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PENTAMETHYLCYCLOPENTADIENYL DERIVATIVES OF TRANSITION METALS

III*. SOME REACTIONS OF PENTAMETHYLCYCLOPENTADIENYLMETAL CARBONYL DERIVATIVES OF COBALT AND MANGANESE

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SUMMARY

Some reactions of $(CH_3)_5C_5Co(CO)_2$ and $(CH_3)_5C_5Mn(CO)_3$ are described. Reactions of $(CH_3)_5C_5Co(CO)_2$ with iodine and with 2-iodoheptafluoropropane give black $(CH_3)_5C_5Co(CO)I_2$ and black $(CH_3)_5C_5Co(CO)[CF(CF_3)_2]I$, respectively. Reaction of $(CH_3)_5C_5Co(CO)I_2$ with triphenylphosphine gives green $(CH_3)_5C_5CoI_2P(C_6H_5)_3$. Reaction of $(CH_3)_5C_5Co(CO)I_2$ with pentafluorophenyllithium gives low yields of yellow $(CH_3)_5C_5Co(CO)(C_6F_5)_2$ and green $(CH_3)_5C_5Co(CO)(C_6F_5)I$. Reaction of $(CH_3)_5C_5Co(CO)_2$ with diphenylacetylene gives the tetraphenylcyclobutadiene derivative $(CH_3)_5C_5CoC_4(C_6H_5)_4$. Reaction of $(CH_3)_5C_5Co(CO)_2$ with 1,7-cyclododecadiyne gives the tricyclic cyclobutadiene derivative $(CH_3)_5C_5CoC_{12}H_{16}$. Reaction of $(CH_3)_5C_5Co(CO)_2$ with dimethyl acetylenedicarboxylate gives red $(CH_3)_5C_5CoC_6(CO_2CH_3)_6$ and green $(CH_3)_5C_5Co[C_6(CO_2CH_3)_6]_2$. The manganese compounds $(CH_3)_5C_5Mn(CO)_2P(C_6H_5)_3$, $[(CH_3)_5C_5Mn(CO)_2NO][PF_6]$, and $[(CH_3)_5C_5Mn(CO)(NO)P(C_6H_5)_3][PF_6]$ have been prepared from $(CH_3)_5C_5Mn(CO)_3$ by methods completely analogous to the preparation of the corresponding unsubstituted cyclopentadienyl derivatives from $C_5H_5Mn(CO)_3$. Some spectroscopic properties of these new compounds are given.

INTRODUCTION

The reactions between acetylpentamethylcyclopentadiene and various metal carbonyls reported in the previous paper of this series[1] make several pentamethylcyclopentadienylmetal carbonyl derivatives readily available for the first time. Their availability allows a comparison of the chemistry of the pentamethylcyclopentadienylmetal carbonyls with that of the corresponding unsubstituted cyclopentadienylmetal carbonyls. This paper describes an exploratory study of some reactions of the penta-

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* For part II of this series see ref. 1.

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TABLE 1. SOME NEW PENTAMETHYLCYCLOPENTADIENYL DERIVATIVES OF COBALT AND MANGANESE PREPARED IN THIS WORK

