

The electrochemical synthesis of η^5 -cyclopentadienylcobalt- η^4 -tetraphenylbutadiene and its reaction with iodine in the presence of electron donor ligands ¹

V.A. Knizhnikov, V.L. Shirokii, A.N. Ryabtsev, N.A. Maier *

Institute of Physical Organic Chemistry of Belarus Academy of Science, Minsk, Belarus

Received 11 June 1996; accepted 1 August 1996

Abstract

η^5 -Cyclopentadienylcobalt- η^4 -tetraphenylbutadienes $\text{RC}_5\text{H}_4\text{CoC}_4\text{H}_2\text{Ph}_4$ (**IIa–d**: **a** R = H; **b** R = Et; **c** R = ⁱPr; **d** R = PhCH₂) have been prepared by simultaneous electrolysis of a respective substituted cyclopentadiene RC_5H_5 and diphenylacetylene in acetonitrile containing up to 0.5% water, using a cobalt anode. The action of iodine on **IIa–d** results in the elimination of the tetraphenylbutadiene ligand and the formation of diiodides $(\text{RC}_5\text{H}_4\text{CoI}_2)_2$ (**IIIa–d**). The reaction of **IIa** with iodine in the presence of electron donor ligands leads to the formation of complexes CpCoI_2L , (L = Ph₃P, Py, Me₂S, dppe), $[\text{CpCoI}_2]^+ \text{I}_3^-$ (L₂ = dipy, phen), $(\text{CpCoI}_2)_2\text{L}$ (L = dppe). © 1997 Elsevier Science S.A.

Keywords: Cobalt; Cyclopentadienyl; Electrochemistry; Tetraphenylbutadiene

1. Introduction

The preparation of η^5 -cyclopentadienylcobalt- η^4 -tetraphenylcyclobutadiene (**I**) by electrolysis of mixtures of cyclopentadiene and diphenylacetylene (tolan) in acetonitrile using a cobalt anode has been reported in the literature [1,2]. A more detailed study of this reaction has revealed that, when the reaction is carried out in the presence of appreciable amounts of water, a complex involving an acyclic four-electron donor ligand η^5 -cyclopentadienylcobalt- η^4 -tetraphenylbutadiene (**IIa**) is formed along with **I**, and when the water content attains a value of ca. 0.5% the complex **IIa** becomes dominant among the reaction products. Taking ethyl-, isopropyl- or benzylcyclopentadiene in the reaction instead of unsubstituted cyclopentadiene, the respective ethylcyclopentadienyl-, isopropylcyclopentadienyl- and benzylcyclopentadienylcobalt tetraphenylbutadienes (**IIb–d**) have been obtained [3].

2. Results and discussion

We have studied the effect of the electrochemical reaction conditions (reagent ratio, current density, nature of supporting electrolyte) on the yield of the compound **IIa**. The d.c. electrolyses were carried out in a thermostated diaphragmless electrochemical cell under argon atmosphere. The experimental conditions and results are presented in Table 1.

At stoichiometric reagent ratio (molar ratio cyclopentadiene:tolan 1:2) the yield of **IIa** depends on the current density *i*. A decrease of current density from 10 to 2.5 mA cm^{−2} leads to a yield increase from 60 to 68% (with tetraethylammonium chloride as supporting electrolyte: Table 1, runs 1–3). At equimolecular reagent ratio, an even higher yield of 78%, calculated with respect to the starting tolan, has been obtained; however, the product yield calculated with respect to cyclopentadiene decreased down to around 39% at the same time (run 4). Similar effects were observed with tetraethylammonium bromide taken as supporting electrolyte (runs 5–8), but the yields of complex **IIa** were about 15–20% lower compared with those in analogous

* Corresponding author.

¹ Dedicated to the memory of Professor Yu.T. Struchkov.

Table 1

Electrochemical synthesis of η^5 -cyclopentadienylcobalt- η^4 -tetraphenylbutadiene (10 mmol tolan)

No. of run	CpH (mmol)	i (mA cm ⁻²)	τ ^c (min)	Q ^d (mF)	Yield (mmol)
1 ^a	5	10	80	44.30	3.02
2 ^a	5	5	160	40.60	3.23
3 ^a	5	2.5	320	42.64	3.39
4 ^a	10	2.5	370	53.70	3.93
5 ^b	5	10	80	40.00	2.28
6 ^b	5	5	160	48.00	2.25
7 ^b	5	2.5	320	40.84	2.47
8 ^b	10	2.5	330	43.25	2.81

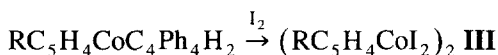
^a With 0.1 N Et₄NCl as supporting electrolyte.^b With 0.1 N Et₄NBr as supporting electrolyte.^c Electrolysis duration.^d Quantity of charge passed.

experiments where chloride salt was used. It should be noted that the formation of **I** in small quantities (approximately 2%) was observed in all cases.

