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Organometallic Chemistry of the Transition Metals. XI. Some New Cyclopentadienyl Derivatives of Cobalt and Rhodium[1,2]

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Received August 6, 1965

The cyclopentadienylmetal dicarbonyls, $C_5H_5M(CO)_2$ (M = Co and Rh), react with iodine in diethyl ether solution to give the corresponding violet-black to brown cyclopentadienylmetal carbonyl diiodides, $C_5H_5MCOI_2$ (M = Co and Rh). The cobalt derivative $C_5H_5CoCOI_2$ reacts with pyridine to form green-black nonionic $C_5H_5Co(NC_5H_5)I_2$. However, $C_5H_5CoCOI_2$ reacts with 2,2′-bipyridyl or *o*-phenanthroline to form the violet-black salts $[C_5H_5Co(C_{10}H_8N_2)I]I$ and $[C_5H_5Co(C_{12}H_8N_2)I]I$, respectively. Triphenylphosphine reacts with $C_5H_5CoCOI_2$ to give the green substitution product $C_5H_5CoI_2P(C_6H_5)_3$. Treatment of $C_5H_5CoI_2P(C_6H_5)_3$ with methylmagnesium bromide in diethyl ether solution gives the red dimethyl derivative $C_5H_5Co(CH_3)_2P(C_6H_5)_3$. Cyclopentadienyldicarbonylcobalt, $C_5H_5Co(CO)_2$, reacts with triphenylphosphine in boiling methylcyclohexane to give red-black $C_5H_5Co(CO)P(C_6H_5)_3$, which reacts with heptafluoropropyl iodide to give black $C_5H_5CoI(C_3F_7)P(C_6H_5)_3$.

Introduction

Studies on $C_5H_5Co(CO)_2$ have indicated its chemistry to resemble greatly that of pentacarbonyliron with C_5H_5Co and $(CO)_3Fe$ residues behaving analogously in various complexes.[3] For example, dienes,[4,5] perfluoroalkyl halides,[4] and dialkyl disulfides[6] react with $C_5H_5Co(CO)_2$ under appropriate conditions to form the complexes C_5H_5Co(diene), $C_5H_5CoCOIR_f$, and $[C_5H_5CoSR]_2$, respectively, corresponding to the iron carbonyl complexes (diene)$Fe(CO)_3$,[7] $R_fFe(CO)_4I$,[8] and $[Fe(CO)_3SR]_2$,[9] respectively.

One characteristic reaction of $Fe(CO)_5$ occurs with halogens to give the tetracarbonyl dihalides $Fe(CO)_4X_2$.[10] The iodide $Fe(CO)_4I_2$ is especially stable. As reported in the preliminary communication,[2] cyclopentadienyldicarbonylcobalt was found to react with iodine to give $C_5H_5CoCOI_2$. Subsequent to this initial report reactions between $C_5H_5CoCOI_2$ and various Lewis bases were studied resulting in the preparation of compounds such as $C_5H_5CoI_2NC_5H_5$, $[C_5H_5Co(C_{10}H_8N_2)I]I$, and $C_5H_5CoI_2P(C_6H_5)_3$. The triphenylphosphine derivative was in turn used as a starting material for the preparation of the compound $C_5H_5Co(CH_3)_2P(C_6H_5)_3$, a moderately stable compound containing two methyl groups σ-bonded to a cobalt atom. Other related studies include the reaction between $C_5H_5Co(CO)_2$ and triphenylphosphine and the preparation of the rhodium analog $C_5H_5RhCOI_2$.

After the appearance of our original communication on $C_5H_5CoCOI_2$ and the completion of most of the work on the cobalt compounds described in this paper, Heck informed the author of similar work from his laboratory[11] on $C_5H_5CoCOI_2$. Fortunately, the duplication between the two independent research programs was relatively minor, mainly occurring on the studies of the reactions of $C_5H_5CoCOI_2$ with pyridine and 2,2′-bipyridyl.

Experimental Section

Infrared spectra (Table I) were taken in potassium bromide pellets and recorded on a Perkin-Elmer Model 21 spectrometer. Since potassium bromide might be expected to exchange halogen with certain metal–halogen complexes upon preparation of pellets,[12] spectra of crucial compounds were also taken in Nujol mulls to establish the absence of this effect. Proton n.m.r. spectra were taken in the indicated solvents and recorded on a Varian A-60 spectrometer.[13] Ultraviolet spectra were taken in dichloromethane solution and recorded on a Cary Model 14 spectrometer. Microanalyses (Tables II and III) and molecular weight determinations (Mechrolab vapor pressure osmometer in benzene solution) were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany, or Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Chromatographic separations were carried out on 80–200 mesh adsorption alumina (Fisher Scientific Co., No. A-540).

Cobaltocene, $(C_5H_5)_2Co$, was purchased in 10% benzene solution from Arapahoe Chemical Co., Boulder, Colo., and converted to $C_5H_5Co(CO)_2$ in nearly quantitative yields by carbonylation at 130° (100 atm. initial pressure).[14] Rhodium trichloride trihydrate was purchased from Englehard Co., Astor, N. J., and converted to $[Rh(CO)_2Cl]_2$ by a procedure kindly furnished

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[1] For part X of this series see R. B. King and M. B. Bisnette, *J. Organometal. Chem.*, **2**, 15 (1964).

[2] For a preliminary communication of some of this work see R. B. King, *Z. Naturforsch.*, **19b**, 1160 (1964).

[3] For a further discussion of this analogy between $C_5H_5Co(CO)_2$ and $Fe(CO)_5$ see ref. 4.

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

[5] A. Nakamura and N. Hagihara, *Bull. Chem. Soc. Japan*, **33**, 425 (1960); **34**, 452 (1961); H. P. Fritz and H. Keller, *Z. Naturforsch.*, **16b**, 348 (1961).

[6] R. B. King, P. M. Treichel, and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 3600 (1961).

