CONTRIBUTION FROM THE RESEARCH CENTER OF THE
HERCULES POWDER COMPANY, WILMINGTON, DELAWARE 1989

Dihalocarbonylcyclopentadienylcobalt Complexes

BY RICHARD F. HECK

Received December 28, 1964

Halogens react with dicarbonylcyclopentadienylcobalt to form dihalocarbonylcyclopentadienylcobalt complexes and carbon monoxide. The dihalocarbonylcyclopentadienylcobalt complexes react very readily with coordinating compounds such as phosphite esters and pyridines. The carbonyl group is replaced first by the coordinating compound and then halogens are replaced, forming ionic compounds.

Introduction

Dicarbonylcyclopentadienylcobalt is known to react with allylic halides to produce carbonyl-π-allyl-π-cyclopentadienylcobalt salts[1] and π-allyl-π-cyclopentadienylcobalt halides.[2] Similarly, perfluoroalkyl iodides react forming iodocarbonyl-π-cyclopentadienylperfluoroalkylcobalt derivatives.[3] It has now been found that an analogous reaction occurs with halogens, forming dihalocarbonyl-π-cyclopentadienylcobalt complexes. The reaction is completely analogous to the

$$C_5H_5Co(CO)_2 + X_2 \longrightarrow C_5H_5Co(CO)X_2 + CO$$

reaction of iron pentacarbonyl with halogens.[4]

$$Fe(CO)_5 + X_2 \longrightarrow Fe(CO)_4X_2 + CO$$

Results

Iodine, bromine, and chlorine react very rapidly with dicarbonylcyclopentadienylcobalt in ether solution. The iodine product is prepared simply by adding an ether solution of 1 mole of iodine to an ether solution of 1 mole of dicarbonylcyclopentadienylcobalt at 0°. A mole of gas is rapidly evolved, and the iodide crystallizes from the solution as shiny dark purple crystals in good yield. The bromide was prepared similarly, but the product is less stable. It is decomposed by light and apparently decomposes slowly at room temperature even in the dark. The chloride must be made at low temperatures because it decomposes rapidly above about $-20°$.

All three halides react readily with a variety of coordinating compounds. Some ligands, such as triphenylphosphine[4a] and piperidine, cause reduction of the complexes to dicarbonylcyclopentadienylcobalt or derivatives of this compound. Phosphite esters and pyridines, on the other hand, first replace carbon monoxide and then may replace halogen, forming ionic products.

Diiodocarbonyl-π-cyclopentadienylcobalt, in methylene chloride solution, reacts very rapidly with 1 mole of 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane (trimethylolpropane phosphite) causing replacement of the carbonyl group by the phosphite ester. If the reaction is carried out in tetrahydrofuran

$$CpCo(CO)I_2 + PO_3C_6H_{11} \longrightarrow CpCo(PO_3C_6H_{11})I_2 + CO$$

solution, a less soluble, probably ionic, monotetrahydrofuran derivative is obtained.

$$CpCo(PO_3C_6H_{11})I_2 + OC_4H_8 \longrightarrow \{CpCo(PO_3C_6H_{11})(OC_4H_8)I\}^+I^-$$

With 1 mole of pyridine, the diiodocarbonylcyclopentadienylcobalt yields diiodopyridinecyclopentadienylcobalt. With *o*-dipyridyl, the ionic complex

$$CpCo(CO)I_2 + NC_5H_5 \longrightarrow CpCo(NC_5H_5)I_2 + CO$$

iododipyridylcyclopentadienylcobalt iodide is obtained.

$$CpCo(CO)I_2 + \text{dipy} \longrightarrow \{CpCo(\text{dipy})I\}^+I^- + CO$$

Similar compounds can be obtained from the dibromo- and dichlorocarbonylcyclopentadienylcobalt complexes. Dichlorocarbonylcyclopentadienylcobalt gave a stable product on reaction with dipyridyl but it was hygroscopic. The product was converted into the nonhygroscopic hexafluorophosphate by reaction with ammonium hexafluorophosphate. Analyses indicated that the product was chlorodipyridylcyclopentadienylcobalt hexafluorophosphate.

The compounds prepared in this work are listed in Table I along with their analyses, infrared carbonyl absorptions, and ultraviolet spectra.