The obtained compounds **IIa–d** are reddish-brown crystalline substances, air-stable and easily dissolved in common organic solvents. Their structures are confirmed by MS, IR and NMR spectroscopy. NMR data are presented in Table 2, and in Table 3 some physico-chemical characteristics of the complexes are given.

In the ¹H NMR spectra of these compounds, a high-field shift of the resonance signal of ethylenic protons belonging to the tetraphenylbutadiene ligand (δ 1.30–1.54 ppm) compared with that of non-coordinated butadiene (δ ~ 5 ppm) is to be noted. Although such an NMR signal shift of ethylenic protons, according to the data known from the literature [4], could be regarded as providing evidence of a coordinated butadiene moiety, an X-ray analysis of the complex **IIa** has been performed to establish its structure. The analysis of the X-ray diffraction pattern of compound **IIa** revealed that the Co(I) atom is coordinated with both C₅H₅ and η -tetraphenylbutadiene ligands, forming a wedge-like sandwich structure as shown in Fig. 1 [5].

In the framework of reactivity studies of monocyclopentadienylcobalt derivatives, we have investigated the reaction of the complexes **II** with iodine. The reactions proceed easily, yielding the respective iodides through elimination of tetraphenylbutadiene ligands:



R = H (**a**), C₂H₅ (**b**), ¹C₃H₇ (**c**), C₆H₅CH₂ (**d**)

The compound **IIIa** is believed to have dimeric structure (see, for example, Ref. [6]). By analogy, we suggest dimeric structures also for the compounds **IIIb–d**.

Stoichiometric quantities of iodine (reagent ratio 1:1) are sufficient for the transformation to be complete. When the amount of iodine taken was less than that required by 1:1 stoichiometry, unreacted **II** compounds

were present among the reaction products. No organocobalt product containing both the tetraphenylbutadiene ligand and iodine could be detected. This result is different from that observed earlier by us [7] for the reaction of η^5 -cyclopentadienylcobalt- η^4 -cyclopentadiene with iodine (reagent ratio 2:1), where η^5 -cyclopentadienyl(η^2 -cyclopentadiene)cobalt iodide with both iodine and cyclopentadiene ligands was isolated from the reaction mixture.

The compounds **IIIa–d** react with triphenylphosphine to give the respective phosphine complexes (RC₅H₄)(Ph₃P)CoI₂ (**IVa–d**), which can also be formed when the compounds **IIa–d** and triphenylphosphine, dissolved in benzene, are allowed to react with iodine: (see Scheme 1)

The elimination of the tetraphenylbutadiene ligand and the formation of the compounds of type (C₅H₅)CoI₂L [L = Py (**V**), Me₂S (**VI**)] also takes place in the reaction of equimolecular amounts of the compound **IIa** with iodine in the presence of pyridine or dimethylsulphide. ¹H NMR studies of the compounds **V** and **VI** were hampered by their poor solubilities in common organic solvents. However, the introduction of benzyl substituent in the cyclopentadienyl ring was found to enhance the solubility of the corresponding pyridine complex, and the structure of [C₆H₅CH₂C₅H₄CoI₂Py] (**VII**) could be confirmed by ¹H NMR spectroscopy. Thus, the signal of the methylene group protons in compound **VII** is located at δ 3.75 ppm (2H), the cyclopentadienyl ligand protons are detected at δ 5.40–5.50 ppm (4H), and the presence of phenyl and pyridine protons is revealed by the signals at δ 7.10–7.90 ppm (10H).

The reaction of **IIa** with iodine in the presence of 2,2'-dipyridyl (dipy) or 1,10-phenanthroline (phen) was found to take a somewhat more complex course compared with that with ligands as discussed above. When equimolecular quantities of **IIa** and iodine were allowed to react, a mixture of products was obtained. However, in the presence of iodine taken in excess, the reaction occurred selectively and led to the formation of com-

Table 2
 ^1H and ^{13}C chemical shifts in the NMR spectra of compounds **IIa–c**