Compound	*Color*	*M.p.*	*Analyses (%) Found (calcd.)*						*Infrared spectrum* $\nu(CO)(cm^{-1})$
			C	*H*	*O*	*Metal*	*Other*	*Mol. Wt.*	
(A) Cobalt compounds									
$Me_5C_5Co(CO)I_2$	black	175–177°	28.0 (27.8)	3.2 (3.1)	3.0 (3.4)	11.4 (12.4)	51.3 (I) (53.4)(I)	426 ($CHCl_3$) (476)	2060(s)
$Me_5C_5Co(CO)[CF(CF_3)_2]I$	black	dec > 160°	32.5 (32.5)	3.0 (2.9)	3.1 (3.1)	10.4 (11.4)	24.6 (I) (24.5)(I)	533 (CH_2Cl_2) (518)	2062 (s)
$[Me_5C_5Co(CO)C_3H_5][PF_6]$	yellow	dec > 200°	41.4 (41.2)	4.7 (4.9)	3.9 (3.9)	14.3 (14.5)	27.8 (F) (28.0)(F)		2065(s)
$Me_5C_5CoI_2P(C_6H_5)_3$	green	179–182°	46.4 (47.2)	4.2 (4.2)	— —	8.3 (8.0)	35.3 (I) (35.9)(I)		none
$Me_5C_5CoI_2P(C_6H_5)_3 \cdot CH_2Cl_2$	green		42.1 (43.7)	4.2 (4.0)		8.0 (7.4)	4.3 (P) (3.9)(P)		none
$Me_5C_5Co(CO)(C_6F_5)_2$	dark yellow	214–216°	49.5 (49.6)	3.2 (2.8)	2.9 (2.9)	10.0 (10.6)	34.1 (F) (34.2)(F)	544 (556)	2064(s)
$Me_5C_5Co(CO)(C_6F_5)I$	green	190–192°	40.4 (39.5)	3.2 (3.3)		11.0 (11.4)		540 (516)	2051(s)
$Me_5C_5CoC_4(C_6H_5)_4$	deep yellow	295–297°	82.6 (82.9)	6.6 (6.4)	0.0 (0.0)	10.6 (10.7)	— —		none
$Me_5C_5CoC_{12}H_{16}$	yellow	140–143°	74.8 (74.5)	8.2 (8.8)	0.0 (0.0)	16.9 (16.6)	— —		none
$Me_5C_5CoC_6(CO_2Me)_6$	red	217–219°	53.8 (54.2)	5.1 (5.3)	30.5 (31.0)	10.5 (9.5)	— —	527 (620)	1730(s)
$Me_5C_5Co[C_6(CO_2Me)_6]_2$	green	127–130°	52.2 (52.8)	5.1 (4.9)	36.5 (36.8)	5.0 (5.6)	— —		1743(s)
(B) Manganese compounds									
$Me_5C_5Mn(CO)_2P(C_6H_5)_3$	pale yellow	177–180° (dec.)	70.8 (71.0)	5.9 (5.9)	6.4 (6.3)		6.2 (P) (6.1)(P)		1915(s), 1855(s)
$[Me_5C_5Mn(CO)_2NO][PF_6]$	yellow	dec. > 190°	34.3 (34.3)	3.6 (3.6)	11.4 (11.4)	13.0 (13.1)	27.2 (F) (27.2)(F)		2104(s), 2062(s) ν(NO) 1825(s)
$[Me_5C_5Mn(CO)(NO)P(C_6H_5)_3][PF_6]$	yellow	192–193°	53.3 (53.2)	4.6 (4.6)	4.9 (4.9)	8.4 (8.4)	17.3 (F) (17.4)(F)		2021(s) ν(NO) 1774(s)

methylcyclopentadienylmetal carbonyls of cobalt and manganese. Future papers of this series will discuss the chemistry of pentamethylcyclopentadienylmetal carbonyls of chromium, molybdenum, tungsten, and iron.

EXPERIMENTAL

Microanalyses (Table 1) were carried out by Pascher Microanalytisches Laboratorium, Bonn, Germany; Meade Microanalytical Laboratory, Amherst, Massachusetts; and Mr. W. Swanson and co-workers of the microanalytical laboratory at the University of Georgia. Molecular weights (Table 1) were determined by a vapor pressure osmometer in the indicated solvents. The infrared spectra in the 2200–1500 cm^{-1} $\nu(CO)$ and $\nu(NO)$ region (Table 1) were taken in dichloromethane solutions and recorded on a Perkin–Elmer Model 621 spectrometer with grating optics. The NMR spectra (Table 2) were taken in the indicated solvents and recorded either on a Perkin–Elmer Hitachi R-20 spectrometer or a Varian HA-100 spectrometer. Melting points were obtained in capillaries and are uncorrected.

TABLE 2

NMR SPECTRA OF SOME PENTAMETHYLCYCLOPENTADIENYL DERIVATIVES OF COBALT AND MANGANESE

Compound	*NMR spectrum*: ^1H, τ(*ppm*) ^{19}F, ϕ(*ppm*)		
	Solvent	Me_5C_5	*Other*[a]
(A) Cobalt compounds			
$Me_5C_5Co(CO)_2$	CS_2	8.11	
$Me_5C_5Co(CO)I_2$	$CDCl_3$	7.84	
$Me_5C_5Co(CO)[CF(CF_3)_2]I$	$CDCl_3$	8.10	CF_3, 66.1 d (~10); CF, too weak for observation
$[Me_5C_5Co(CO)C_3H_5][PF_6]$	$(CD_3)_2CO$	8.02	CH_2, 6.49 d(6), 7.44 d(12); CH, 5.41 tt(6, 12)
$Me_5C_5CoI_2P(C_6H_5)_3$	$CDCl_3$	8.33	C_6H_5, ~2.2 to ~3.2 (very broad)
$Me_5C_5CoI_2P(C_6H_5)_3 \cdot CH_2Cl_2$	$CDCl_3$	8.34	C_6H_5, ~2.3(br), ~2.7, ~3.1 br; CH_2Cl_2, 4.91 s
$Me_5C_5CoC_4(C_6H_5)_4$	$CDCl_3$	8.59	C_6H_5, 2.99
$Me_5C_5CoC_{12}H_{16}$	$CDCl_3$	8.27	CH_2, ~8.3(br), ~8.6(br)
$Me_5C_5CoC_6(CO_2Me)_6$	$CDCl_3$	8.34	CH_3CO_2, 6.30 s
(B) Manganese compounds			
$Me_5C_5Mn(CO)_3$	$CDCl_3$	8.14	
$Me_5C_5Mn(CO)_2P(C_6H_5)_3$	$CDCl_3$	8.45	C_6H_5, 2.75(br)
$[Me_5C_5Mn(CO)_2NO][PF_6]$	CD_3CN	8.01	
$[Me_5C_5Mn(CO)(NO)P(C_6H_5)_3][PF_6]$	CD_3CN	8.34	C_6H_5, 2.54

(a) s=singlet, d=doublet, t=triplet, tt=triplet of triplets, (br)=broad. Coupling constants in Hz given in parentheses.

