interaction with the one or two phosphorus atoms of the coordinated phosphorus ligands. The chemical shifts of the π-C_5H_5 protons occurred in the range τ 5.8–5.9 and were thus appreciably higher than those in the unsubstituted compounds $(CH_3)_3EFe(CO)_2C_5H_5$. Replacement of carbonyl groups with the more weakly π-accepting trivalent phosphorus ligands would be expected to increase the electron density on the metal atom. Some of this electron density can be transferred to the antibonding orbitals of the π-C_5H_5 ring. This would be expected to increase the shielding of the protons of the π-C_5H_5 ring and hence raise their chemical shift. The fact that the chemical shifts in all of the trivalent phosphorus derivatives in Table III are the same regardless of the π-accepting qualities of the phosphorus ligand and of the remaining number of carbonyl groups can be attributed to the fact that replacement of one carbonyl group in the $(CH_3)_3EFe(CO)_2C_5H_5$ compounds with a more weakly π-accepting phosphorus ligand increases the electron density in the π-C_5H_5 antibonding orbitals to near the saturation point. Additional electron density obtained either by substitution of the second carbonyl group with a more weakly π-accepting ligand or by use of still more weakly π-accepting phosphorus ligands is not fed into the π-C_5H_5 antibonding orbitals. Instead this extra electron density appears to be fed into the $(CH_3)_3E$ group by increased dπ–dπ bonding between the iron atom and the silicon or tin atom. This suggestion is supported by the steady increase in the nmr chemical shifts of the $(CH_3)_3E$ protons of the $(CH_3)_3EFeL_2C_5H_5$ compounds with the following variation of the L ligands: 2CO (least) $\sim$ CO, $P(OC_6H_5)_3$ < CO, $P(C_6H_5)_3$ < diphos (greatest). Except for the first approximate equality, this sequence corresponds to decreasing π-acceptor ability of the L ligands. Increasing the dπ–dπ bonding between the iron atom and the silicon or tin atoms increases the negative charge on the silicon or tin atom and hence decreases its electronegativity. Prior data[15] suggest that a decrease in the electronegativity of an atom increases the chemical shift of an attached methyl group.

The methyl resonances of the trimethyltin derivatives exhibited satellites corresponding to coupling of the methyl protons with the magnetically active tin isotopes ^{117}Sn and ^{119}Sn. The resolution of the spectra did not permit unequivocal separation of the coupling with the two different tin isotopes which differ by only about 4%. The values given in Table III may be regarded as an average of these two coupling constants. Progressive substitution of carbonyl groups in $(CH_3)_3SnFe(CO)_2C_5H_5$ with more weakly π-accepting trivalent phosphorus ligands lowers the $J(Sn–CH_3)$ coupling constant. The increased dπ–dπ iron–tin bonding which occurs upon substitution with more weakly π-accepting ligands increases the involvement of the d orbitals in the bonding of the tin atom which may lower the s character of the tin orbitals bonding to the methyl groups. Flitcroft and Kaesz[16] indicate that a reduction in the s character of the tin orbital in the $Sn–CH_3$ bond leads to a reduction in the $J(Sn–CH_3)$ coupling constant in agreement with our observations.

Acknowledgment.—We are indebted to the National Science Foundation for generous support of this work under Grant GP-7081. We are also indebted to Dr. William Atwell of Dow-Corning Corp. for generous samples of trimethylchlorosilane and to Dr. William Considine of M and T Chemical Corp. for generous samples of trimethyltin chloride.

[15] H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 722 (1961).
[16] N. Flitcroft and H. D. Kaesz, *J. Am. Chem. Soc.*, **85**, 1377 (1963).

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Cyclopentadienylcobalt Derivatives of Chelating Aromatic Ligands

BY RICHARD F. HECK

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A series of five-coordinate cyclopentadienylcobalt complexes has been prepared by allowing diiodocarbonylcyclopentadienylcobalt(III) to react with *ortho*-substituted benzene derivatives containing phenolic, amino, and thiophenolic groups, in the presence of a base. The products are probably best formulated as cobalt(I) derivatives with *o*-quinoidal-type ligands rather than as five-coordinate cobalt(III) complexes.

