

Preliminary communication

THE PREPARATION AND CHEMISTRY OF A ZEROVALENT COBALT(0) COMPLEX CONTAINING ONLY ISOCYANIDE LIGANDS

YASUHIRO YAMAMOTO* and HIROSHI YAMAZAKI

The Institute of Physical and Chemical Research, Wako-shi, Saitama, 351 (Japan)

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Summary

Reaction of $\text{Co}_2(\text{CO})_8$ with 2,6-xylyl isocyanide at 80–90°C gave a zerovalent isocyanide complex of cobalt, $\text{Co}_2(\text{C}_9\text{H}_9\text{N})_8$ (I). The structure and reactions of I are discussed.

The reaction between octacarbonyldicobalt and isocyanides give $[\text{Co}(\text{RNC})_5][\text{Co}(\text{CO})_4]$ [1]. Recently Manning et al. have reported that reinvestigation of the aforementioned reaction afforded neutral complexes of type $[\text{Co}_2(\text{RNC})_m(\text{CO})_{8-m}]$ ($m = 1, 2$ or 3), together with $[\text{Co}(\text{RNC})_5][\text{Co}(\text{CO})_4]$ [2]. However, zerovalent cobalt complexes bearing isocyanides as the sole ligand have not been synthesized as yet*, although there are various zerovalent isocyanide complexes of Ni, Pd, Pt, Cr Mo, etc. [3]. We wish to report the preparation and reactions of the zerovalent complex of cobalt which contains only isocyanide ligands.

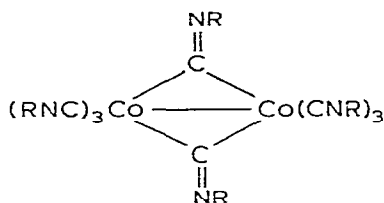
A mixture of $\text{Co}_2(\text{CO})_8$ and 2,6-xylyl isocyanide (1/10 molar ratio) in toluene was heated at 80–90°C for 0.5–1.0 h under a nitrogen atmosphere. The resulting reddish brown solution was chromatographed on alumina using benzene as an eluant to give the dimeric, reddish brown complex, $\text{Co}_2(\text{C}_9\text{H}_9\text{N})_8$ (I)**, 60–70%, m.p. 194–196°C (decomposed under nitrogen). Similar reactions with *t*-butyl or cyclohexyl isocyanide gave $[\text{Co}(\text{RNC})_5][\text{Co}(\text{CO})_4]$ as the main product without producing the cobalt(0) complex.

Compound I is air-sensitive, even in the solid state, and it is soluble in unsaturated hydrocarbons, but poorly soluble in alcohols. The molecular weight obtained by cryoscopy in benzene agreed with the calculated value. The

* Recently, the preparation and X-ray crystallography of $\text{Co}_2(\text{t-BuNC})_8$ appeared after this paper was submitted (G.K. Barker, A.M.R. Galas, M. Green, J.A.K. Howard, F.G.A. Stone, T.W. Turney, A.J. Welch, and P. Woodward, *J. Chem. Soc. Chem. Commun.*, (1977) 256).

** Found: C, 74.12; H, 6.21; N, 9.75. $\text{C}_{72}\text{H}_{72}\text{Co}_2\text{N}_8$ calcd.: C, 74.09; H, 6.22; N, 9.60%.

infrared spectrum (KBr) showed broad absorptions due to the terminal isocyanide groups at 2048 cm^{-1} and to the bridged isocyanide groups at 1675 cm^{-1} . The spectrum in $\text{C}_6\text{H}_5\text{Cl}$ at 23°C showed five absorptions due to the terminal isocyanide groups at 2126 , 2092 (sh), 2055 , 2027 , and 1997 cm^{-1} and two due to the bridged ones at 1684 and 1678 cm^{-1} . The spectrum remained unchanged when was measured at -80°C . The spectroscopic results suggest that compound I has a doubly isocyanide-bridged structure in the solid state and in solution in view of the known structure of $\text{Co}_2(\text{CO})_8$ [4].

