Cyclopentadienylcobalt Complexes **Containing** Two Phosphine Ligands

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Abstract—The ionic complexes $[C_5H_5Co(L)(Ph_2PMe)I]^+$ $[I]^-$ (L = Ph₃P and Ph₂PMe) were prepared by the reactions of cyclopentadienyl(triphenylphosphine)cobalt and cyclopentadienyl(methyldiphenylphosphine)-cobalt diiodides with methyldiphenylphosphine. The treatment of these complexes with sodium tetraphenylborate results in the formation of $[C_5H_5Co(L)(Ph_2PMe)I]^+[BPh_4]^-$ compounds.

Earlier we showed that treatment of cyclopentadienyl(tetraphenylbutadiene)cobalt with iodine in the presence of equimolar amounts of monodentate electron-donor ligands results in cleavage of the four-electron-donor butadiene ligand to form cyclopentadienylcobalt diiodide $C_5H_5Co(L)I_2$ complexes (L = Ph₃P [1], Me₂S, C₅H₅N [2]) in high yields. Treatment of equimolar mixtures of cyclopentadienyl(tetraphenylbutadiene)cobalt with 2,2'-dipyridyl or 1,10-phenanthroline with excess iodine gives ionic compounds $[C_5H_5Co(L_2)I]^+[I_3]^-$ (L₂ = Dipy, Phen [2]). This latter result led us to suggest that using excess monodentate ligands would allow us to obtain ionic complexes of cyclopentadienylcobalt with two monodentate ligands. To confirm this suggestion, we have studied the action of diphenylmethylphosphine on cyclopentadienvl(triphenylphosphine)cobalt and cyclopentadienyl-(methyldiphenylphosphinecobalt) diiodides. The latter compound we obtained for the first time.

The diphenylmethylphosphine complex of cyclopentadienylcobalt diiodide was prepared both by the reaction of iodine with an equimolar mixture of cyclopentadienyl(tetraphenylbutadiene)cobalt with diphenylmethylphosphine and by the reaction of diphenylmethylphosphine with cyclopentadienylcobalt diiodide.



The ¹H NMR spectrum of compound **I** in $(CD_3)_2CO$ contains a singlet of cyclopentadienyl protons at δ 5.25 ppm (5H). Methyl protons appear as a doublet at δ 2.53 ppm (3H, *J* 11.1 Hz). Phenyl protons give two multiplets at δ 7.5–7.7 (6H) and 7.9–8.2 ppm (4H).

The mass spectrum of the compound contains a molecular ion peak. The principal fragment ions and their relative intensities are shown in Table 1.

We found that the reactions of cyclopentadienyl-(triphenylphosphine)cobalt and cyclopentadienyl-(methyldiphenylphosphine)cobalt with diphenylmethylphosphine give rise to compounds containing two phosphine ligands bound to a cobalt atom.

Treatment of solutions of compounds II and III in methylene chloride with sodium tetraphenylborate resulted in replacement of the I^- anion by a tetraphenylborate group.



 Table 1. Mass spectrum of cyclopentadienyl(methyldiphenylphosphine)cobalt diiodide (I)

Ion	m/z	I, %	Ion	m/z	I, %
$\overline{C_{18}H_{18}CoI_2P^+}$	578	2	$C_{13}H_{13}P^+$	200	100
$C_{18}H_{18}CoIP^+$	451	20	$C_{12}H_{15}P^+$	185	89
C ₅ H ₅ CoI ⁺ ₂	378	3	C ₅ H ₅ Co ⁺	124	9
$C_{18}H_{18}CoP^+$	324	5	$C_6H_5P^+$	108	41
$C_{13}H_{13}CoP^+$	259	10	$C_6H_5^+$	77	82
C ₅ H ₅ CoI ⁺	251	97	$C_5H_5^+$	65	74

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 $L = Ph_3P$ (II), Ph_2PMe (III).

Compounds II-V are colored solid substances soluble in polar organic solvents. The structure of the compounds was proved by the ¹H NMR and IR spectra (Table 2) and by the elemental analyses.



$$L = Ph_3P$$
 (IV), Ph_2PMe (V).