Experimental

Diiodocarbonylcyclopentadienylcobalt.—In a gasometric apparatus[5] at 0°, filled with ether-saturated carbon monoxide, were placed 20 ml. of 0.1 *M* dicarbonyl-π-cyclopentadienylcobalt in ether and 40 ml. of 0.05 *M* iodine in ether. The black solution evolved 44 ml. of gas (1.3 mmoles) within 90 sec. and the reaction stopped. A black crystalline solid had separated from the solution. The solvent was evaporated at room temperature, and the residue was dissolved in about 5 ml. of chloroform and filtered to remove a small quantity of insoluble green material. The addition of 5 ml. of ether and 5 ml. of pentane to the chloroform solution and cooling in Dry Ice gave shiny dark purple crystals of the product. There was obtained 0.53 g. (65.5%), m.p. 185° dec. More material can be obtained by concentrating the mother liquors. The analytical sample was recrystallized from a small quantity of chloroform by adding ether. The compound was stable in the air, at least for several days.

The compound could also be prepared in methylene chloride solution.

---

[1] E. O. Fischer and R. D. Fischer, *Z. Naturforsch.*, **16b**, 475 (1961).

[2] R. F. Heck, *J. Org. Chem.*, **28**, 604 (1963).

[3] R. B. King, P. M. Treichel, and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 3593 (1961).

[4] W. Hieber and G. Bader, *Chem. Ber.*, **61B**, 1717 (1928).

[4a] NOTE ADDED IN PROOF.—R. B. King, *Z. Naturforsch.*, **19b**, 1160 (1964), has also reported the synthesis of diiodocarbonylcyclopentadienylcobalt and finds that triphenylphosphine replaces carbon monoxide in the complex. Apparently both reduction and substitution occur with this ligand

[5] R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **83**, 1097 (1961).

TABLE I

DIHALOCARBONYLCYCLOPENTADIENYLCOBALT COMPLEXES AND DERIVATIVES

Compound	M.p., °C.	Ultraviolet bands, mμ (ε)	Found		Calculated		
			% C	% H	Formula	% C	% H
π-$C_5H_5Co(CO)_2$[a,b]	. . .	235 (8000) 247 (7900) 295 (4100)[c]	. . .	. . .	. . .	. . .	. . .
π-$C_5H_5Co(C_3H_5)I$[2]	95.5–97	229 (8500) 275 (12,000) 540 (sh) (400)[c]	. . .	. . .	. . .	. . .	. . .
π-$C_5H_5Co(CO)I_2$[d]	185 dec.	258 (16,000) 265 (16,000) 272 (16,000) 535 (1600)[c]	17.84	1.54[e]	$C_6H_5OI_2Co$	17.75	1.24
π-$C_5H_5Co(CO)Br_2$[f]	>300	244 263 460 (sh) 528 690[c]	23.57	1.82	$C_6H_5OBr_2Co$	23.11	1.62
π-$C_5H_5Co(PO_3C_6H_{11})I_2$	198–200 dec.	288 (6600) 271 (8000) 400 (sh) (850) 535 (840)[c]	24.52	3.19	$C_{11}H_{16}O_3PI_2Co$	24.47	2.99
π-$C_5H_5Co(NC_5H_5)I_2$	158–159 dec.	228 (15,200) 278 (17,300) 435 (sh) (1570) 640 (1850)[c]	26.51	2.48	$C_{10}H_{10}NI_2Co$	26.28	2.21
$[\pi$-$C_5H_5Co(N_2C_{10}H_{10})I]^+I^-$	>300	294 (23,800) 430 (1680) 540 (1420)[g]	33.68	2.82[h]	$C_{15}H_{13}N_2I_2Co$	33.73	2.45
$[\pi$-$C_5H_5Co(N_2C_{10}H_{10})Br]^+Br^- \cdot CH_3OH$	>300	244 (17,300) 273 (19,300) 311 (sh) (11,000) 405 (825) 540 (1010)[g]	40.10	3.82	$C_{16}H_{17}Br_2N_2OCo$	40.70	3.63
$[\pi$-$C_5H_5Co(N_2C_{10}H_{10})Cl]^+Cl^-$	>300	240 (16,900) 287 (16,400) 300 (15,500) 310 (sh) (11,000) 534 (790)[g]	. . .	. . .	. . .	. . .	. . .
$[\pi$-$C_5H_5Co(N_2C_{10}H_{10})Cl]^+PF_6^-$	. . .	. . .	39.10	3.08	$C_{15}H_{13}ClF_6PN_2Co$	39.11	2.84

[a] E. O. Fischer and R. Jira, *Z. Naturforsch.*, **10b**, 355 (1955); T. S. Piper, F. A. Cotton, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **1**, 165 (1955). [b] ν_{CO} 1965, 2035 cm.$^{-1}$ in methylene chloride solution. [c] Methylene chloride solution. [d] ν_{CO} 2080 cm.$^{-1}$ in methylene chloride solution. [e] Found: I, 62.50. Calcd.: I, 62.54. [f] ν_{CO} 2105 cm.$^{-1}$ in methylene chloride solution. [g] Methanol solution. [h] Found: N, 4.91. Calcd.: N, 5.25.