[7] For a review on (diene)$Fe(CO)_3$ complexes see R. Pettit and G. F. Emerson in "Advances in Organometallic Chemistry," F. G. A. Stone and R. West, Ed., Vol. 1, Academic Press, New York, N. Y., 1964, p. 1 ff.

[8] R. B. King, S. L. Stafford, P. M. Treichel, and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 3604 (1961).

[9] W. Hieber and P. Spacu, *Z. anorg. allgem. Chem.*, **233**, 353 (1937); W. Hieber and C. Scharfenberg, *Ber.*, **73**, 1012 (1940); W. Hieber and W. Beck, *Z. anorg. allgem. Chem.*, **305**, 265 (1960); S. F. A. Kettle and L. E. Orgel, *J. Chem. Soc.*, 3890 (1960); R. B. King, *J. Am. Chem. Soc.*, **84**, 2460 (1962); **85**, 1584 (1963); R. B. King and M. B. Bisnette, *Inorg. Chem.*, **4**, 1663 (1965).

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

[11] R. F. Heck, *Inorg. Chem.*, **4**, 855 (1965).

[12] V. W. Meloche and G. E. Kalbus, *J. Inorg. Nucl. Chem.*, **6**, 104 (1958).

[13] The ^{19}F spectrum of $C_5H_5CoI(C_3F_7)P(C_6H_5)_3$ was studied in dichloromethane solution on a Varian DP-60 spectrometer. However, an insufficiently strong spectrum was obtained.

[14] R. B. King, "Organometallic Syntheses," Academic Press, New York, N. Y., 1965, vol. 1, p. 115.

TABLE I

INFRARED SPECTRA[a] (CM.$^{-1}$)

Compound	ν_{CH}	ν_{CO}	Other bands
$C_5H_5CoCOI_2$	3030 vw	2045 s	1405 m, 1340 vw, 1006 vw, 935 vw, 877 w, 835 s, 826 m
$C_5H_5RhCOI_2$[c]	3050 w	2065 s	1400 m, 1342 vw, 1002 w, 985 vw, 872 vw, 838 m, 818 m
$C_5H_5CoI_2NC_5H_5$	3050 w	...	1595 w, 1482 w, 1440 m, 1410 m, 1213 w, 1069 w, 830 m, 752 m
$[C_5H_5Co(C_{10}H_8N_2)I]I$[c]	2975 w	...	1595 m, 1490 w, 1470 m, 1440 m, 1415 m, 1314 m, 1275 w, 1240 w, 1153 m, 1102 w, 1070 w, 1030 w, 1020 vw, 1008 vw, 868 vw, 843 w, 825 w, 805 w, 771 s, 724 m
$[C_5H_5Co(C_{10}H_8N_2)I][PF_6]$	3050 vw	...	1598 w, 1490 vw, 1469 w, 1445 w, 1420 w, 1305 vw, 896 w, 877 m 834 s,[b] 825 sh, 764 w, 736 vw, 725 w
$[C_5H_5Co(C_{12}H_8N_2)I]I$[c]	2970 vw	...	1593 w, 1511 w, 1455 vw, 1426 m, 1405 m, 1345 vw, 1302 vw, 1226 vw, 1150 w, 1140 w, 1101 vw, 1088 vw, 1052 w, 1046 vw, 1006 w, 990 w, 948 w, 944 sh, 881 vw, 871 vw, 861 w, 847 s, 836 m, 828 m, 781 w, 741 vw, 723 w, 714 s, 692 vw
$C_5H_5CoI_2P(C_6H_5)_3$[c]	3000 vw	...	1474 m, 1428 s, 1406 w, 1350 vw, 1180 w, 1152 w, 1115 w, 1087 m, 1067 w, 1024 vw, 1013 vw, 994 w, 855 vw, 833 m, 822 m, 744 m, 721 vw, 696 m, 688 m
$C_5H_5Co(CH_3)_2P(C_6H_5)_3$	3000 vvw 2875 vvw 2825 vw	...	1472 w, 1425 w, 1165 w, 1130 vw, 1110 vw, 1085 m, 1021 vw, 1008–1000 vw, 994 vw, 835 vw, 807 w, 803 w, 745 w, 738 w, 692 m
$C_5H_5CoCOP(C_6H_5)_3$	3020 vw	1905 m	1580 vw, 1478 w, 1430 m, 1305 vw, 1185 m, 1180 m, 1115 m, 1087 vw, 1066 vw, 992 vw, 855 vw, 841 vw, 804 vw, 751 m, 744 w, 718 s, 694 m
$C_5H_5CoI(C_3F_7)P(C_6H_5)_3$	*d*	...	1480 w, 1430 m, 1410 w, 1314 m, 1220 m, 1180 m, 1154 m, 1084 w, 1071 w, 1068 w, 1061 w 1034 w, 996 w, 974 w, 963 w, 939 vw, 838 m, 827 w, 796 m, 744 m, 715 m, 695 sh, 691 m

[a] These spectra were taken in potassium bromide pellets and recorded on a Perkin-Elmer Model 21 spectrometer. [b] This strong absorption arises from the PF_6^- anion [c] These spectra were also taken in Nujol mulls. A similar spectrum was obtained. [d] The ν_{CH} bands in this spectrum were too weak to be unequivocally observed.