A nitrogen atmosphere was routinely provided for the following operations: (a) carrying out reactions with metal carbonyl derivatives; (b) handling filtered solutions of organometallic compounds; (c) filling evacuated vessels containing organometallic compounds.

The pentamethylcyclopentadienylmetal carbonyls $(CH_3)_5C_5Co(CO)_2$ and $(CH_3)_5C_5Mn(CO)_3$ were prepared by the methods discussed in the previous paper of this series[1] using the sources indicated there for the commercially purchased raw materials. The other reagents were purchased from the usual commercial sources. The reported reactions involving unsubstituted cyclopentadienyl derivatives analogous to the reactions involving pentamethylcyclopentadienyl derivatives discussed below are cited after the titles.

Preparation of $(CH_3)_5C_5Co(CO)I_2$[2]

A solution of 0.4 g (1.6 mmoles) of $(CH_3)_5C_5Co(CO)_2$ in 100 ml of degassed diethyl ether was treated with a solution of 0.4 g (1.57 mmoles as I_2) of iodine dissolved in 150 ml of diethyl ether. After stirring for 7 h at room temperature the precipitate was filtered, washed with diethyl ether and petroleum ether, and dried to give 0.70 g (93% yield) of black $(CH_3)_5C_5Co(CO)I_2$, m.p. 175–177°.

The reaction between $(CH_3)_5C_5Co(CO)_2$ and iodine was also carried out in benzene and in dichloromethane. In these two cases, the $(CH_3)_5C_5Co(CO)I_2$ reaction product remained in solution and was isolated by removal of the solvent at 25°/35 mm followed by crystallization of the residue from mixtures of dichloromethane and hexane.

Preparation of $(CH_3)_5C_5Co(CO)[CF(CF_3)_2]I$[3,4]

A mixture of 0.5 g (2.0 mmoles) of $(CH_3)_5C_5Co(CO)_2$, 1.0 ml (2.6 g, 8.8 mmoles) of 2-iodoheptafluoropropane, and 20 ml of benzene was kept at 25° for 90 h. Solvent was then removed at 25°/35 mm. Product was isolated by sublimation at 80–95°/0.05 mm and purified by recrystallizing several times from mixtures of dichloromethane and hexane to give 0.73 g (71% yield) of red-black $(CH_3)_5C_5Co(CO)[CF(CF_3)_2]I$.

Reaction of $(CH_3)_5C_5Co(CO)_2$ *with allyl iodide*[5,6]

A mixture of 0.60 g (2.4 mmoles) of $(CH_3)_5C_5Co(CO)_2$, 0.7 ml (1.3 g, 7.7 mmoles) of allyl iodide, and 10 ml of redistilled tetrahydrofuran was kept at 25° for 72 h. Solvent was removed at 25°/35 mm. The residue was extracted with two 30 ml portions of pentane. A small amount of unidentified brown-red solid ($\sim$10 mg) was isolated from these pentane extracts by concentration and cooling.

The solid left from the pentane extraction was extracted with two 40 ml portions of water. The resulting orange aqueous solution was treated with 1.0 g of solid ammonium hexafluorophosphate. The yellow precipitate was removed by filtration. It was dissolved in dichloromethane. The dichloromethane solution was dried over anhydrous magnesium sulfate. Product was precipitated from the filtered dichloromethane solution by adding excess hexane to give 0.21 g (21% yield) of yellow $[(CH_3)_5C_5Co(CO)C_3H_5][PF_6]$.

The black residue left after the extractions with pentane and water was dissolved in 60 ml of dichloromethane and this solution treated with 100 ml of hexane. This solution was dried over anhydrous magnesium sulfate. After filtering off the drying agent, the filtrate was concentrated at 25°/35 mm to give 0.27 g (24% yield) of black $(CH_3)_5C_5Co(CO)I_2$ identified by its infrared spectrum, proton NMR spectrum, and elemental analyses (*Anal.*: Found: C, 30.0; H, 2.9; O, 3.7; I, 55.7. Calculated values see Table 1).

Reaction of $(CH_3)_5C_5Co(CO)I_2$ with triphenylphosphine[2]

A mixture of 0.4 g (0.84 mmoles) of $(CH_3)_5C_5Co(CO)I_2$, 0.23 g (0.91 mmoles) of triphenylphosphine, and 75 ml of tetrahydrofuran was boiled under reflux for 10 h. Solvent was removed from the reaction mixture at 25°/35 mm. The residue was crystallized from a mixture of acetone and hexane and then washed with 200 ml of hexane and dried to give 0.28 g (47% yield) of dark green $(CH_3)_5C_5CoI_2P(C_6H_5)_3$.