Dibromocarbonylcyclopentadienylcobalt.—This compound was prepared as described for the iodo complex above, except that 2.0 ml. of 1.0 *M* bromine in methylene chloride was added instead of the ethereal iodine solution. Within 1 min., 50.4 ml. of gas (1.5 mmoles) was evolved and the reaction stopped. A dark purple solid separated during the reaction. The solvent was evaporated at 0°, and the solid was recrystallized immediately from chloroform by adding ether. Very dark purple crystals were obtained in good yield. The compound turns green rapidly at room temperature in the light, but can be kept in the dark at −10° for at least several days.

Dichlorocarbonylcyclopentadienylcobalt.—In a nitrogen-filled bottle, capped with a rubber-lined metal cap with two holes in it for "hypodermic" injections, was placed 20 ml. of 0.1 *M* dicarbonylcyclopentadienylcobalt in methylene chloride. The solution was cooled in a Dry Ice–acetone mixture and stirred magnetically while 50 ml. of chlorine gas was injected by means of a lubricated syringe. The solution turned dark, and dark purple crystals separated. If the mixture is allowed to warm up, the purple solid decomposes into a green amorphous material. The dichloro complex was too unstable to be analyzed.

Diiodo(4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane)cyclopentadienylcobalt.—To a solution of 0.41 g. of diiodocarbonylcyclopentadienylcobalt in 15 ml. of methylene chloride was added 1.0 ml. of 1.0 *M* 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane[6] in ether. After 10 min., the solution was evaporated to 3 or 4 ml. under vacuum and 30 ml. of ether was added. The black solid formed was separated and recrystallized by dissolving it in a minimum of methylene chloride and adding three times the volume of ether. The yield of shiny black crystals was 0.30 g. (49%).

Treating the product with tetrahydrofuran and recrystallizing from methylene chloride–ether and then twice from methanol gave brown crystals, m.p. 205–208° dec., which seem to be the complex with 1 mole of tetrahydrofuran added.

Anal. Calcd. for $C_{11}H_{16}O_3PI_2Co \cdot C_4H_8O$: C, 29.63; H, 3.95. Found: C, 29.53; H, 4.50.

Diiodopyridinecyclopentadienylcobalt.—In a gasometric apparatus[5] at 0° filled with methylene chloride saturated carbon monoxide was placed a solution of 0.41 g. of diiodocarbonylcyclopentadienylcobalt in 10 ml. of methylene chloride and 1.5 ml. of 1.0 *M* pyridine in methylene chloride. Gas was rapidly evolved, and a green precipitate was formed. In 2 hr., 19 ml. (0.7 mmole) of gas was evolved and the reaction stopped. The product was separated by filtration and air dried. The green compound was slightly soluble in chloroform and methylene chloride and insoluble in methanol and water.

Iododipyridylcyclopentadienylcobalt Iodide.—In the gaso-

---

(6) W. S. Wadsworth, Jr., and W. D. Emmons, *J. Am. Chem. Soc.*, **84**, 610 (1962).

metric apparatus[5] at 0° filled with methylene chloride saturated carbon monoxide was placed a solution of 0.41 g. of diiodocarbonylcyclopentadienylcobalt in 10 ml. of methylene chloride, and 1.0 ml. of 1.0 *M* dipyridyl in methylene chloride was added. The reaction was complete in less than 1 min. A brown precipitate was formed and 25 ml. of gas (0.8 mmole) was evolved. The insoluble product was separated by centrifuging and then recrystallized by dissolving it in about 40 ml. of warm methanol and adding ether. Short black needles of the product crystallized from the solution. There was obtained 0.30 g. of product.

Bromodipyridylcyclopentadienylcobalt Bromide.—To the crude dibromocarbonylcyclopentadienylcobalt prepared from 2 mmoles of dicarbonylcyclopentadienylcobalt as described above (not recrystallized) was added 50 ml. of methylene chloride. The solution at room temperature was centrifuged to remove a small amount of insoluble material, and then 2.0 ml. of 1.0 *M* dipyridyl in methylene chloride was added. A purple solid soon crystallized from the solution. The product was separated by centrifuging and recrystallized three times from methanol by adding ether. About 0.1 g. of purple needles was obtained.