TABLE II

$C_5H_5MCOI_2$ COMPOUNDS

Compound	Preparation[a]	Solvent	Yield, %	Color	Proton n.m.r.,[b] $\tau(C_5H_5)$	Analyses, %	C	H	I	O	Metal	Mol. wt.
$C_5H_5CoCOI_2$	(a) $C_5H_5Co(CO)_2 + I_2$	(a) $(C_2H_5)_2O$	87	Purple-black	4.35	Calcd.	17.8	1.2	62.5	3.9	14.5	406
						Found	18.1	1.2	62.8	3.8	14.3	398
	(b) $C_5H_5Co(CO)_2 + ICl$	(b) CH_2Cl_2	57									
$C_5H_5RhCOI_2$	$C_5H_5Rh(CO)_2 + I_2$	$(C_5H_5)_2O$	98	Brown-purple	4.09[c]	Calcd.	16.0	1.1	56.4	3.6	22.9	
						Found	15.7	1.2	57.7	3.5	21.5	

[a] All reactions were carried out at room temperature. [b] These spectra were taken in chloroform solution. [c] The resolution of this spectrum was insufficient for unequivocal observation of the predicted splitting due to coupling between the protons and the ^{103}Rh nucleus. In $C_5H_5Rh(CO)_2$ J_{Rh-H} is only 0.5 c.p.s.

TABLE III

COMPOUNDS PREPARED FROM $C_5H_5CoCOI_2$

Compound	Preparation[a]	Solvent	Yield, %	Color (solid) and m.p., °C.	Color in acetone soln.	Analyses, %	C	H	I	N or P	Co	Other
$C_5H_5CoI_2NC_5H_5$	$C_5H_5CoCOI_2$ + pyridine	Benzene	87	Black	Deep green	Calcd.	26.3	2.2	55.6	3.1 (N)		
						Found	27.0	2.1	55.2	3.0 (N)		
$[C_5H_5Co(C_{10}H_8N_2)I]I$	$C_5H_5CoCOI_2$ + 2,2′-bipyridyl	Benzene	89	Black	Deep purple	Calcd.	33.7	2.4	47.6	5.2 (N)	11.0	
						Found	33.2	2.7	48.0	5.4 (N)	10.5	
$[C_5H_5Co(C_{10}H_8N_2)I][PF_6]$	$[C_5H_5Co(C_{10}H_8N_2)I]I + NH_4PF_6$	H_2O	28[c]	Purple-black		Calcd.	32.6	2.4	23.0	5.1 (N)		20.7 (F)
						Found	32.4	2.5	23.0	5.0 (N)		20.2 (F)
$[C_5H_5Co(C_{12}H_8N_2)I]I$	$C_5H_5CoCOI_2$ + *o*-phenanthroline	Benzene	62	Black	Deep purple	Calcd.	36.6	2.3	45.4	5.0 (N)	10.6	
						Found	36.9	2.4	46.4	5.0 (N)	11.0	
$C_6H_5CoI_2P(C_6H_5)_3$	$C_5H_5CoCOI_2 + (C_6H_5)_3P$	CH_2Cl_2[b]	95	Green, 176–178	Green	Calcd.	43.1	3.1	39.7	4.8 (P)	9.2	640 (mol. wt.)
						Found	43.6	3.2	39.5	4.7 (P)	8.9	585 (mol. wt.)

[a] All of these preparations were carried out at room temperature. [b] Benzene may also be used but less satisfactorily. [c] The relatively low yield in this reaction probably arises from incompletely dissolving the $[C_5H_5Co(C_{10}H_8N_2)I]I$ used as a starting material in the aqueous reaction medium. Much undissolved starting material was removed by filtration prior to adding the aqueous solution of NH_4PF_6.

by McCleverty.[15] Treatment of $[Rh(CO)_2Cl]_2$ with sodium cyclopentadienide[16] in petroleum ether solution readily furnished sufficient orange liquid $C_5H_5Rh(CO)_2$ (~17% yield) for preparation and characterization of $C_5H_5RhCOI_2$.

Preparation of the $C_5H_5MCOI_2$ Compounds.—Filtered solutions of 10 ml. (14 g., 77.8 mmoles) of $C_5H_5Co(CO)_2$ in ~50 ml. of anhydrous diethyl ether and of 20 g. (78.8 mmoles as I_2) of iodine in ~500 ml. of anhydrous diethyl ether were mixed under nitrogen. Gas evolution and formation of a black precipitate occurred immediately. After stirring 3 days to assure complete reaction, the black crystalline precipitate was filtered, washed with diethyl ether and pentane, and dried to give 27.4 g. (87% yield) of $C_5H_5CoCOI_2$.

The preparation of $C_5H_5RhCOI_2$ was carried out in an analo-

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[15] The author is indebted to Dr. McCleverty for kindly furnishing in advance of publication the crucial details of the preparation of $[Rh(CO)_2Cl]_2$ to be described by J. A. McCleverty and G. Wilkinson, *Inorg. Syn.*, **8**, in press.

[16] E. O. Fischer and K. Bittler, *Z. Naturforsch.*, **16b**, 225 (1961).

gous manner but using only 0.36 g. (1.6 mmoles) of $C_5H_5Rh(CO)_2$ and 0.46 g. (1.8 mmoles as I_2) of iodine.

Reactions between $C_5H_5CoCOI_2$ and the Nitrogen Bases Pyridine, 2,2′-Bipyridyl, and *o*-Phenanthroline.—A solution of $C_5H_5CoCOI_2$ in the indicated solvent (generally benzene) was treated with excess of the nitrogen derivative likewise dissolved in the indicated solvent at room temperature (see Table II). Frequently carbon monoxide evolution was measured by attachment to a mercury-filled gas buret. After stirring for several hours at room temperature, the product was filtered, washed, dried, and generally used without further purification. Only in the case of $[C_5H_5Co(C_{10}H_8N_2)I]I$ was the product recrystallized from a mixture of acetone and diethyl ether.

Preparation of $C_5H_5CoI_2P(C_6H_5)_3$.—A solution of 8.12 g. (20 mmoles) of $C_5H_5CoCOI_2$ in 200 ml. of dichloromethane was treated dropwise with a solution of 5.76 g. (22 mmoles) of triphenylphosphine in 60 ml. of dichloromethane with magnetic stirring at room temperature. Rapid gas evolution occurred and the original dark purple color of $C_5H_5CoCOI_2$ became dark green. After stirring overnight at room temperature, the reaction mixture was filtered and ~50 ml. of hexane added to the filtrate. Solvent was gradually removed at ~25° (30 mm.) until precipitation of the dark green crystals appeared complete. The product was then filtered, washed with diethyl ether and pentane, and dried to give 12.25 g. (95% yield) of dark green $C_5H_5CoI_2P(C_6H_5)_3$, m.p. 160–163° dec.