The dichloromethane adduct listed in Table 1 was obtained if the reaction between $(CH_3)_5C_5Co(CO)I_2$ and triphenylphosphine was carried out in dichloromethane rather than tetrahydrofuran. A mixture of 0.31 g (0.65 mmoles) of $(CH_3)_5C_5Co(CO)I_2$, 0.183 g (0.70 mmoles) of triphenylphosphine, and 30 ml of dichloromethane was stirred at 25° for 48 h. Solvent was removed at 25°/30 mm and the green residue crystallized several times from mixtures of dichloromethane and hexane to give 0.35 g (68% yield) of deep green $(CH_3)_5C_5CoI_2P(C_6H_5)_3 \cdot CH_2Cl_2$.

Reaction of $(CH_3)_5C_5Co(CO)I_2$ with pentafluorophenyllithium

A solution of 0.50 g (3.0 mmoles) of pentafluorobenzene in 75 ml of diethyl ether was cooled to −78° and treated at that temperature with 1.5 ml (~2.2 mmoles) of n-butyllithium (commercial hexane solution). After 1.5 h at −78° this pentafluorophenyllithium solution was treated dropwise at −78° with a solution of 0.5 g (1.05 mmoles) of $(CH_3)_5C_5Co(CO)I_2$ in 100 ml of diethyl ether. The reaction mixture was stirred for 30 minutes at −78° and then allowed to warm to room temperature. Solvent was then removed from the reaction mixture at 25°/35 mm. The residue was extracted with 50 ml of hot hexane in two portions and the concentrated hexane solution chromatographed on a 3 × 50 cm Florisil column. The first band (yellow) was eluted with hexane but evaporation of this eluate gave a negligible amount of material which was not investigated further. The second band (orange) was eluted with a 1/1 mixture of hexane and dichloromethane. Evaporation of this eluate and crystallization of the residue from a mixture of dichloromethane and hexane by cooling a concentrated solution to −78° gave 0.03 g (5.1% yield) of dark yellow $(CH_3)_5C_5Co(CO)(C_6F_5)_2$, m.p. 214–216°. The third and major band (yellow-green) was also eluted with a 1/1 mixture of dichloromethane and hexane. Evaporation of this eluate and low-temperature crystallization of the residue from a mixture of dichloromethane and hexane gave 0.05 g (9.2% yield) of green $(CH_3)_5C_5Co(CO)(C_6F_5)I$, m.p. 190–192°.

Preparation of $(CH_3)_5C_5CoC_4(C_6H_5)_4$[7]

A. Thermal reaction. A mixture of 0.75 g (3.0 mmoles) of $(CH_3)_5C_5Co(CO)_2$, 0.80 g (4.5 mmoles) of diphenylacetylene, and 50 ml of xylene was boiled under reflux for 22 h. Solvent was removed at 30–40°/1 mm. A solution of the residue in a 1/4 mixture of dichloromethane and hexane was chromatographed on a 2 × 60 cm Florisil column. The yellow band was eluted with a 1/3 to 1/2 mixture of dichloromethane and hexane. Evaporation of the eluate at 25°/35 mm followed by several recrystallizations from mixtures of dichloromethane and hexane gave 0.355 g (29% yield) of deep yellow $(CH_3)_5C_5CoC_4(C_6H_5)_4$, m.p. 295–297°.

B. Photochemical reaction. A mixture of 0.50 g (2.0 mmoles) of $(CH_3)_5C_5Co(CO)_2$, 0.60 g (3.37 mmoles) of diphenylacetylene, and ~100 ml of hexane was exposed for 36 h to the ultraviolet irradiation from an H444GS mercury spotlamp placed 11 cm from the Pyrex reaction vessel (the heat from the lamp caused the hexane solvent to boil). After the reaction period was over, the solvent was removed at 25°/35 mm. Chromatography and crystallization as described in procedure *A* above gave a 30% yield of $(CH_3)_5C_5CoC_4(C_6H_5)_4$ identical to the material prepared by the thermal procedure described above.

Reaction of $(CH_3)_5C_5Co(CO)_2$ with 1,7-cyclododecadiyne[8]

A mixture of 0.5 g (2.0 mmoles) of $(CH_3)_5C_5Co(CO)_2$, 0.35 g (2.2 mmoles) of 1,7-cyclododecadiyne (from Farchan Laboratories, Willoughby, Ohio), and 35 ml of n-octane was boiled under reflux for 22 h. Solvent was removed at 50°/35 mm. The residue was extracted with three 10 ml portions of hexane. The combined hexane extracts were chromatographed on a 2 × 40 cm Florisil column. The yellow band was eluted with hexane. Evaporation of the eluate from this band gave crude $(CH_3)_5C_5CoC_{12}H_{16}$ which was purified further by a second similar chromatography and sublimation at 90°/0.01 mm to give 0.24 g (34% yield) of pale yellow $(CH_3)_5C_5CoC_{12}H_{16}$.