Chlorodipyridylcyclopentadienylcobalt Hexafluorophosphate.—A sample of dichlorocarbonylcyclopentadienylcobalt was prepared exactly as described above and to the reaction mixture, cooled in a Dry Ice–acetone mixture, was added 2.0 ml. of 1.0 *M* dipyridyl in methylene chloride. The cold solution was centrifuged, and the purple solid obtained was dried under vacuum. The crude product was recrystallized from methanol by adding an equal volume of ether. The crystalline product was then dissolved in 25 ml. of methanol, and a solution of 0.5 g. of ammonium hexafluorophosphate in 5 ml. of methanol was added. The purple precipitate was filtered off and air dried. About 0.1 g. of the hexafluorophosphate was obtained.

CONTRIBUTION FROM THE MCPHERSON AND EVANS CHEMICAL LABORATORIES
THE OHIO STATE UNIVERSITY, COLUMBUS, OHIO 43210

The Synthesis of Thiocyanatopentacarbonylmanganese(I) and Studies on Manganese–Thiocyanate Bonding[1]

BY MICHAEL F. FARONA[2] AND ANDREW WOJCICKI

Received January 4, 1965

The synthesis of thiocyanatopentacarbonylmanganese(I) by the reaction of sodium pentacarbonylmanganate(−I) and thiocyanogen chloride is reported. Infrared spectral and, where appropriate, electrical conductance studies suggest that the complex is S-bonded in the solid state, almost completely N-bonded in acetonitrile, and that equilibrium between the two linkage isomers prevails in dichloromethane, 1,2-dichloroethane, chloroform, and ethyl acetate. A possible explanation for the different modes of metal–thiocyanate attachment in the isoelectronic $Mn(CO)_5SCN$ (solid state) and $Cr(CO)_5NCS^-$ ion is presented. Attempted preparations of dithiocyanatotetracarbonyliron(II) have been unsuccessful.

Introduction

Thiocyanato complexes of the transition elements have received considerable attention during recent years.[3–11] The ambidentate nature of the ligand has stimulated a number of investigations primarily directed at the elucidation of various factors which influence the two modes (M–SCN and M–NCS) of metal–thiocyanate attachment[3–7] and at the development of physicochemical techniques for the diagnosis of the type of binding.[5–11]

The reported studies did establish that both steric[3,4] and electronic[4–7] factors affect the nature of M–CNS bonding in complexes containing metals in intermediate and high oxidation states. Nevertheless, a complete explanation of the metal's preference for the sulfur end of the ligand in some compounds, and for the nitrogen end in others, is still lacking at present. Furthermore, neglected in all investigations have been complexes of low-valent metals. Although the literature does contain isolated reports of the synthesis of few compounds, for example, $Fe(CO)_2(P(C_2H_5)_3)_2(NCS)_2$[12,13] and $Rh(CO)L_2CNS$[14] ($L = P(C_6H_5)_3$, $As(C_6H_5)_3$, $Sb(C_6H_5)_3$), these were not prepared for a study of the bonding.

In order to fill this void we have commenced an investigation of thiocyanato derivatives of the metal carbonyls. Such compounds are expected to possess many properties in common with the carbonyl halides[15] and hence may provide systems ideally suited to a systematic study of various factors that influence one mode of metal–thiocyanate attachment in preference to the other. Structurally, the complexes should exhibit several different geometries, which would render possi-

---

[1] Presented in part at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 5–10, 1964, and at the Eighth International Conference on Coordination Chemistry, Vienna, Austria, Sept. 7–11, 1964.

[2] Based on the Ph.D. thesis submitted by M. F. F. to The Ohio State University, Aug. 1964.

[3] F. Basolo, W. H. Baddley, and J. L. Burmeister, *Inorg. Chem.*, **3**, 1202 (1964).

[4] J. L. Burmeister and F. Basolo, *ibid.*, **3**, 1587 (1964).

[5] P. C. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.*, 1912 (1960).

[6] J. Lewis, R. S. Nyholm, and P. W. Smith, *ibid.*, 4590 (1961).

[7] A. Turco and C. Pecile, *Nature*, **191**, 66 (1961).

[8] M. M. Chamberlein and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **81**, 6412 (1959).

[9] C. Schäffer, Special Publication No. 13, The Chemical Society, London, 1959, p. 153.

[10] A. Tramer, *J. chim. phys.*, **59**, 232 (1962).

[11] O. W. Howarth, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc.*, 3335 (1964).

[12] G. Booth and J. Chatt, *ibid.*, 2099 (1962).

[13] Henceforth NCS designates N-bonding and SCN S-bonding; CNS denotes that either the bonding is not known or both isomers are present in equilibrium.

[14] L. Vallarino, *J. Chem. Soc.*, 2287 (1957).

[15] For a discussion of metal carbonyl halides see J. Chatt, P. L. Pauson, and L. M. Venanzi, "Organometallic Chemistry," H. Zeiss, Ed., Reinhold Publishing Co., New York, N. Y., 1960, Chapter 10.