The analytical sample, m.p. 176–178°, was recrystallized further from a mixture of dichloromethane and hexane.

Preparation of $C_5H_5Co(CH_3)_2P(C_6H_5)_3$.—A mixture of 3.5 ml. (10.5 mmoles) of a commercial (Arapahoe) 3 *M* solution of methylmagnesium bromide in diethyl ether and an additional 50 ml. of anhydrous diethyl ether was treated with 1.28 g. (2 mmoles) of $C_5H_5CoI_2P(C_6H_5)_3$. After stirring for ~90 min. at room temperature the reaction mixture was hydrolyzed with 50 ml. of a saturated aqueous solution of ammonium chloride. After 1 hr. the upper diethyl ether layer was separated from the filtered reaction mixture. The water layer was extracted with ~25-ml. portions of diethyl ether until the ether extracts were colorless. The combined ether layers were dried over anhydrous sodium sulfate.[17] After filtration from the drying agent, solvent was removed from the filtrate at ~25° (30 mm.), leaving red crystals.

A solution of this crude $C_5H_5Co(CH_3)_2P(C_6H_5)_3$ in ~40 ml. of diethyl ether was chromatographed on a 2 × 50 cm. alumina column. The chromatogram was developed with diethyl ether and the single orange band eluted with diethyl ether.[17] Removal of solvent from the filtered eluate left red crystals which were washed with ~25 ml. of pentane at −78° and dried to give up to 0.141 g. (17% yield[18]) of red crystalline $C_5H_5Co(CH_3)_2P(C_6H_5)_3$, m.p. 138–141° dec.

Anal. Calcd. for $C_{25}H_{26}CoP$: C, 72.1; H, 6.2; Co, 14.2; P, 7.5. Found: C, 71.6; H, 6.2; Co, 13.5; P, 7.3.

Proton N.m.r. Spectrum (CS_2 Solution).—Resonances were found at τ 2.62 (unresolved singlet), τ 5.46 (singlet), and τ 9.83 (doublet, J = 6 c.p.s.) of approximate relative intensities 15:5:6 corresponding to the fifteen phenyl protons, the five π-cyclopentadienyl protons, and the six methyl protons, respectively.

Preparation of $C_5H_5Co(CO)P(C_6H_5)_3$.—A mixture of 5.0 ml. (7.0 g., 38.9 mmoles) of $C_5H_5Co(CO)_2$, 12.5 g. (47.7 mmoles) of triphenylphosphine, and 250 ml. of methylcyclohexane was boiled 24 hr. under reflux with magnetic stirring under nitrogen. Cooling the red-black reaction mixture to room temperature precipitated red crystals. After several hours these were filtered, washed with two 50-ml. portions of diethyl ether, then 50 ml. of pentane, and dried to give 12.88 g. (80% yield) of red-black crystalline $C_5H_5Co(CO)P(C_6H_5)_3$, m.p. 140–143°.

Upon standing even in a closed vial at −10°, samples of $C_5H_5Co(CO)P(C_6H_5)_3$ gradually became black over periods of 1 week or more.

Anal. Calcd. for $C_{24}H_{20}CoOP$: C, 69.6; H, 4.8; P, 7.5. Found: C, 69.0; H, 4.8; P, 7.3.

Reaction between $C_5H_5Co(CO)P(C_6H_5)_3$ and Iodine.—A solution of 1.04 g. (2.5 mmoles) of $C_5H_5Co(CO)P(C_6H_5)_3$ in 50 ml. of dichloromethane was treated with 1.27 g. (5 mmoles as I_2) of iodine. Gas evolution occurred and the reaction mixture became green. After stirring for 3 days at room temperature to assure complete reaction, the reaction mixture was shaken in several portions with a total of 80 ml. of a ~6% aqueous solution of sodium thiosulfate 5-hydrate to assure removal of excess iodine. The dichloromethane layer was dried over anhydrous sodium sulfate. After filtration from the drying agent, solvent was removed from the filtrate at ~25° (30 mm.). The green-black solid which remained was washed with diethyl ether and pentane and dried. After one recrystallization from a mixture of dichloromethane and hexane, 1.039 g. (65% yield) of dark green $C_5H_5CoI_2P(C_6H_5)_3$, m.p. 175–177°, was obtained. The product was identified by comparison of its infrared spectrum with that of authentic $C_5H_5CoI_2P(C_6H_5)_3$ obtained as described above from $C_5H_5CoCOI_2$ and triphenylphosphine.

Preparation of $C_5H_5CoI(C_3F_7)P(C_6H_5)_3$.—A mixture of 1.04 g. (2.5 mmoles) of $C_5H_5Co(CO)P(C_6H_5)_3$, 1.0 ml. (2.06 g., 6.95 mmoles) of heptafluoro-*n*-propyl iodide, $CF_3CF_2CF_2I$, and 50 ml. of pure benzene was boiled under reflux for 22 hr. under nitrogen. The black mixture was then cooled to room temperature and filtered, and the solvent was removed from the filtrate at ~25° (30 mm.). A filtered solution of the black residue in 50 ml. of diethyl ether was chromatographed on a 2 × 50 cm. alumina column. The chromatogram was developed with diethyl ether. A single dark brown band appeared. This band was eluted with diethyl ether. Solvent was removed from the filtered eluate at ~25° (30 mm.), leaving brown crystals. These brown crystals were washed with pentane and dried. After one recrystallization from a mixture of diethyl ether and hexane, 0.378 g. (22% yield) of black crystalline $C_5H_5CoI(C_3F_7)P(C_6H_5)_3$, m.p. 173–174° dec., was obtained.