Reaction of $(CH_3)_5C_5Co(CO)_2$ with dimethyl acetylenedicarboxylate

A mixture of 0.5 g (2.0 mmoles) of $(CH_3)_5C_5Co(CO)_2$, 1.0 ml (1.16 g, 8.16 mmoles) of dimethyl acetylenedicarboxylate, and 200 ml of redistilled tetrahydrofuran was exposed for 25 h to the irradiation from an H444GS mercury spotlamp placed 10 cm from the Pyrex flask containing the reaction mixture. After the reaction period was over, solvent was removed from the reaction mixture at 25°/35 mm. An extract of the residue in a 1/3 mixture of dichloromethane and petroleum ether was chromatographed on a 1.5 × 60 cm Florisil column. After washing the column with a mixture of dichloromethane and hexane the dark band was eluted with acetone. Evaporation of the acetone eluate at 25°/35 mm followed by crystallization from a mixture of dichloromethane and hexane gave 0.059 g (4.3% yield) of green $(CH_3)_5C_5Co[C_6(CO_2CH_3)_6]_2$, m.p. 127–130°. After removing this product from the chromatography column, the next band (orange) was eluted with methanol. Evaporation of the methanol eluate at 25°/35 mm followed by crystallization of the residue from a mixture of dichloromethane and hexane gave 0.17 g (14% yield) of red $(CH_3)_5C_5CoC_6(CO_2CH_3)_6$, m.p. 218–219°.

Reactions of $(CH_3)_5C_5Co(CO)_2$ which did not yield definite products

1. Reaction of 0.5 g (2.0 mmoles) of $(CH_3)_5C_5Co(CO)_2$ with 0.5 g (2.87 mmoles) of 1,7-cyclotridecadiyne in boiling 2,2,5-trimethylhexane for 19 h resulted only in recovery of unchanged $(CH_3)_5C_5Co(CO)_2$.
2. Reactions of $(CH_3)_5C_5Co(CO)_2$ with the Lewis base ligands $(C_6H_5)_3P$, $(CH_3O)_3P$, and C_6H_5CN in boiling methylcyclohexane gave yellow to green very air-sensitive products which could not be purified and characterized.

Preparation of $(CH_3)_5C_5Mn(CO)_2P(C_6H_5)_3$[9]

A mixture of 0.2 g (0.76 mmoles) of $(CH_3)_5C_5Mn(CO)_3$ and 0.50 g (1.91 mmoles) of triphenylphosphine in 50 ml of cyclohexane was exposed to ultraviolet irradiation for 80 min. Solvent was then removed at 25°/35 mm. A concentrated solution of the residue in a 1/10 mixture of dichloromethane and hexane was chromatographed on a 2 × 30 cm Florisil column prepared in hexane. The yellow band was eluted with a mixture of dichloromethane and hexane. Evaporation of the eluate at 25°/35 mm left a yellow residue which was dried at 25°/0.01 mm for 24 h to remove any unreacted $(CH_3)_5C_5Mn(CO)_3$. Crystallization of this residue from a mixture of dichloromethane and hexane followed by careful washing with pentane gave 0.18 g (48% yield) of pale yellow $(CH_3)_5C_5Mn(CO)_2P(C_6H_5)_3$, m.p. 177–180° (dec.).

Preparation of $[(CH_3)_5C_5Mn(CO)_2NO][PF_6]$[10]

A solution of 0.4 g (1.45 mmoles) of $(CH_3)_5C_5Mn(CO)_3$ in 10 ml of freshly distilled acetonitrile was treated dropwise with a solution of 0.255 g (1.45 mmoles) of nitrosonium hexafluorophosphate ($[NO][PF_6]$; purchased from Ozark-Mahoning, Tulsa, Oklahoma) in 5 ml of dry acetonitrile during 5 min. After stirring an additional 30 min at room temperature, the acetonitrile was removed at 25°/35 mm. Crystallization of the residue several times from mixtures of dichloromethane with benzene or toluene gave 0.56 g (92% yield) of yellow $[(CH_3)_5C_5Mn(CO)_2NO][PF_6]$.

Reaction of $(CH_3)_5C_5Mn(CO)_3$ with $[NO][SbF_6]$ in dichloromethane solution by a similar procedure gave the yellow hexafluoroantimonate $[(CH_3)_5C_5Mn(CO)_2NO][SbF_6]$ which was not analysed but instead converted to the hexafluorophosphate salt by metathesis with ammonium hexafluorophosphate in acetone solution.

Preparation of $[(CH_3)_5C_5Mn(CO)(NO)P(C_6H_5)_3][PF_6]$[11]

A mixture of 0.25 g (0.49 mmoles) of $[(CH_3)_5C_5Mn(CO)_2NO][PF_6]$, 0.20 g (0.76 mmoles) of triphenylphosphine, and 20 ml of methanol was boiled under reflux for 90 min. Solvent was removed from the reaction mixture at 40°/35 mm. The residue was washed with benzene to remove any unreacted triphenylphosphine. Crystallization several times from mixtures of dichloromethane and toluene gave 0.26 g. (81% yield) of $[(CH_3)_5C_5Mn(CO)(NO)P(C_6H_5)_3][PF_6]$.