Introduction

Stable coordination complexes of group VIII metal ions with the dianions of toluene-3,4-dithiol, catechol, *o*-phenylenediamine, and related derivatives have recently been reported by Balch, Röhrscheid, and Holm.[1] *o*-Phenylenediamidocyclopentadienylcobalt(III) was also reported recently from the reaction of *o*-phenylenediamine with dicarbonylcyclopentadienylcobalt(I) and oxygen.[2] These reports prompted us to attempt to prepare the complete series of related chelates with oxygen

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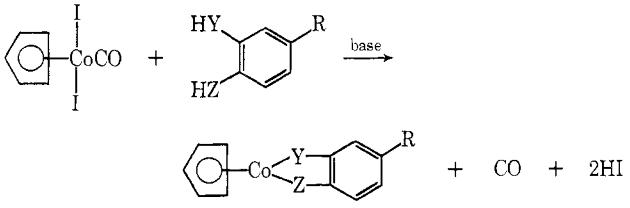
[1] A. L. Balch, F. Röhrscheid, and R. H. Holm, *J. Am. Chem. Soc.*, **87**, 2301 (1965).

[2] T. Joh, N. Hagihara, and S. Murahashi, *Bull. Chem. Soc. Japan*, **40**, 661 (1967).

and sulfur atoms replacing the nitrogen atoms in *o*-phenylenediamidocyclopentadienylcobalt(III). Five-coordinate cobalt(III) derivatives are often proposed as intermediates in replacement reactions, but few such complexes are stable enough to be isolated. It appeared that support for the existence of these intermediates might be found if the above-mentioned complexes could be prepared.

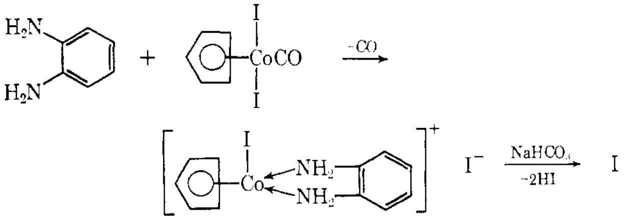
Results and Discussion

A general route to the desired compounds was found in the reaction of diiodocarbonylcyclopentadienylcobalt(III)[3,4] with the necessary *ortho*-disubstituted benzene derivative and a base to remove 2 mol of hydrogen iodide from the reactants.

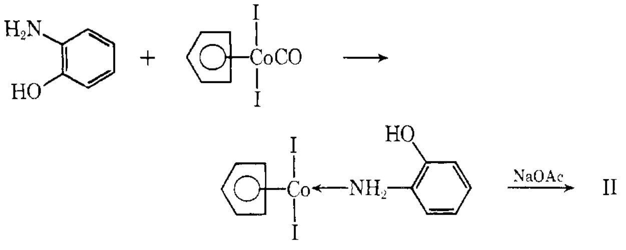


	Y	Z	R
I	NH	NH	H
II	NH	O	H
III	NH	S	H
IV	O	O	H
V	O	S	H
VI	S	S	CH_3

In two examples intermediate complexes were isolated from this reaction when the base was omitted. *o*-Phenylenediamine and diiodocarbonylcyclopentadienylcobalt(III) reacted to form iodo-*o*-phenylenediaminecyclopentadienylcobalt(III) iodide. The complex salt VII readily lost 2 mol of hydrogen iodide on treatment with aqueous sodium bicarbonate or stronger bases to produce I. Mixtures of VII and I did not appear to produce appreciable amounts of a mono(hydrogen iodide) adduct of I judging by the ultraviolet–visible spectrum of the mixture. A similar situation was found in the reaction of *o*-aminophenol with diiodocarbonylcyclopentadienylcobalt(III). The covalent complex VIII obtained probably did not have the phenolic hydroxyl coordinated in the complex. This complex also lost 2 mol of hydrogen iodide on treatment with sodium acetate or triethylamine. Mixtures of VIII and II also failed to show spectral evidence for the existence of a mono(hydrogen iodide) adduct.



VII



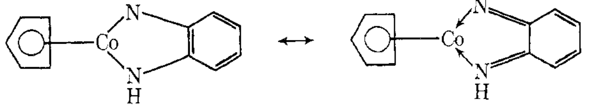
VIII

The complexes obtained from diiodocarbonylcyclopentadienylcobalt(III) and benzylamine or ethylenediamine do not lose hydrogen iodide to produce stable products with weak bases or even with strong aqueous sodium hydroxide. The conjugation between chelating groups appears necessary to produce a stable five-coordinate complex.

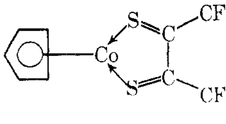
All of the five-coordinate complexes prepared are nicely crystalline, intensely blue to purple materials. All have charge-transfer absorption bands in their visible spectra with extinction coefficients above 10,000. Only the complex from catechol (IV) is hydrolytically unstable and it must be protected from moisture. The complexes are generally soluble in organic solvents and they are sublimable under vacuum. The complexes show no tendency to react with another ligand to form six-coordinate complexes.