Anal. Calcd. for $C_{26}H_{20}CoF_7IP$: C, 45.7; H, 2.9; P, 4.6; F, 19.5; I, 18.6; Co, 8.6; mol. wt., 682. Found: C, 46.1; H, 3.1; P, 4.5; F, 19.4; I, 18.6; Co, 8.6; mol. wt., 676.

Ultraviolet and Visible Spectra (Extinction Coefficients Given in Parentheses).—$C_5H_5CoCOI_2$: Maxima at 221 mμ (14,100), 255 mμ (17,400, broad maximum), and 538 mμ (1660) in dichloromethane solution (dark purple). $C_5H_5RhCOI_2$: Maxima at 222 mμ (17,100), 434 mμ (2120), and 528 mμ (1210, shoulder) in dichloromethane solution (brown). $C_5H_5CoI_2NC_5H_5$: Maxima at 219 mμ (21,500), 278 mμ (19,300), 443 mμ (1760), and 638 mμ (2110) in dichloromethane solution (intense green). $C_5H_5CoI_2P(C_6H_5)_3$: Maxima at 267 mμ (18,700) and 589 mμ (1710) in dichloromethane solution (deep inky blue-green). $C_5H_5CoIC_3F_7P(C_6H_5)_3$: Maxima at 263 m$\mu$ (23,300) and 486 mμ (2060) in dichloromethane solution (yellow-brown).

In dilute dioxane solution the compounds $C_5H_5CoCOI_2$, $C_5H_5CoI_2NC_5H_5$, and $C_5H_5CoI_2P(C_6H_5)_3$ decomposed within a few minutes to give a yellow solution with maxima at 289 mμ (4500–8200) and 365 mμ (1580–2040).

Molar Conductance Measurements (Acetone Solution, Concentration Range Studied Given in Parentheses).—$C_5H_5CoCOI_2$: 6.5 ± 0.6 ohm^{-1} cm.^{2} mole^{-1} (7×10^{-4} to 2.9×10^{-3} *M*). $C_5H_5RhCOI_2$: 6.6 ohm^{-1} cm.^{2} mole^{-1} (5.9×10^{-4} *M*). $C_5H_5CoI_2NC_5H_5$: 4 ± 0.8 ohm^{-1} cm.^{2} mole^{-1} (4×10^{-4} to 1.6×10^{-3} *M*). $[C_5H_5Co(C_{10}H_8N_2)I]I$: 202 ± 15 ohm^{-1} cm.^{2} mole^{-1} (3.7×10^{-4} to 1.3×10^{-3} *M*). $[C_5H_5Co(C_{12}H_8N_2)I]I$: 185 ± 20 ohm^{-1} cm.^{2} mole^{-1} (6.5×10^{-4} to 1.6×10^{-3} *M*). $C_5H_5CoI_2P(C_6H_5)_3$: 13 ± 0.8 ohm^{-1} cm.^{2} mole^{-1} (4.7×10^{-4} to (1.7×10^{-3} *M*).

Discussion

Cyclopentadienylcarbonyldiiodocobalt, $C_5H_5CoCOI_2$, forms black, apparently air-stable, crystals sparingly soluble in pentane and diethyl ether but more soluble in dichloromethane, benzene, and tetrahydrofuran

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[17] These solutions were somewhat air-sensitive and so were kept under nitrogen.

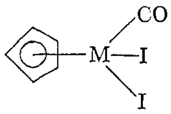
[18] The yields in the preparation of $C_5H_5Co(CH_3)_2P(C_6H_5)_3$ were very erratic ranging from a minimum of ~1% to this maximum of 17%.

to give deep purple solutions. It cannot be sublimed by heating at 0.1 mm. Its spectroscopic properties are in accord with the expected structure I (M = Co). Thus, its infrared spectrum exhibits a single sharp strong ν_{CO} band at 2045 cm.$^{-1}$ (potassium bromide pellet) or 2068 cm.$^{-1}$ (halocarbon oil mull) due to the single carbonyl group. The single resonance at τ 4.35 in its proton n.m.r. spectrum confirms the presence of five equivalent π-cyclopentadienyl protons.

Formally, the cobalt atom in $C_5H_5CoCOI_2$ may be considered in the oxidation state +3 since the two iodine atoms and the π-cyclopentadienyl ring each act as uninegative ligands. Moreover, a π-cyclopentadienyl ring may be considered to occupy three coordination positions of the metal atom.[19] Thus, $C_5H_5CoCOI_2$ (I, M = Co) is a hexacoordinate complex of cobalt (III) corresponding to the very extensive series of octahedral cobalt(III) ammines and related complexes.[20]

The formal +3 oxidation state of the cobalt atom in $C_5H_5CoCOI_2$ is a relatively high one for the metal in a metal carbonyl complex. The resulting relatively high positive charge on the cobalt atom reduces the partial dπ–pπ double bonding ("back bonding") between the cobalt atom and the carbon atom of the carbonyl ligand and thus the bond order of this cobalt–carbon bond. This is reflected in the relatively high frequency of the ν_{CO} band in the infrared spectrum of $C_5H_5CoCOI_2$ cited above. In addition, this diminution of the cobalt–carbon bond order weakens the bond between the cobalt atom and the carbonyl group to the extent that the single carbonyl group in $C_5H_5CoCOI_2$ is readily replaced with other ligands upon reaction at room temperature. This facile replacement of the carbonyl group in $C_5H_5CoCOI_2$ with other ligands permits the synthesis of novel cyclopentadienyl cobalt complexes. The several such compounds described both in this paper and also by Heck[11] appear to be a mere sample of the cobalt complexes which should be preparable from $C_5H_5CoCOI_2$.