EXPERIMENTAL

The IR spectra were recorded in KBr pellets on a Protege-460 spectrophotometer. The ¹H NMR spectra were recorded on a Tesla BS-567A spectrometer for solutions in $(CD_3)_2CO$ against TMS. The mass spectrum of cyclopentadienyl(methyldiphenylmethylphosphine)cobalt diiodide was obtained on an MX-1320 instrument, ionizing energy 35 eV. The starting cyclopentadienyl(tetraphenylbutadiene)cobalt and cyclopentadienyl(triphenylphosphine)cobalt diiodides were synthesized by published procedures [1].

All operations were carried out under argon using anhydrous organic solvents.

Table 2. ¹H NMR spectra (δ , ppm) of compounds II–V

Comp. no.	C ₅ H ₅	C ₆ H ₅	CH ₃
II III	5.23 s (5H) 5.78 s (5H)	7.4–8.2 m (25H) 7.3–8.1 m (20H)	2.50 d (3H) 1.8 d (3H), 1.9 d (3H)
IV	5.21 s (5H)	6.7–7.1 m (12H) 7.3–8.0 m (33H)	2.50 d (3H)
V	5.67 s (5H)	6.7–7.05 m (12H) 7.25–7.9 m (28H)	1.8 d (3H), 1.9 d (3H)

Cyclopentadienyl(methyldiphenylphosphine)cobalt diiodide (I). *a*. A solution of 0.127 g of iodine in 25 ml of benzene was added to a solution of 0.24 g of cyclopentadienyl(tetraphenylbutadiene)cobalt and 0.1 g of methyldiphenylphosphine in 50 ml of benzene. The reaction mixture was stirred for 2 h and filtered. The resulting solution was reduced to 10 ml in a vacuum and treated with 75 ml of hexane. A precipitate formed and was separated, washed with hexane, and dried in a vacuum. Reprecipitation from benzene gave 0.24 g (83%) of compound **I**, mp 153– 155°C. Found, %: C 37.56; H 3.30; I 43.72. $C_{18}H_{18}$. Col₂P. Calculated, %: C 37.40; H 3.14; I 43.91.

b. To a suspension of 0.378 g of cyclopentadienylcobalt diiodide in 75 ml of benzene, 0.2 g of diphenylmethylphosphine was added. The reaction mixture was stirred for 8 h and filtered. The reaction product was isolated and purified as in procedure *a*. We obtained 0.44 g (76%) of compound **I**, mp 154–155°C.

Bis(methyldiphenylphosphine)cyclopentadienyliodocobalt iodide (III). To a solution of 0.289 g of cyclopentadienyl(methyldiphenylphosphine)cobalt diiodide in 50 ml of methylene chloride, 0.1 g of methyldiphenylphosphine was added. The reaction mixture was stirred for 10 h and filtered. The resulting solution was treated with 40 ml of hexane and reduced to 50 ml in a vacuum. A precipitate formed and was separated, sequentially washed with ether and pentane, and dried in a vacuum. Reprecipitation from methylene chloride gave 0.31 g (80%) of compound **III**, mp 98–100°C. Found, %: C 48.01; H 4.28; I 32.40. $C_{31}H_{31}CoI_2P_2$. Calculated, %: C 47.84; H 4.01; I 32.61.

Similarly, from 0.32 g of cyclopentadienyl(triphenylphosphine)cobalt diiodide and 0.1 g of methyldiphenylphosphine we obtained 0.32 g (76%) of compound **II**, mp 47–49°C. Found, %: C 51.68; H 4.22; I 29.96. $C_{36}H_{33}CoI_2P_2$. Calculated, %: C 51.45; H 3.96; I 30.20.

Bis(methyldiphenylphosphine)cyclopentadienyliodocobalt tetraphenylborate (V). To a solution of 0.389 g of compound **III** in 75 ml of methylene chloride, 0.171 g of sodium tetraphenylborate was added. The reaction mixture was stirred for 12 h and filtered. The resulting solution was concentrated in a vacuum until crystallization began and treated with hexane. The precipitate was separated, washed with ether and pentane, and dried in a vacuum. Reprecipitation from benzene gave 0.39 g (80%) of compound V, mp 109–111°C. Found, %: C 68.31; H 5.52; I 12.84. $C_{55}H_{51}$ · BCoIP₂. Calculated, %: C 68.06; H 5.30; I 13.07.

Similarly, from 0.42 g of compound **II** and 0.171 g of sodium tetraphenylborate we obtained 0.41 g (79%) of compound **IV**, mp 75–77°C. Found, %: C 70.03; H 5.34; I 12.02. $C_{60}H_{53}BCoIP_2$. Calculated, %: C 69.79; H 5.17; I 12.29.

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