Infrared Spectra

The infrared spectra of dichloromethane solutions in the $\nu(CO)$ and $\nu(NO)$ regions are given in Table 1. The infrared spectra of the new compounds were also taken in potassium bromide pellets. The frequencies observed in some of these spectra in the 1650 to 700 cm^{-1} region are listed below.

A. $(CH_3)_5C_5Co(CO)I_2$. Bands at 1485 w, 1469 w, 1454 w, 1427 w, 1400 vw, 1376 w, 1371 m, 1355 w, 1158 w, 1072 vw, and 1006 m cm^{-1}.

B. $(CH_3)_5C_5Co(CO)[CF(CF_3)_2]I$. $\nu(CF)$ frequencies at 1286 m, 1253 s, 1241 s(sh), 1202 m, and 1173 s cm^{-1}; other bands at 1473 w(br), 1430 vw, 1381 w, 1113 w, 1003 m, 925 m, 876 w, 866 m, 737 m, and 703 m cm^{-1}.

C. $[(CH_3)_5C_5Co(CO)C_3H_5][PF_6]$. $\nu(PF)$ frequency at 837 s cm^{-1}; other bands at 1502 vw, 1482 vw, 1463 vw, 1434 vw, 1397 w, 1384 w, 1080 vw, 1030 w, 1014 vw, and 1003 vw cm^{-1}.

D. $(CH_3)_5C_5Co(CO)(C_6F_5)_2$. Bands at 1629 m, 1608 w, 1501 s, 1440 vs, 1389 w, 1384 w, 1380 m, 1367 w, 1348 w, 1340 w, 1262 w, 1158 vw, 1115 w, 1061 s, 1055 s, 1021 m, 960 s, 954 s, 771 m, 755 m, and 739 w cm^{-1}.

E. $(CH_3)_5C_5Co(CO)(C_6F_5)I$. Bands at 1628 w, 1607 w, 1507 s, 1476 w, 1451 s, 1433 s, 1379 m, 1366 w(sh), 1344 w, 1266 w, 1161 w, 1115 w, 1061 s, 1022 m, 959 s, 771 m, and 740 w cm^{-1}.

F. $(CH_3)_5C_5CoC_4(C_6H_5)_4$. Bands at 1595 m, 1495 m, 1445 w, 1398 w, 1381 w, 1066 w, 1026 w, 910 w, 778 w, 745 m, and 699 s cm^{-1}.

G. $(CH_3)_5C_5CoC_{12}H_{16}$. Bands at 1475 w, 1434 s, 1400 w, 1377 m, 1370 m, 1332 w, 1314 m, 1281 w, 1221 m, 1085 w, 1067 vw, 1044 vw, 1025 m, 927 vw, 802 w, and 760 w cm^{-1}.

H. $(CH_3)_5C_5CoC_6(CO_2CH_3)_6$. Bands at 1615 s, 1460 m, 1452 m, 1440 m, 1391 w, 1384 m, 1377 w, 1344 w, 1260 s, 1230 m, 1215 s, 1154 w, 1115 w, 1010 m, 981 w, 955 vw, 923 vw, 867 vw, 832 w, 787 w, 779 vw, 759 vw, 730 w, and 701 w cm^{-1}.

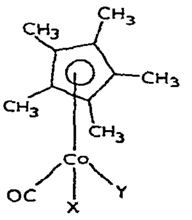
I. $(CH_3)_5C_5Co[C_6(CO_2CH_3)_6]_2$. Bands at 1625 w, 1443 s, 1410 w, 1360 w, 1326 w, 1230 vs(br), 1168 (sh), 1098 vw, 1065 vw, 1017 w, 987 m, 956 vw(sh), 905 w, 853 m, 828 vw, 800 vw, 796 w, 783 vw, and 755 w cm^{-1}.

Mass spectrum of $(CH_3)_5C_5CoC_{12}H_{16}$

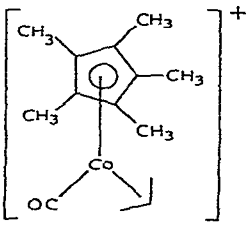
The mass spectrum of $(CH_3)_5C_5CoC_{12}H_{16}$ was measured at 70 eV on a Perkin–Elmer Hitachi RMU-6 mass spectrometer with a 210° chamber temperature and a 135° sample temperature. The following ions containing cobalt and with an intensity of at least 10% that of the parent molecular ion were observed with the relative intensities being given in parentheses: $C_{10}H_{15}CoC_{12}H_{16}^+$ (*i.e.* $C_{22}H_{31}Co^+$; 100), $C_{22}H_{29}Co^+$ (25), $C_{22}H_{25}Co^+$ (25), $C_{17}H_{16}Co^+$ (15), $C_{12}H_{10}Co^+$ (12), $C_{10}H_{15}Co^+$ (24), $C_{10}H_{13}Co^+$ (30), and Co^+ (10). A strong metastable ion observed at *m/e* 344 corresponds to the reaction $C_{22}H_{29}Co^+ \rightarrow C_{22}H_{25}Co^+ + 2H_2$.