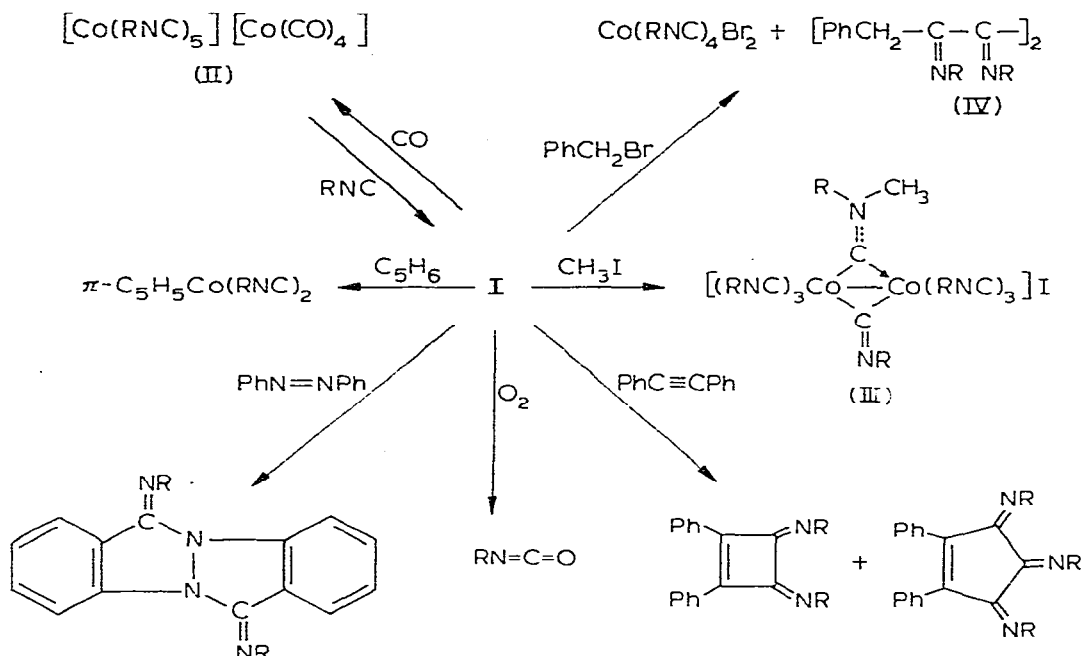


One would have expected to see at least two sets of methyl resonances in the proton NMR spectrum. The spectrum in $\text{C}_6\text{H}_5\text{Cl}$ showed only one sharp singlet at δ 2.13 ppm. The singlet broadened at low temperatures, but complete separation of the broad signal was not observed at -90°C . We could not determine whether this NMR behavior is due to fluxionality in solution or to an accidental degeneracy.

Ligand exchange of I with free 2,6-xylyl isocyanide in $\text{C}_6\text{H}_5\text{Cl}$ was examined by variable-temperature NMR spectroscopy. The two methyl resonances of the free and coordinated isocyanide broadened on warming and coalesced at 127°C . The broad singlet sharpened at higher temperatures. This change is reversible. It is of interest to note that the rate of ^{14}CO exchange with $\text{Co}_2(\text{CO})_8$ in toluene is immeasurably rapid at room temperature [5].

When I was treated with CO (30 kg/cm^2 at 40°C), disproportionation to cobalt(I) and cobalt(-I) occurred to afford $[\text{Co}(\text{C}_9\text{H}_9\text{N})_5][\text{Co}(\text{CO})_4]$ (II) which was obtained from the reaction of $\text{Co}_2(\text{CO})_8$ and $\text{C}_9\text{H}_9\text{N}$ at room temperature. The reaction of I with cyclopentadiene in toluene at reflux gave $\pi\text{-C}_5\text{H}_5\text{Co}(\text{C}_9\text{H}_9\text{N})_2^*$, compared with $\pi\text{-C}_5\text{H}_5\text{Co}(\text{CO})_2$ [6] obtained from $\text{Co}_2(\text{CO})_8$ and C_5H_6 . The reaction with toluene in toluene at reflux gave 3,4-bis-(2,6-xylylimino)-1,2-diphenylcyclobutene [7] and 3,4,5-tris(2,6-xylylimino)-1,2-diphenylcyclopentene [7]. A similar reaction with azobenzene gave 6*H*,12*H*-indazolo-[2,1, α]-6,12-diiminoindazole [8]. The treatment of $\text{Co}_2(\text{CO})_8$ with Na-Hg produced $\text{NaCo}(\text{CO})_4$ [9], but similar reduction of I did not occur. This may be due to steric hindrance of the bulky isocyanide ligands and to the relatively high electron density on the cobalt atom, arising from the high electron-releasing ability of isocyanide. Metal anions with all isocyanide ligands have not been obtained hitherto, although those having CO as the sole ligand have been isolated in the various metals [10]. Molecular oxygen reacted with oxidation of isocyanide to isocyanate, which was identified as an urea deriva-

* The elemental analysis was satisfactory, also another organic compound which was formulated as $(\text{C}_5\text{H}_6)_2(\text{C}_9\text{H}_9\text{N})_4$ was isolated, which will be reported elsewhere.



tive. The reaction of I with bromine and iodine gave $\text{Co}(\text{C}_9\text{H}_9\text{N})_4\text{X}_2$ ($\text{X} = \text{Br}$ or I). On treatment with CH_3I , methylation on a nitrogen atom of a bridging isocyanide ligand occurred to give an ionic 1/1 adduct III. The infrared spectrum of III in CH_2Cl_2 showed three absorptions due to the terminal isocyanide groups at 2154, 2116, and 2098 cm^{-1} , an absorption due to the RNC bridge at 1722 cm^{-1} , and a new one due to the C—N stretching frequency at 1513 cm^{-1} . These absorptions due to the terminal and the bridging groups are higher than those of the starting complex, reflecting the oxidation state. The proton NMR spectrum in CD_2Cl_2 showed three kinds of methyl groups at δ 2.20 (14 CH_3), 2.30 (2 CH_3), and 4.17 ($\text{CH}_3\text{—N}$) ppm. The reaction of I with benzyl bromide readily took place to give $\text{Co}(\text{C}_9\text{H}_9\text{N})_4\text{Br}_2$ and the tetraimino derivative IV*.

Studies on the reactions and catalytic activity of I and derived compounds are in progress.

References

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* The elemental analysis was satisfactory.