The green-black nonionic water-insoluble complex $C_5H_5CoI_2NC_5H_5$ obtained from $C_5H_5CoCOI_2$ and pyridine has already been adequately discussed in both a preliminary communication[2] and Heck's paper.[11] Analogous treatment of $C_5H_5CoCOI_2$ with 2,2′-bipyridyl gave a black salt formulated as the ionic derivative $[C_5H_5Co(C_{10}H_8N_2)I]I$. Characteristic of this material and indicative of its ionic formulation are its solubility in water to give a dark purple aqueous solution and the high conductivity (~200 ohm^{-1} cm.^{2} mole^{-1}) of its likewise dark purple acetone solution. Final and most conclusive evidence for the formulation $[C_5H_5Co(C_{10}H_8N_2)I]I$ is the immediate precipitation of a violet-black salt of composition $[C_5H_5Co(C_{10}H_8N_2)I][PF_6]$ from the aqueous solutions of the corresponding iodide upon treatment with aqueous ammonium hexafluorophosphate. The characterization of the hexafluorophosphate salt included an analysis for iodine which clearly established that the ammonium hexafluorophosphate had only removed half of the iodine in $[C_5H_5Co(C_{10}H_8N_2)I]I$.



I

Reaction between $C_5H_5CoCOI_2$ and o-phenanthroline forms a black material which appears to be entirely analogous to but less soluble than the product obtained from 2,2′-bipyridyl. Elemental analyses, solubility in water to give deep purple solutions, and the high conductivity of the acetone solutions (~175 ohm^{-1} cm.^{2} mole^{-1}) established this material to be the corresponding $[C_5H_5Co(C_{12}H_8N_2)I]I$.

Reactions of $C_5H_5CoCOI_2$ with the monodentate ligand pyridine and the bidentate ligand 2,2′-bipyridyl yielded the neutral species $C_5H_5CoI_2NC_5H_5$ and the monovalent cation $[C_5H_5Co(C_{10}H_8N_2)I]^+$. By a logical extension of this principle, the tridentate ligand 2,2′,2″-terpyridyl should give the bivalent cation $[C_5H_5Co(C_{15}H_{11}N_3)]^{+2}$ with breakage of both cobalt–iodine bonds in $C_5H_5CoCOI_2$. Treatment of $C_5H_5CoCOI_2$ with 2,2′,2″-terpyridyl in benzene or tetrahydrofuran solution produced an immediate *orange-brown* precipitate too insoluble in water or acetone for satisfactory purification. The relatively pale orange color of this material contrasting with the green-black color of $C_5H_5CoI_2NC_5H_5$ and the violet-black color of $[C_5H_5Co(C_{10}H_8N_2)I]I$ suggested scission of both of the cobalt–iodine bonds in $C_5H_5CoCOI_2$. Elemental analyses of this orange-brown material suggested it to be a mixture but were consistent with $[C_5H_5Co(C_{15}H_{11}N_3)]I_2$ as a major component of this mixture.

All of these amine derivatives of $C_5H_5CoCOI_2$ have the nitrogen atom in a pyridine ring system. Reactions of $C_5H_5CoCOI_2$ with ammonia itself or the completely aliphatic amines ethylenediamine or diethylenetriamine gave light brown amorphous solids. When isolated in the usual manner these materials contained no metal carbonyl groups as deduced from the infrared spectrum but appreciable amounts of oxygen which could only have come from the oxygen or moisture of the air or from the diethyl ether used to wash some of these materials. The insolubility of these materials prevented metathesis studies as a chemical tool for the elucidation of their nature.

The reaction between $C_5H_5CoCOI_2$ and triphenylphosphine was also investigated and found to give dark green air-stable $C_5H_5CoI_2P(C_6H_5)_3$ in nearly quantitative yield contrary to the implication of Heck in his paper.[11] The low equivalent conductance of this complex in dilute acetone solutions (~13 ohm^{-1} cm.^{2} mole^{-1}) supports the nonionic formulation.

Recently Yamazaki and Hagihara[21] prepared some stable green σ-bonded alkyl complexes of the type C_5-

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[19] For suitable reviews of the chemistry of cyclopentadienyl derivatives see P. L. Pauson, *Quart. Rev.* (London), **9**, 391 (1955); E. O. Fischer and H. P. Fritz, *Advan. Inorg. Chem. Radiochem.*, **1**, 55 (1959); and G. Wilkinson and F. A. Cotton, *Progr. Inorg. Chem.*, **1**, 1 (1959).

[20] For a summary of Co(III) complexes see F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, New York, N. Y., 1962, pp. 726–730.

[21] H. Yamazaki and N. Hagihara, *Bull. Chem. Soc. Japan*, **37**, 907 (1964).

$H_5Ni(R)(C_6H_5)_3$ by treatment of the halide $C_5H_5NiClP(C_6H_5)_3$ with alkylmagnesium halides. Similar treatment of $C_5H_5CoI_2P(C_6H_5)_3$ with methylmagnesium bromide in diethyl ether solution gave an erratic yield of red crystalline $C_5H_5Co(CH_3)_2P(C_6H_5)_3$ (II). This compound appeared to be fairly stable in air at room temperature in the solid state but was appreciably oxidized in solution over a period of 1 hr. preventing reliable solution molecular weight determinations. The proton n.m.r. spectrum of $C_5H_5Co(CH_3)_2P(C_6H_5)_3$ supports the proposed structure II exhibiting resonances at τ 2.62 (unresolved singlet), τ 5.46 (singlet), and τ 9.83 (doublet, $J = 6$ c.p.s.) corresponding to the fifteen phenyl protons, the five cyclopentadienyl protons, and the six methyl protons, respectively. The doublet methyl resonance arises from coupling between the methyl protons and the ^{31}P nucleus of the triphenylphosphine ligand. The fair stability of $C_5H_5Co(CH_3)_2P(C_6H_5)_3$ contrasts with the apparent complete instability of the unknown[22] $(CH_3)_2Fe(CO)_4$, suggesting that π-cyclopentadienyl and tertiary phosphine ligands are more efficient than carbonyl groups in stabilizing transition metal–alkyl σ bonds.