Substituted derivatives with substituents in the six-membered ring have been prepared, but generally these materials were less stable than the parent compounds and very difficult to purify. The 4-nitro derivative of I was obtained reasonably pure and showed a shift of 36 $m\mu$ to higher wavelengths in its charge-transfer band from that of compound I.

Thus, five-coordinate derivatives of formally cobalt(III) are readily prepared from chelating aromatic amines, thiols, phenols, π-$C_5H_5Co(CO)I_2$, and bases. The fact that only chelating aromatic derivatives undergo the reaction, however, suggests that the new hetero five-membered rings produced may have considerable resonance energy. Alternatively, the complexes may be essentially all in the form of cobalt(I) derivatives chelated to *o*-quinoidal-type ligands and thus attain the krypton configuration for cobalt, *e.g.*



The related complex obtained from dicarbonylcyclopentadienylcobalt(I) and bis(trifluoromethyl)dithietene,[5] on the basis of X-ray diffraction studies,[6] has been assigned the dithione structure rather than the dithiolate structure



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(3) R. F. Heck, *Inorg. Chem.*, **4**, 855 (1965).

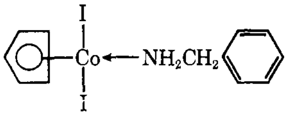
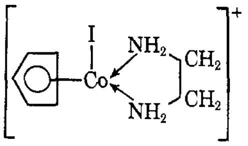
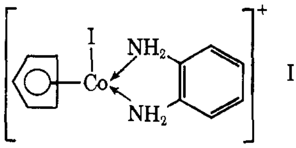
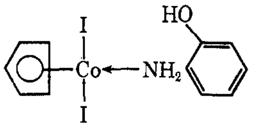
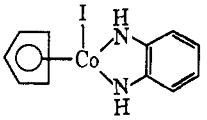
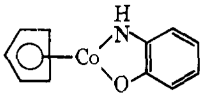
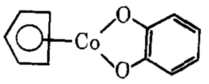
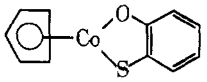
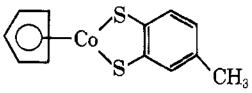
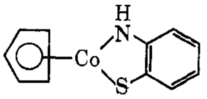
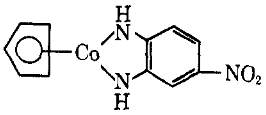
(4) R. B. King, *Z. Naturforsch.*, **19b**, 1160 (1964).

(5) R. B. King, *J. Am. Chem. Soc.*, **85**, 1587 (1963).

(6) H. W. Baird and B. M. White, *ibid.*, **88**, 4744 (1966).

TABLE I

CYCLOPENTADIENYLCOBALT(III) DERIVATIVES

Compound	Mp, °C	Color of solid (color of soln)	Spectrum, λ_{max} (ϵ)	Analyses, %					
				Calcd.			Found		
				C	H	Other	C	H	Other
	158–159	Black (green)	634 (1950)[a] 277 (20,200)[a]	29.71	2.28	2.89 (N)	29.80	2.90	2.72 (N)
	186–187 dec	Black (purple)	553 (1300)[a] 278 (13,000)[a] 220 (30,100)[a] 557 (1350)[b] 280 (14,500)[b]	19.64	3.06	6.55 (N)	19.42	3.10	6.41 (N)
	None	Black (purple)	524 (9200)[a,c] 404 (3500)[a,c] 270 (11,900)[a]	27.18	2.70	5.77 (N)	27.46	2.87	5.65 (N)
	144–145	Black (green)	577 (7300)[a] 264 (7200)[a]	27.12	2.48	2.88 (N)	27.38	2.57	2.72 (N)
	153–154	Green (red-purple)	530 (22,600)[a] 258 (14,100)[a] 521 (20,500)[b] 252 (13,700)[b]	57.40	4.82	12.17 (N)	57.85	5.00	12.06 (N)
	None	Bronze (blue)	578 (19,700)[a] 276 (10,900)[a] 587 (20,400)[b] 275 (10,100)[b]	57.16	4.36	6.06 (N)	57.68	4.77	6.06 (N)
	None	Purple (blue)	719 (19,000)[b] 287 (13,700)[b]	56.92	3.91	...	57.61	4.00	...
	None	Black (blue)	635 (13,700)[b] 300 (8450)[b]	53.23	3.65	12.92 (S)	53.11	4.10	12.42 (S)
	200.0–201.5	Purple (blue)	586 (11,900)[b] 290 (31,800)[b]	51.79	3.40	23.04 (S)	52.16	4.13	22.5 (S)
	165–166 dec	Purple (blue)	571 (17,100)[b] 274 (25,400)[b] 239 (19,200)[b]	53.44	4.08	5.67 (N)	53.00	4.20	5.35 (N)
	None	Bronze (purple)	566 (31,000)[b] 431 (13,000)[b] 254 (9300)[b]	48.02	3.66	15.27 (N)	46.74	4.00	14.50 (N)