Compound	$\delta^1\text{H}$ (ppm)					$\delta^{13}\text{C}$ (ppm) ^a				
	Solvent	Ph	Cp	=CH–	R	=HCPh	=C(Ph)–	Cp	R	C–
1	2	3	4	5	6	7	8	9	10	11
IIa	CCl_4	6.70–7.10 (20H)	4.48 (5H)	1.44 (2H)	—	52.17 (2C)	96.01 (2C)	84.10 (5C)	—	137.86 (2C) 144.53 (2C)
IIb	$(\text{CD}_3)_2\text{CO}$	6.87–7.23 (20H)	4.62 (2H) 3.85 (2H)	1.51 (2H)	1.20 (3H) 2.14 (2H)	52.50 (2C)	96.25 (2C)	80.34 (2C) 85.91 (2C) 105.40 (1C)	12.65 (1C) 19.88 (1C)	138.02 (2C) 144.92 (2C)
IIc	$(\text{CD}_3)_2\text{CO}$	6.96–7.30 (20H)	4.72 (2H) 3.75 (2H)	1.54 (2H)	1.24 (6H) 2.42 (1H)	52.50 (2C)	96.25 (2C)	78.75 (2C) 86.63 (2C) 109.82 (1C)	23.86 (2C) 26.25 (1C)	138.03 (2C) 144.98 (2C)
IIId	CCl_4	6.65–7.32 (25H)	4.36 (2H) 3.86 (2H)	1.30 (2H)	3.30 (2H)	53.00 (2C)	96.35 (2C)	81.01 (2C) 86.02 (2C) 101.95 (1C)	33.33 (1C)	137.66 (2C) 141.34 (1C) 144.30 (2C)

^a The ^{13}C NMR spectra were recorded with CDCl_3 as solvent.

Table 3
Physico-chemical characteristics of the complexes II–IV

Compound	Anal. Found (%)			Formula	Calc. (%)			M.p. (°C)	Yield (%)	MS, m/z (ion)
	C	H	I		C	H	I			
I	2	3	4	5	6	7	8	9	11	12
IIa	82.01	5.78	—	C ₃₃ H ₂₇ Co	82.15	5.64	—	208–210	65	482 (C ₃₃ H ₂₇ Co ⁺), 417 (C ₂₈ H ₂₂ Co ⁺), 358 (C ₂₈ H ₂₂ ⁺), 281 (C ₂₂ H ₁₇ ⁺), 238 (C ₁₄ H ₁₁ Co ⁺), 124 (C ₅ H ₅ Co ⁺), 65 (C ₅ H ₅ ⁺)
IIb	82.50	6.28	—	C ₃₅ H ₃₁ Co	82.34	6.12	—	162–164	66	510 (C ₃₅ H ₃₁ Co ⁺), 482 (C ₃₃ H ₂₇ Co ⁺), 417 (C ₂₈ H ₂₂ Co ⁺), 358 (C ₂₈ H ₂₂ ⁺), 281 (C ₂₂ H ₁₇ ⁺), 238 (C ₁₄ H ₁₁ Co ⁺), 152, (C ₇ H ₉ Co ⁺), 124 (C ₅ H ₅ Co ⁺), 93 (C ₇ H ₉ ⁺), 77 (C ₆ H ₅ ⁺)
IIc	82.57	6.41	—	C ₃₆ H ₃₃ Co	82.43	6.34	—	198–200	70	624 (C ₃₆ H ₃₃ Co ⁺), 482 (C ₃₃ H ₂₇ Co ⁺), 417 (C ₂₈ H ₂₂ Co ⁺), 358 (C ₂₈ H ₂₂ ⁺), 281 (C ₂₂ H ₁₇ ⁺), 238 (C ₁₄ H ₁₁ Co ⁺), 179 (C ₁₄ H ₁₁ ⁺), 166 (C ₈ H ₁₁ Co ⁺), 124 (C ₅ H ₅ Co ⁺), 107 (C ₈ H ₁₁ ⁺)
IId	83.77	6.00	—	C ₄₀ H ₃₃ Co	83.90	5.81	—	199–201	67	572 (C ₄₀ H ₃₃ Co ⁺), 417 (C ₂₈ H ₂₂ Co ⁺), 358 (C ₂₈ H ₂₂ ⁺), 281 (C ₂₂ H ₁₇ Co ⁺), 238 (C ₁₄ H ₁₁ Co ⁺), 214 (C ₁₂ H ₁₁ Co ⁺), 179 (C ₁₄ H ₁₁ ⁺), 155 (C ₁₂ H ₁₁ ⁺)
IIIa	16.01	1.48	67.00	C ₅ H ₅ CoI ₂	15.89	1.33	67.17	—	90	406 (C ₇ H ₉ CoI ₂ ⁺), 279 (C ₇ H ₉ CoI ⁺), 253 (C ₅ H ₇ CoI ⁺), 186 (CoI ⁺), 152 (C ₇ H ₉ Co ⁺), 93 (C ₇ H ₉ ⁺)
IIIb	21.00	2.34	62.67	C ₇ H ₉ CoI ₂	20.75	2.23	62.53	140–142	87	