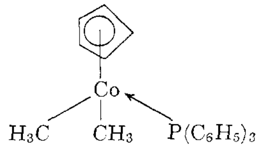
The successful preparations of $C_5H_5CoI_2P(C_6H_5)_3$ and $C_5H_5Co(CH_3)_2P(C_6H_5)_3$ prompted consideration of the preparations of other cobalt compounds containing both π-cyclopentadienyl and triphenylphosphine ligands. In view of the obvious interest in many laboratories throughout the world in reactions between metal carbonyl derivatives and triphenylphosphine,[23] the lack of a literature report of the reaction between $C_5H_5Co(CO)_2$ (available for more than 10 years) and triphenylphosphine was curious.[24] Hayter and Williams,[25] however, have prepared the dark red-violet derivative $C_5H_5CoCOP(CH_3)_2P(CH_3)_2CoCOC_5H_5$ (III) from tetramethylbiphosphine and $C_5H_5Co(CO)_2$. In III the biphosphine nucleus is preserved and each phosphorus atom is donating its lone pair to the cobalt atom just as phosphorus atoms in tertiary phosphines do in their numerous complexes with transition metals. It was therefore not at all surprising that dark red crystalline $C_5H_5Co(CO)P(C_6H_5)_3$ was obtained from $C_5H_5Co(CO)_2$ and triphenylphosphine. The proposed nature of this product was confirmed by the presence of a single sharp metal carbonyl band at 1905 cm.$^{-1}$ suggestive of a single carbonyl group bonded to the cobalt atom.

A characteristic feature of $C_5H_5Co(CO)P(C_6H_5)_3$ is its instability. Even when stored at $-10°$ in a closed vial under nitrogen it gradually became black. The presumably analogous brown crystalline solid obtained from tris(dimethylamino)phosphine[26] and $C_5H_5Co(CO)_2$ in boiling methylcyclohexane was too unstable for purification and characterization.

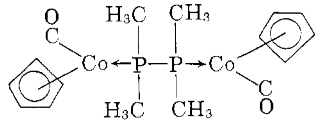
Since $C_5H_5Co(CO)P(C_6H_5)_3$ was available from $C_5H_5Co(CO)_2$ and triphenylphosphine in up to 80% yield, an investigation of its chemistry was feasible and of interest for comparison with the corresponding chemistry of $C_5H_5Co(CO)_2$.

Perfluoroalkyl iodides react readily with $C_5H_5Co(CO)_2$ to give black crystalline compounds of the type $C_5H_5Co(CO)R_fI$.[4] Similar treatment of $C_5H_5Co(CO)P(C_6H_5)_3$ with heptafluoropropyl iodide in boiling benzene gave black crystalline $C_5H_5CoI(C_3F_7)P(C_6H_5)_3$ (IV). Unfortunately, the percentage of fluorine in this compound was so low due to the heavy iodine and triphenylphosphine ligands that only a partial ^{19}F spectrum of the heptafluoropropyl group could be observed even in a ~30% dichloromethane solution.

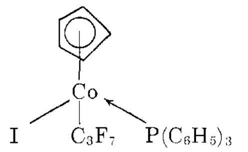
Iodine reacts readily with $C_5H_5Co(CO)P(C_6H_5)_3$ in dichloromethane solution to give a 65% yield of $C_5H_5CoI_2P(C_6H_5)_3$ identical with material obtained from $C_5H_5CoCOI_2$ and triphenylphosphine as described above. Thus it is possible to replace one carbonyl group of $C_5H_5Co(CO)_2$ with iodine and the other carbonyl group of $C_5H_5Co(CO)_2$ with triphenylphosphine in either of the two possible sequences to give ultimately $C_5H_5CoI_2P(C_6H_5)_3$. Allyl iodide also iodinates $C_5H_5Co(CO)P(C_6H_5)_3$ to give some $C_5H_5CoI_2P(C_6H_5)_3$. However, the major product is a yellow allyltriphenylphosphonium salt of a complex presently unidentified cyclopentadienylcobalt iodide anion.



II



III



IV

Some reactions between $C_5H_5Co(CO)_2$ and halogens other than iodine were also studied, but our investigations in this area were not generally as extensive as those of Heck.[11] In general, our results are in agreement with those of Heck so they will not be discussed in detail here. We also investigated the reactions between $C_5H_5Co(CO)_2$ and certain interhalogen compounds. Iodine monochloride was found to react with $C_5H_5Co(CO)_2$ in dichloromethane solution to give the *diiodide* $C_5H_5CoCOI_2$ rather than the mixed iodochloride $C_5H_5CoCOClI$. The $C_5H_5CoCOI_2$ formed in this reaction was identified by conversion with triphenylphosphine to $C_5H_5CoI_2P(C_6H_5)_3$ and comparison of the latter with a sample obtained from authentic $C_5H_5CoCOI_2$ and triphenylphosphine.

The preparation of $C_5H_5CoCOI_2$ from $C_5H_5Co(CO)_2$

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(22) G. Braun, Thesis, Technischen Hochschule, München, 1960.

(23) For a recent review discussing metal carbonyl complexes with tertiary phosphines see T. A. Manuel in "Advances in Organometallic Chemistry," F. G. A. Stone and R. West, Ed., Academic Press, New York, N. Y., Vol. 3, 1966, in press. The author is indebted to Dr. Manuel for a preprint of this manuscript.

(24) In their paper describing the discovery of $C_5H_5Co(CO)_2$ [*J. Inorg. Nucl. Chem.*, **1**, 165 (1955)], T. S. Piper, F. A. Cotton, and G. Wilkinson describe the reactions between $C_5H_5Co(CO)_2$ and phosphorus trihalides to give green solids which could not be obtained pure owing to their insolubility in nonreactive solvents.