DISCUSSION

The reactions of $(CH_3)_5C_5Co(CO)_2$ with iodine to give $(CH_3)_5C_5Co(CO)I_2$ (I: X=Y=I) and with a representative perfluoroalkyl iodide $(CF_3)_2CFI$ to give the corresponding $(CH_3)_5C_5Co(CO)R_fI$ derivative (I: X=I, Y=R_f; R_f=$CF(CF_3)_2$ in this case) are completely analogous to previously reported reactions of $C_5H_5Co(CO)_2$ already cited in the Experimental Section. The major product from the reaction of $(CH_3)_5C_5Co(CO)_2$ with allyl iodide is the cation $[(CH_3)_5C_5Co(CO)C_3H_5]^+$ (II) analogous to the cation $[C_5H_5Co(CO)C_3H_5]^+$ obtained as the major product from the corresponding reaction of $C_5H_5Co(CO)_2$ with allyl iodide[5]. However, the reaction of $(CH_3)_5C_5Co(CO)_2$ with allyl iodide also gave appreciable quantities of the diiodide $(CH_3)_5C_5Co(CO)I_2$ (I: X=Y=I) by the allyl iodide acting as an iodinating agent. This resembles the recently observed[12] iodination of $(CH_3)_5C_5Ir(CO)_2$ with allyl iodide to give $(CH_3)_5C_5Ir(CO)I_2$.



(I)

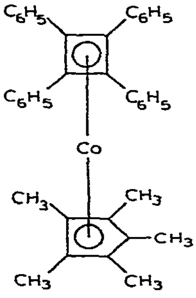


(II)

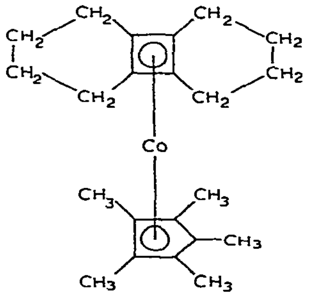
Some reactions of $(CH_3)_5C_5Co(CO)I_2$ were investigated. Reaction of $(CH_3)_5$-$C_5Co(CO)I_2$ with triphenylphosphine resulted in displacement of the carbonyl group to give the triphenylphosphine derivative $(CH_3)_5C_5CoI_2P(C_6H_5)_3$ analogous to the corresponding reaction with $C_5H_5Co(CO)I_2$[2]. However, in the preparation of $(CH_3)_5C_5CoI_2P(C_6H_5)_3$ dichloromethane had to be avoided as a solvent because of the formation of a stable 1/1 solvate identified not only by elemental analyses but also by the CH_2Cl_2 resonance in its proton NMR spectrum.

The triphenylphosphine derivative $C_5H_5CoI_2P(C_6H_5)_3$ has been reported to react with certain alkyls of magnesium or lithium to give compounds of the types $C_5H_5Co(R)IP(C_6H_5)_3$ and $C_5H_5CoR_2P(C_6H_5)_3$[2,13]. However, no stable products of the types $C_5H_5Co(CO)R_2$ or $C_5H_5Co(CO)RI$ have ever been prepared by reactions of $C_5H_5Co(CO)I_2$ with metal alkyls or aryls although a few compounds of these types, particularly those with perfluoroalkyl groups, have been prepared by other methods[3,4,14]. The reaction of the pentamethylcyclopentadienyl derivative $(CH_3)_5C_5$-$Co(CO)I_2$ with pentafluorophenyllithium has now been found to give low yields of both green $(CH_3)_5C_5Co(CO)(C_6F_5)I$ (I: $X=I$, $Y=C_6F_5$) and yellow $(CH_3)_5C_5Co$-$(CO)(C_6F_5)_2$ (I: $X=Y=C_6F_5$) which could be readily separated by column chromatography. The infrared spectra of these compounds exhibited the expected single $\nu(CO)$ frequency and the expected infrared frequencies from pentafluorophenyl groups[15].