IIIc	22.76	2.52	60.59	$C_8H_{11}CoI_2$	22.88	2.64	60.44	110–112	76	420 ($C_8H_{11}CoI_2^+$), 313 (CoI_2^+), 293 ($C_8H_{11}CoI^+$), 267 ($C_6H_9CoI^+$), 186 (CoI^+), 166 ($C_8H_{11}Co^+$), 107 ($C_8H_{11}^+$)
IIIId	30.95	2.41	54.18	$C_{12}H_{11}CoI_2$	30.80	2.37	54.24	—	73	486 ($C_{12}H_{11}CoI_2^+$), 341 ($C_{12}H_{11}CoI^+$), 313 (CoI_2^+), 214 ($C_{12}H_{11}Co^+$), 186 (CoI^+), 155 ($C_{12}H_{11}^+$)
IVa	43.21	3.23	39.87	$C_{23}H_{20}CoI_2P$	43.12	3.12	39.69	173–175	78	640 ($C_{23}H_{20}CoI_2P^+$), 513 ($C_{23}H_{20}CoIP^+$), 386 ($C_{23}H_{20}CoP^+$), 378 ($C_5H_5CoI_2^+$), 321 ($C_{18}H_{15}CoP^+$), 313 (CoI_2^+), 262 ($C_{18}H_{15}P^+$), 251 ($C_5H_5CoI^+$), 77 ($C_6H_5^+$), 65 ($C_5H_5^+$)
IVb	45.18	3.75	38.06	$C_{25}H_{24}CoI_2P$	44.94	3.62	37.99	178–180	72	668 ($C_{25}H_{24}CoI_2P^+$), 575 ($C_{18}H_{15}CoI_2P^+$), 541 ($C_{25}H_{24}CoIP^+$), 414 ($C_{25}H_{24}CoP^+$), 406 ($C_7H_9CoI_2^+$), 279 ($C_7H_9CoI^+$), 262 (C_{18} 152 ($C_7H_9Co^+$), 93 ($C_7H_9^+$), 77 ($C_6H_5^+$)
IVc	46.00	4.01	37.13	$C_{26}H_{26}CoI_2P$	45.78	3.84	37.20	179–181	67	682 ($C_{26}H_{26}CoI_2P^+$), 575 ($C_{18}H_{15}CoI_2P^+$), 555 ($C_{26}H_{26}CoIP^+$), 420 ($C_8H_{11}CoI_2^+$), 293 ($C_8H_{11}CoI^+$), 262 ($C_{18}H_{15}P^+$), 166 ($C_8H_{11}Co^+$), 186 (CoI^+), 107 ($C_8H_{11}^+$)
IVd	49.51	3.45	34.52	$C_{30}H_{26}CoI_2P$	49.34	3.59	34.76	171–174	63	730 ($C_{30}H_{26}CoI_2P^+$), 603 ($C_{30}H_{26}CoIP^+$), 575 ($C_{18}H_{15}CoI_2P^+$), 468 ($C_{12}H_{11}CoI_2^+$), 341 ($C_{12}H_{11}CoI^+$), 262 ($C_{18}H_{15}P^+$), 214 ($C_{12}H_{11}Co^+$), 186 (CoI^+), 155 ($C_{12}H_{11}^+$)

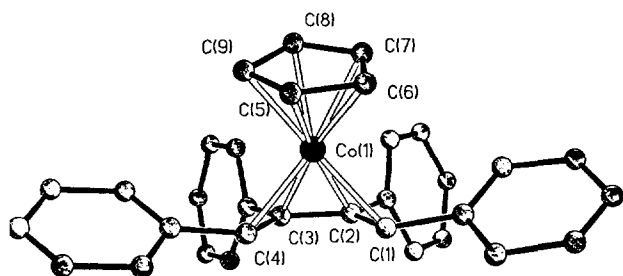


Fig. 1. Molecular structure of η^5 -cyclopentadienyl- η^4 -tetraphenylbutadiene (**IIa**).

plexes having composition $(C_5H_5)CoI_4L_2$ [L_2 = dipy (**VIII**); phen (**IX**)].

In the 1H NMR spectrum of **VIII**, the singlet of cyclopentadienyl protons is found at δ 6.15 ppm (5H), dipyriddy protons are revealed as two doublets: at δ 8.50 ppm (2H) and δ 10.0 ppm (2H), and two triplets: at δ 7.85 ppm (2H) and δ 8.26 ppm (2H).

