_3$
(II); $R=C_6H_5$



(III); $R=CH_3$

The reaction of I and II with acrylonitrile gave only 2-methylglutaronitrile, and not adiponitrile, as the hydrodimer of acrylonitrile. However, from the reaction of III with acrylonitrile, neither hydrodimer nor dimer could be obtained, though propionitrile was formed. According to our experimental results, the formation of 2-methylglutaronitrile is considered to proceed through the second addition of acrylonitrile to the 1-cyanoethyl group of the complex. In the case of the 2-cyanoethyl complex, however, the decomposition of the cyanoethyl group may occur before the dicyanobutyl complex is formed by the second insertion of acrylonitrile, resulting in the failure to obtain any type of dimer, though propionitrile is formed.