[a] In methanol solution. [b] In methylene chloride solution. [c] Band is concentration dependent. Reported values at 4.1 × 10^{-5} M.

Experimental Section

Diiodo(benzylamine)cyclopentadienylcobalt(III).—To a solution of 7.65 g (15 mmol) of π-$C_5H_5Co(CO)I_2$[3,4] in 150 ml of methylene chloride was added 30 ml of a 1.0 M solution of benzylamine in methylene chloride. The resulting solution was stirred at room temperature for 1 hr and then filtered. The black solid obtained, 5.6 g, mp 133°, was recrystallized by dissolving it in a minimum of methylene chloride and then adding about three times the volume of ether. Long black needles slowly formed. There was obtained 1.82 g of product, mp 154°. A second crop of 1.7 g, mp 159°, was also isolated.

Iodo(ethylenediamine)cyclopentadienylcobalt(III) Iodide.—A 1 M solution (5 ml) of ethylenediamine in methylene chloride was added to a solution of 2.55 g (5 mmol) of $C_5H_5Co(CO)I_2$[3,4] in 50 ml of methylene chloride. After being stirred 1 hr at room temperature, the solution was concentrated on the steam bath to about 30 ml and 2.4 g of a black powder was filtered from the solution. The material was recrystallized by dissolving it in a minimum of methanol and then adding ether.

Iodo(*o*-phenylenediamine)cyclopentadienylcobalt(III) Iodide.—A mixture of 0.51 g (1 mmol) of $C_5H_5Co(CO)I_2$[3,4] and 1.1 g (1 mmol) of *o*-phenylenediamine was stirred with 10 ml of methylene chloride at room temperature for 1 hr. The black solid which precipitated was removed by filtration and dried. There was obtained 0.45 g of product.

Diiodo(2-hydroxyaniline)cyclopentadienylcobalt(III).—A mixture of 0.81 g (2 mmol) of $C_5H_5Co(CO)I_2$[3,4] and 0.22 g (2 mmol) of *o*-aminophenol was stirred in 20 ml of methylene chloride, After 1 hr more methylene chloride was added to dissolve the solid present, 25 ml of hexane was also added, and the solution was concentrated on the steam bath to about 25 ml. The black crystalline solid formed was isolated by filtration (0.37 g) and recrystallized by dissolving in methylene chloride, adding hexane, and concentrating on the steam bath until crystals began to appear. On cooling, shiny black crystals were obtained weighing 0.2 g.

***o*-Phenylenediamidocyclopentadienylcobalt(III).**—A solution of 1 g of sodium hydroxide in 10 ml of water was added to 2.0 g of iodo(*o*-phenylenediamine)cyclopentadienylcobalt(III) iodide, prepared from $C_5H_5Co(CO)I_2$ as described above, and 50 ml of ether in a separatory funnel, and the mixture was shaken for about 5 min. The lower aqueous phase was then separated and another 10 ml of water containing 1 g of sodium hydroxide was added. After shaking again the aqueous layer was removed, an additional 50 ml of ether was added, and the ether phase was washed twice with water. After drying, the ether was removed under reduced pressure and the greenish crystals obtained were recrystallized from about 250 ml of hexane. There was obtained 0.69 g of product.

The nmr spectrum of the compound in deuteriochloroform at 60 MHz showed a sharp singlet from the cyclopentadienyl hydrogens at δ 4.98 ppm with relative area 74, a broad singlet at δ 8.5–10 ppm with relative area $\sim$22 from the amide hydrogens, and a sharp singlet at δ 6.95 ppm of relative area 64 from the aromatic hydrogens.