In the 1H NMR spectrum of **IX**, the cyclopentadienyl group protons are detected at δ 6.35 ppm (5H), the protons of the phenanthroline ligand give two doublets: at δ 8.95 ppm (2H) and δ 10.35 ppm (2H), and a multiplet in the region of δ 8.10–8.45 ppm (4H).

The data from the 1H NMR spectra provide evidence for the equivalence of the two nitrogen-containing cycles, both in **VIII** and **IX**, i.e. for the bidentate character of the ligand coordination to cobalt. Taking this into account, it could be suggested that the **VIII** and **IX** molecules are stable 18-electron species $[(C_5H_5)CoIL_2]^+$, with I_3^- counter-ions in the outer sphere.

X-ray structural analysis data provided a convincing confirmation of the suggested structure (Fig. 2) [8].

In $[(C_5H_5)Co(dipy)]^+$ (Fig. 2), the Co(III) atom is coordinated with an η^5 - C_5H_5 ligand, a practically planar π -donor dipyriddy ligand, and an iodine atom.

The reaction of η^5 -cyclopentadienylcobalt- η^4 -tetraphenylbutadiene with iodine in the presence of 1,2-bis(diphenylphosphino)ethane (dppe) proceeds in an

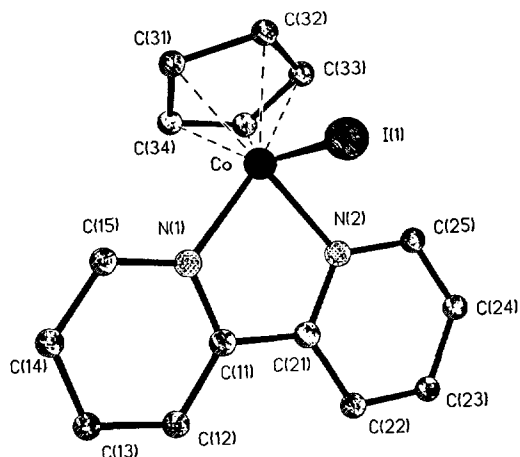
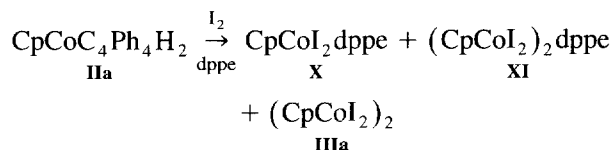


Fig. 2. Molecular structure of $[\eta^5-C_5H_5Co(dppe)I]^+$ (cation of **VIII**, the counter-ion I_3^- is omitted).

even more complex manner. We have found that, within the interval of reagent ratios **IIa**:dppe: I_2 from 1:0.5:1 to 1:1:1, a mixture of three products is formed:



The yields of the compounds **X**, **XI** and **IIIa** depend on the quantities of dppe and iodine used. Thus, at equimolecular **IIa**/iodine ratio, the increase in amount of dppe from 0.55 to 1.0 mol/mol **IIa** resulted in a substantial yield increase of the unsymmetric mononuclear complex **X** and a corresponding yield decrease for the binuclear complex **XI** and the dimeric iodide **IIIa** (molar product ratios found were 2.5:2.5:1 and 7.5:0.5:0.25 respectively). At 1.5-fold dppe excess, the complex **X** becomes the only organocobalt product of the reaction.

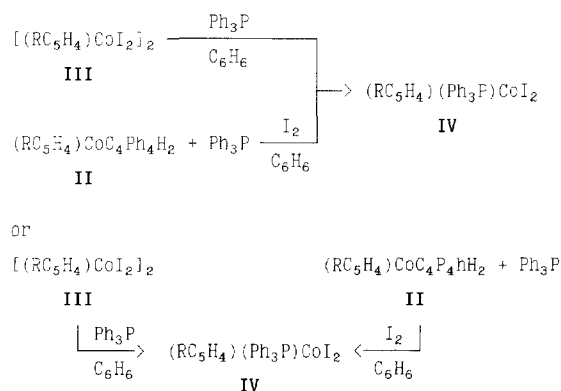
It should be pointed out that in all experiments with equimolecular **IIa**/iodine ratios, some quantity of unreacted **IIa** was always present in the reaction mixtures. This may be caused by a partial consumption of iodine in a by-reaction with dppe. Applying a fairly small (less than 10%) excess of iodine led to a complete transformation of **IIa**.

The complex **XI** reacts with dppe to give the compound **X**, which can also be obtained in a moderate yield by the reaction of dppe with the diiodide **IIIa**:



The synthesized complexes **X** and **XI** are solid coloured air-stable substances. Their structures have been confirmed by the respective data obtained from IR and 1H NMR spectra, and from elemental analysis.