(25) R. G. Hayter and L. F. Williams, *J. Inorg. Nucl. Chem.*, **26**, 1977 (1964).

(26) For a description of metal carbonyl complexes of tris(dimethylamino)phosphine see R. B. King, *Inorg. Chem.*, **2**, 936 (1963).

and iodine suggested the preparation of the analogous rhodium compound $C_5H_5RhCOI_2$. The reaction between $C_5H_5Rh(CO)_2$ and iodine in diethyl ether solution at room temperature proceeded rapidly with gas evolution to give a nearly quantitative yield of purple-brown crystalline $C_5H_5RhCOI_2$. The expected structure I (M = Rh) is confirmed by the presence of a π-cyclopentadienyl resonance at τ 4.09 in the proton n.m.r. spectrum and a strong metal carbonyl band at 2065 cm.$^{-1}$ in the infrared spectrum.

Acknowledgment.—The author is indebted to Mr. M. B. Bisnette and Mr. A. Fronzaglia for experimental assistance and to the U. S. Air Force Office of Scientific Research for partial support of this work under Grant No. AF-AFOSR-580-64.

CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT LABORATORIES,
UNION CARBIDE CORPORATION, PLASTICS DIVISION, BOUND BROOK, NEW JERSEY

Tetraneophyltin[1] and Its Derivatives: The Effects of Steric Hindrance in Organotin Chemistry

BY WALTER T. REICHLE

Received August 5, 1965

Tetraneophyltin has been prepared and its chemical reactions and derivatives subjected to study. The very severe steric crowding inhibits tin–carbon bond cleavage reactions in the tetraneophyltin or chloride displacement reactions in trineophyltin chloride. By various techniques the following compounds were prepared: $[C_6H_5C(CH_3)_2CH_2]_3SnX$: X = F, Cl, Br, I, OH, $S_{1/2}$, N_3, NO_3, ClO_4, O_2CCH_3, O_2CCF_3, O_2CH. The fluoride is a low-melting, hydrocarbon-soluble derivative; the acetate, formate, and perfluoroacetate have normal ester carbonyl absorptions (1650–1700 cm.$^{-1}$). The nitrate and perchlorate are both bidentate ligands attached to five-coordinate tin atoms; all other derivatives have four-coordinate tin atoms. Neither the hydrosulfide nor the oxide (X = SH, $O_{1/2}$) could be prepared. The infrared, nuclear magnetic resonance, and Mössbauer spectra of these compounds have been correlated.

Introduction

Generally speaking, the effect of steric crowding about a reaction center has been explored in depth only in organocarbon chemistry.[2] In organotin chemistry there are relatively few examples of compounds and their reactions which have a sterically hindered tin atom as the focal point of the investigation.

Bähr and Gelius[3,4] prepared tetramesityltin and similar hindered tetraaryltin compounds. These showed considerably depressed reactivities with attacking electrophiles as did tetra-9-fluorenyltin and tetra-1-indenyltin, which were prepared by other investigators.[5] Seyferth[6] prepared tetra(trimethylsilylmethyl)tin and found that its tin–carbon bond cleavage reactions had to be carried out under severe conditions. Recently,[7] a synthetic study of the neopentyltin compounds was reported. It was observed that both the tendency toward tin–carbon bond formation as well as bond cleavage of these compounds was considerably depressed, relative to unhindered alkyl analogs. These authors noted the facile formation of bis(trineopentyltin) oxide and hexaneopentylditin. Bis-9-phenanthryltin has also been prepared and found not to undergo the normal disproportionation to the tetra-9-phenanthryltin and tin metal on heating and to be approximately dimeric in solution.[8] Krause and Weinberg prepared the stable di-*t*-butyl- and di-*t*-amyltin dihydroxides.[9] Here, steric crowding presumably prevented dehydration to the polydialkyltin oxides. Tri-2-tolyltin hydroxide was found to have an unusually high melting point (215°) without decomposition to the oxide and water.[10] Unexpectedly, the di-*t*-butyltin difluoride was found to be a fairly insoluble substance of high melting point (260° dec.),[11] quite comparable in its properties with the trialkyltin fluorides which seem to polymerize by Sn–F–Sn bridging.[12]

The purpose of this paper is to present the physical properties and some chemical reactions of a wide range of derivatives of a single severely hindered tin compound (tetraneophyltin) in order to be able to find what changes, relative to unhindered systems, occur. Inspection of Fisher–Hirschfelder[13] models of tetraneophyltin indicates that the tin atom is virtually enveloped in hydrocarbon. The phenyl groups protrude straight into space from the molecule. The underlying methyl and methylene groups seem to shield the tin atom

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(1) Neophyl = $C_6H_5C(CH_3)_2CH_2$–

(2) M. S. Newman, Ed., "Steric Effects in Organic Chemistry," John Wiley and Sons, New York, N. Y., 1956.

(3) G. Bähr and R. Gelius, *Ber.*, **91**, 812 (1958).

(4) G. Bähr and R. Gelius, *ibid.*, **91**, 818 (1958).

(5) H. Zimmer and H. W. Sparmann, *ibid.*, **87**, 645 (1954).

(6) D. Seyferth, *J. Am. Chem. Soc.*, **79**, 5881 (1957).

(7) H. Zimmer, I. Hechenbleikner, O. A. Homberg, and M. Danzik, *J. Org. Chem.*, **29**, 2632 (1964).

(8) G. Bähr and R. Gelius, *Ber.*, **91**, 829 (1958).

(9) E. Krause and K. Weinberg, *ibid.*, **63**, 381 (1930).

(10) A. Stern and E. I. Becker, *J. Org. Chem.*, **29**, 3220 (1964).

(11) E. Krause and K. Weinberg, *Ber.*, **63**, 383 (1930).

(12) H. C. Clark, R. J. O'Brien, and J. Trotter, *Proc. Chem. Soc.*, 85 (1963).

(13) These represent covalently bonded atoms which have approximately the van der Waal's radius.