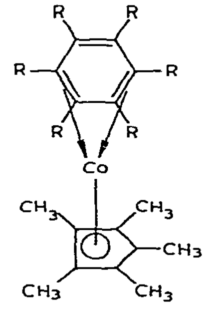
The reactions of $(CH_3)_5C_5Co(CO)_2$ with diphenylacetylene to give the tetraphenylcyclobutadiene derivative $(CH_3)_5C_5CoC_4(C_6H_5)_4$ (III) and with 1,7-cyclododecadiyne to give the tricyclic cyclobutadiene derivative $(CH_3)_5C_5CoC_{12}H_{16}$ (IV) are again completely analogous to previously reported reactions of $C_5H_5Co(CO)_2$ already cited in the Experimental Section. The reaction of $(CH_3)_5C_5Co(CO)_2$ with dimethyl acetylenedicarboxylate gave the red substituted benzene derivative $(CH_3)_5$-$C_5CoC_6(CO_2CH_3)_6$ (V: $M=Co$, $R=CO_2CH_3$) as the major organocobalt product. No precedent for this reaction has yet been observed in the chemistry of $C_5H_5Co(CO)_2$. However, the rhodium and iridium analogues $(CH_3)_5C_5MC_6(CO_2CH_3)_6$ (V: $M=Rh$ and Ir; $R=CO_2CH_3$) have been reported[16]. The rhodium compound $(CH_3)_5C_5$-$RhC_6(CO_2CH_3)_6$ (V: $M=Rh$; $R=CO_2CH_3$) was shown by NMR to have the limiting structure at room temperature but to have fluxional[17] properties at 155° whereas the iridium compound $(CH_3)_5C_5IrC_6(CO_2CH_3)_6$ (V: $M=Ir$; $R=CO_2CH_3$) failed to exhibit any fluxional properties even at 167°. The cobalt compound $(CH_3)_5$-$C_5CoC_6(CO_2CH_3)_6$ prepared in this work (V: $M=Co$; $R=CO_2CH_3$) exhibited only a single sharp resonance from all 18 protons of the six carbomethoxy groups at ~30°.



(III)



(IV)



(V)

Furthermore, cooling to $-50°$ failed to broaden this carbomethoxy resonance indicating that even at fairly low temperatures a fluxional process making the carbomethoxy protons equivalent takes place in $(CH_3)_5C_5CoC_6(CO_2CH_3)_6$ (V: M=Co; R=CO_2CH_3). These NMR data on the cobalt complex $(CH_3)_5C_5CoC_6(CO_2CH_3)_6$ (V: M=Co; R=CO_2CH_3) combined with the previously reported[16] data on the rhodium and iridium analogues indicate that the rearrangement processes become slower in going down the column of the periodic table from cobalt through rhodium to iridium. This is in accord with previously observed trends on other types of fluxional organometallic molecules such as the cyclooctatetraene complexes $C_8H_8M(CO)_3$ (M=Fe, Ru, and Os)[17,18].

The reaction between $(CH_3)_5C_5Co(CO)_2$ and dimethyl acetylenedicarboxylate besides giving the red $(CH_3)_5C_5CoC_6(CO_2CH_3)_6$ (V: M=Co, R=CO_2CH_3) discussed above also gave a green product of stoichiometry $(CH_3)_5C_5Co[C_6(CO_2CH_3)_6]_2$ in rather low yield. Speculation on the nature of this second product seems premature until crystal structure data become available. Furthermore, the relatively small quantities of this complex currently available have precluded a study of reactions which might clarify its structure.

The successful preparation of $C_5H_5Co(CO)P(C_6H_5)_3$ from $C_5H_5Co(CO)_2$ and triphenylphosphine[2] made of interest the reactions of $(CH_3)_5C_5Co(CO)_2$ with triphenylphosphine and similar Lewis base ligands. However, in our hands such reactions when carried out in boiling methylcyclohexane gave yellow to green products too air-sensitive for proper characterization. Presumably, the electron releasing tendencies of the five methyl substituents in the pentamethylcyclopentadienyl ring load the cobalt atom in $(CH_3)_5C_5CoL_2$ and $(CH_3)_5C_5Co(CO)L$ with so much negative charge that it is extremely sensitive to oxidation.

During the course of this work some reactions of the manganese compound $(CH_3)_5C_5Mn(CO)_3$ were investigated. These reactions resulted in the preparation and characterization of the new pentamethylcyclopentadienylmanganese compounds $(CH_3)_5C_5Mn(CO)_2P(C_6H_5)_3$, $[(CH_3)_5C_5Mn(CO)_2NO][PF_6]$, and $[(CH_3)_5C_5Mn(CO)(NO)P(C_6H_5)_3][PF_6]$ by reactions completely analogous to those suitable for the preparation of the corresponding unsubstituted cyclopentadienylmanganese carbonyl derivatives. Our efforts to explore the chemistry of pentamethylcyclopentadienylmanganese carbonyl derivatives have been limited by the availability of the $(CH_3)_5C_5Mn(CO)_3$ starting material in only 12% yield from the reaction of $Mn_2(CO)_{10}$ with acetylpentamethylcyclopentadiene[1].

The proton NMR spectra (Table 2) of the new pentamethylcyclopentadienylmetal derivatives of cobalt and manganese all exhibited the sharp singlet resonances from the 15 equivalent protons of the pentamethylcyclopentadienyl rings. Alternative structures for any of the new compounds with diene-bonded pentamethylcyclopentadiene ligands are thereby excluded. The directions of the chemical shift changes of these pentamethylcyclopentadienyl protons with changes of the structure of the complexes in accord with observations made even in the earliest work[19] with pentamethylcyclopentadienylmetal carbonyl derivatives.

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