In the 1H NMR spectrum of **X** (acetone- d_6), the



Scheme 1.

signal of phenyl protons is located in the δ 7.30–8.25 ppm range, the cyclopentadienyl protons give a singlet at δ 5.90 ppm, and the signals from methylene groups are represented by two broadened peaks at δ 3.35 and 3.45 ppm. In the ^1H NMR spectrum of **XI** (CDCl_3), the phenyl protons are revealed in the δ 7.10–7.45 ppm region, the singlet of cyclopentadienyl protons is located at δ 4.82 ppm, and the signal from methylene groups is a broadened peak at δ 2.56 ppm.

3. Experimental

All operations were carried out in argon atmosphere. ^{13}C and ^1H NMR spectra were recorded with a Bruker WH-360 spectrometer using 360.13 and 90.53 MHz frequencies respectively. Mass spectra were obtained with an MX-1320 instrument. The X-ray structural analyses were performed by S.E. Nefedov and I.L. Eremenko, guided by Professor Yu.T. Struchkov [5,8].

3.1. Alkylcyclopentadienylcobalt tetraphenylbutadienes (**IIa–d**)

A solution of 5 or 10 mmol of the corresponding cyclopentadiene and 10 mmol diphenylacetylene in 75 ml of electrolyte medium was electrolysed with d.c. current maintained at current density values of 2.5, 5 or 10 mA cm^{-2} (manual control). The electrolytic cell used was of diaphragmless type, fitted with a stirrer and coaxial cylindric electrode set: two steel cathodes of total surface area 100 cm^2 and a cobalt anode of 100 cm^2 area disposed between them. 0.1 N tetraethylammonium chloride or bromide solution in acetonitrile with around 0.5% water content was used as electrolyte medium. A copper coulometer was used to measure the quantity of electric charge passed.

After the required quantity of electric charge had passed, the reaction mixture was diluted with a 10-fold excess of water, and the products extracted with hexane. The extract was dried over anhydrous magnesium sulphate. After removal of the solvent, the residue was chromatographed on a column filled with 100/160 μm silica using hexane/benzene (1:1) as eluent. The solvent from the solution thus obtained was evaporated under reduced pressure, and the solid residue dried in vacuo.

3.2. Cyclopentadienylcobalt diiodide (**IIIa**)

To a solution of 0.5 mmol cyclopentadienylcobalt tetraphenylbutadiene (**IIa**) in 50 ml of benzene, a solution of 0.5 mmol iodine in 15 ml of benzene was added. The reaction mixture was stirred for 1 h. The precipitate formed was separated from the solvent, washed with ether and dried in vacuo.

Ethylcyclopentadienylcobalt diiodide (**IIIb**) was prepared in a similar way.

3.3. Isopropylcyclopentadienylcobalt diiodide (**IIIc**)

To a solution of 0.5 mmol isopropylcyclopentadienylcobalt tetraphenylbutadiene in 50 ml of benzene, a solution of 0.5 mmol iodine in 15 ml of benzene was added. The reaction mixture was stirred for 1 h and then filtered. The filtrate was concentrated to a volume of 10 ml by removal of the solvent under vacuum, and 70 ml of pentane was added to the resulting solution. The precipitate formed was separated, washed many times with pentane and dried in vacuo. The compound was purified by repeated precipitation from benzene.

Benzylcyclopentadienylcobalt diiodide (**IIId**) was prepared by a similar procedure.

3.4. Alkylcyclopentadienyl(triphenylphosphine)cobalt diiodides (**IVa–d**)

To a solution of 0.5 mmol of the corresponding compound (**Ia–d**) and 0.5 mmol triphenylphosphine in 50 ml of benzene, a solution of 0.5 mmol iodine in 15 ml of benzene was added. The mixture was stirred for 2 h and then filtered. The filtrate was concentrated by removal of the solvent under vacuum, and then treated with 60 ml of pentane. The precipitate was separated, washed with pentane and dried in vacuo.

The compounds were purified by repeated precipitation from benzene.

3.5. Cyclopentadienyl(pyridine)cobalt diiodide (**V**)

To a solution of 0.24 g (0.5 mmol) cyclopentadienylcobalt tetraphenylbutadiene and 0.08 g (1 mmol) pyridine in 50 ml of benzene, a solution of 0.127 g (0.5 mmol) iodine in 25 ml of benzene was added. The reaction mixture was stirred for 1 h. The precipitate formed was separated from the solvent and dissolved in methylene dichloride. The solution was filtered, concentrated by removal of solvent under vacuum, and treated with pentane (75 ml). The precipitate formed was filtered, washed with pentane, and dried in vacuo. 0.17 g (74%) of the compound **V** was obtained, m.p. 160–162 $^{\circ}\text{C}$.