***o*-Phenyleneamidooxidocyclopentadienylcobalt(III).**—A mixture of 0.8 g (2 mmol) of $C_5H_5Co(CO)I_2$,[3,4] 0.22 g (2 mmol) *o*-aminophenol, 30 ml of methylene chloride, and a solution of 5 g of anhydrous sodium acetate dissolved in 30 ml of water was stirred at room temperature for 1 hr. The blue methylene chloride layer was separated, the aqueous layer was extracted again, and the combined extracts were washed with water, dried over magnesium sulfate, and concentrated under reduced pressure. After recrystallization from hexane, 0.27 g of bronze-colored crystals was obtained.

***o*-Phenylenedioxidocyclopentadienylcobalt(III).**—A mixture of 0.16 g (4 mmol) of $C_5H_5Co(CO)I_2$,[3,4] 0.22 g (2 mmol) of catechol, 20 ml of methylene chloride, and 4 ml of 1 *M* triethylamine in methylene chloride was stirred at room temperature for 1 hr and then evaporated to dryness under reduced pressure. The product was extracted from the residue with several portions of hot hexane. The combined extracts were filtered, concentrated until crystals began to appear, and cooled to 0°. The purple crystals were isolated by filtration and quickly dried under reduced pressures because the compound hydrolyzed rapidly in moist air. There was obtained 0.17 g of product.

The nmr spectrum of the compound in deuterated acetone at 60 MHz showed sharp singlets at δ 5.57 and 7.01 ppm with relative areas of 5 and 4, respectively.

***o*-Phenyleneoxidothioxidocyclopentadienylcobalt(III).**—A mixture of 4.8 g (12 mmol) of $C_5H_5Co(CO)I_2$,[3,4] 1.5 g (12 mmol) of monothiocatechol, 320 ml of methylene chloride, and 24 ml of 1 *M* triethylamine in methylene chloride was stirred at room temperature for 1 hr, and the solution was concentrated under reduced pressure. The product was extracted from the residue with a 2:1 mixture of hexane and methylene chloride. When the blue compound was completely extracted, the extracts were concentrated on a steam bath to about 30 ml and allowed to cool to room temperature. The black solid obtained was dissolved in about 20 ml of boiling chloroform, 100 ml of pentane was added, and the solution was quickly filtered. On standing, the filtrate deposited small black prisms. There was obtained 0.028 g of product. More product could be obtained by evaporating the solvent from the mother liquors and subliming the residue at 140° ($\sim$1 mm). This gave about 0.030 g more of the product.

4-Methyl-1,2-phenylenedithioxidocyclopentadienylcobalt(III).—A mixture of 1.0 g (2.5 mmol) of $C_5H_5Co(CO)I_2$,[3,4] 0.28 g (2 mmol) of 3,4-toluenedithiol, 20 ml of methylene chloride, and a solution of 5 g of sodium acetate dissolved in 30 ml of water was stirred at room temperature for 1 hr. The methylene chloride phase was separated, and the aqueous phase was extracted again. The combined extracts and original methylene chloride solution were then washed with water and dried over magnesium sulfate. The solvent was evaporated at room temperature under reduced pressure, and the residue was recrystallized from hexane to give 0.47 g of product.

***o*-Phenyleneamidothioxidocyclopentadienylcobalt(III).**—A mixture of 0.8 g (2 mmol) of $C_5H_5Co(CO)I_2$, 0.25 g (2 mmol) of *o*-aminothiophenol, 20 ml of methylene chloride, and 4 ml 1 *M* triethylamine in methylene chloride was stirred at room temperature for 1 hr, and the solvent was evaporated under reduced pressure. The product was extracted from the residue with several portions of hot hexane. Concentrating the purple extracts and cooling gave 0.092 g of long purple needles of the product.

The nmr spectrum of this compound in deuteriochloroform at 60 MHz had a sharp singlet at δ 5.17 ppm from the cyclopentadienyl protons and a complex multiplet at δ 6.7–7.8 ppm from the aromatic protons and the amide hydrogen.

4-Nitro-1,2-phenylenediamidocyclopentadienylcobalt(III).—A mixture of 0.8 g (2 mmol) of $C_5H_5Co(CO)I_2$, 0.31 g (2 mmol) of 4-nitro-1,2-phenylenediamine, 50 ml of methylene chloride, and 5 ml of 1 *M* triethylamine in methylene chloride was stirred for 1 hr at room temperature. The solution was filtered, the residue was extracted with methylene chloride until the extracts were nearly colorless, and then the extracts were diluted with about 25 ml of hexane. Concentrating the solution to about 25 ml on the steam bath and cooling gave 0.14 g of purple-bronze crystals of the product. Another 0.1 g of product was obtained by concentrating the mother liquors further.

Acknowledgment.—The experimental work was carried out with the assistance of Mr. Joseph Keelins.