Anal. Found: C, 26.33; H, 2.30; I, 55.81; N, 3.37. $\text{C}_{10}\text{H}_{10}\text{CoI}_2\text{N}$ Calc.: C, 26.29; H, 2.21; I, 55.55; N, 3.07%.

In a similar way, from 0.24 g (0.5 mmol) of cyclopentadienylcobalt tetraphenylbutadiene, 0.062 g of dimethyl sulphide and 0.127 g (0.5 mmol) of iodine, 0.16 g (73%) of cyclopentadienyl(dimethylsulphide)cobalt diiodide (**VI**) was obtained, m.p. 182–183 $^{\circ}\text{C}$.

Anal. Found: C, 18.93; H, 2.70; I, 57.45; S, 7.23. $\text{C}_7\text{H}_{11}\text{CoI}_2\text{S}$ Calc.: C, 19.11; H, 2.52; I, 57.69; S, 7.29%.

3.6. *Benzylcyclopentadienyl(pyridine)cobalt diiodide (VII)*

To a solution of 0.57 g (1 mmol) benzylcyclopentadienylcobalt tetraphenylbutadiene and 0.158 g (2 mmol) pyridine in 100 ml of benzene, a solution of 0.254 g (1 mmol) iodine in 50 ml of benzene was added dropwise. The reaction mixture was stirred for 1 h and then filtered. The solution obtained was concentrated by removal of solvent under vacuum, and then treated with pentane (75 ml). The precipitate formed was then transferred to a Soxhlet apparatus and the reaction product extracted with ether. The mixture obtained was concentrated to a volume of about 10 ml, the crystals formed were separated from the solvent, washed with pentane and dried in vacuo. 0.35 g (64%) of the compound **VII** was obtained, m.p. 120–122 °C.

Anal. Found: C, 37.48; H, 3.06; I, 46.44; N, 2.43. $C_{17}H_{16}CoI_2N$ Calc.: C, 37.32; H, 2.95; I, 46.39; N, 2.56%.

3.7. *Cyclopentadienyl(2,2'-dipyridyl)cobalt tetraiodide (VIII)*

To a solution of 0.24 g (0.5 mmol) cyclopentadienylcobalt tetraphenylbutadiene and 0.11 g (0.7 mmol) 2,2'-dipyridyl in 50 ml of benzene, 0.254 g (1 mmol) of iodine in 50 ml of benzene was added. The reaction mixture was stirred for 1 h. The precipitate formed was filtered, washed with 15 ml of benzene and then dissolved in methylene dichloride. The solution obtained was filtered and concentrated to a volume of about 10 ml by removing the solvent under vacuum. The crystals formed were separated from the solvent, washed with ether, then pentane, and dried in vacuo. 0.3 g (76%) of the compound **VIII** was obtained, m.p. 166–168 °C.

Anal. Found: C, 22.72; H, 1.63; I, 64.48; N, 3.67. $C_{15}H_{13}CoI_4N$ Calc.: C, 22.87; H, 1.66; I, 64.43; N, 3.56%.

By a similar procedure, from 0.24 g (0.5 mmol) of cyclopentadienylcobalt tetraphenylbutadiene, 0.108 g (0.6 mmol) of 1,10-phenanthroline and 0.252 g (1 mmol) of iodine, 0.33 g (81%) of cyclopentadienyl(1,10-phenanthroline)cobalt tetraiodide (**IX**) was obtained, m.p. 190–192 °C.

Anal. Found: C, 25.45; H, 1.58; I, 62.44; N, 3.29. $C_{17}H_{13}CoI_4N$ Calc.: C, 25.15; H, 1.61; I, 62.63; N, 3.45%.

3.8. *The reaction of cyclopentadienylcobalt tetraphenylbutadiene with iodine in the presence of bis(diphenylphosphino) ethane (dppe)*

(a) To a solution of 0.24 g (0.5 mmol) of **IIa** and 0.1 g (0.25 mmol) of dppe in 50 ml of benzene, a solu-

tion of 0.127 g (0.5 mmol) of iodine in 20 ml of benzene was added under vigorous stirring. The mixture was stirred for 2 h, and then filtered. The solution obtained was concentrated by removal of solvent under vacuum, and then treated with pentane. The precipitate formed was separated from the solvent, washed with pentane and dried in vacuo. After repeated precipitation from methylene dichloride, 0.14 g (48%) of the compound **XI** was obtained, m.p. 139–141 °C.

Anal. Found: C, 37.22; H, 2.73; I, 43.81. $C_{36}H_{34}Co_2I_4P_2$ Calc.: C, 37.47; H, 2.79; I, 43.98%.

In the residue obtained after evaporation of pentane/benzene solution, the initial **IIa** was detected by mass spectrometry.

The precipitate obtained by filtration of the reaction mixture was treated with methylene dichloride. The suspension was filtered, the solution concentrated by the removal of solvent under vacuum, and treated with pentane. The precipitate formed was filtered, washed with pentane and dried in vacuo. After repeated precipitation from methylene dichloride, 0.094 g of the compound **X** was obtained, m.p. 159–162 °C.

Anal. Found: C, 47.56; H, 3.72; I, 32.74. $C_{31}H_{29}CoI_2P_2$ Calc.: C, 47.97; H, 3.77; I, 32.70%.

The residue obtained after extraction of the compound **X** was washed with ether, then pentane, and dried in vacuo. 0.037 g of **IIIa** was obtained.

(b) After performing operations similar to those described above, from 0.48 g (1 mmol) of compound **IIa**, 0.4 g (1 mmol) of dppe and 0.28 g (1.1 mmol) of iodine, the following compounds were isolated: 0.56 g of **X**, 0.053 g of **XI**, and 0.018 g of **IIIa**. No initial compound **IIa** was detected in the reaction mixture.

3.9. *Cyclopentadienylcobalt diiodide-bis(diphenylphosphino)ethane*

(a) To a solution of 0.24 g (0.5 mmol) **IIa** and 0.302 g (0.75 mmol) dppe in 50 ml of benzene, a solution of 0.13 g iodine in 20 ml benzene was added. The reaction mixture was stirred for 1.5 h, the precipitate formed was separated from the solvent. The reaction products were extracted from the precipitate with methylene dichloride; the extract was filtered, concentrated, and treated with pentane. The precipitate formed was filtered, washed with pentane and dried in vacuo. After repeated precipitation from methylene dichloride, 0.29 g (75%) of the compound **X** was obtained.

(b) To a solution of 0.29 g (0.25 mmol) **XI** in 70 ml of benzene, 0.1 g (0.25 mmol) of dppe was added. The reaction mixture was stirred for 0.5 h. The precipitate formed was filtered, washed with ether, then pentane, and dried in vacuo. 0.35 g (90%) of the compound **X** was isolated.

(c) To a suspension of 0.19 g (0.5 mmol) **IIIa** in 20 ml of benzene, 0.2 g (0.5 mmol) of dppe was added.

The reaction mixture was stirred for 4 h. The precipitate was then separated from the solvent. The reaction product was extracted from the precipitate with methylene dichloride. The solution obtained was filtered, then concentrated and treated with pentane. The precipitate formed was filtered, washed with ether, then pentane, and dried in vacuo. 0.16 g (41%) of the compound X was isolated.

References

- [1] V.L. Shirokii, A.V. Mosin, N.A. Maier and Yu.A. Oldekop, *Zh. obshch. khim.*, 55(10) (1985) 2399.
- [2] V.L. Shirokii, A.V. Mosin, N.A. Maier and Yu.A. Oldekop, *Vestsi AN BSSR, ser. khim. navuk*, 3 (1987) 72.
- [3] V.L. Shirokii, V.A. Knizhnikov, A.V. Mosin, M.G. Novikova, N.A. Maier and Yu.A. Oldekop, *Metall. Khim.*, 4(5) (1991) 1059.
- [4] H. Yamazaki and Y. Wakatsuki, *J. Organomet. Chem.*, 149(3) (1978) 377.
- [5] V.L. Shirokii, V.A. Knizhnikov, A.V. Mosin, S.E. Nefedov, I.L. Eremenko, A.I. Yanovskii and Yu.T. Struchkov, *Metall. Khim.*, 6(3) (1993) 22.
- [6] W.-S. Lee and H.H. Brintzinger, *J. Organomet. Chem.*, 209(3) (1981) 401.
- [7] V.A. Knizhnikov, V.L. Shirokii, A.B. Sutormin, M.G. Novikova, N.A. Maier and Yu.A. Oldekop, *Metall. Khim.*, 2(5) (1989) 1160.
- [8] V.L. Shirokii, V.A. Knizhnikov, A.V. Mosin, S.E. Nefedov, I.L. Eremenko, A.I. Yanovskii and Yu.T. Struchkov, *Metall. Khim.*, 6(1) (1993) 26.