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STABILIZATION OF NEGATIVE CHARGE BY THE COBALTICINIUM NUCLEUS

II*. ACIDITY OF HYDROXY-2,3,4,5-TETRAARYL AND HYDROXY-2,3,4,5-TETRAALKYL COBALTICINIUM AND RHODICINIUM SALTS

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Summary

Hydroxy-2,3,4,5-tetra-substituted cobalticinium and rhodicinium salts exist in proteolytic equilibrium with stable cyclopentadienone complexes. The changes in IR, UV and NMR spectra upon dissociation are described. Acidity constants, K_a, have been determined spectrophotometrically for the following hydroxymetallocinium salts, $C_5R_4OH\,M\overset{+}{C}_5H_5$: R = CH_3, M = Co, 4.30 ± 0.07; R = C_6H_5, M = Co, 2.42 ± 0.05; R = C_6F_5, M = Co, —0.60 ± 0.10; R = C_6H_5, M = Rh, 2.54 ± 0.03; R = C_6F_5, M = Rh, —0.41 ± 0.10.

The acidity increases with increasing electronegativity of the R group and decreases slightly when Co^{III} is replaced by Rh^{III}. The lower acidity of the Rh compounds reflects a slightly lower electronegativity of Rh as compared to Co.

Introduction

Cyclopentadienyl tetraalkyl- or tetraaryl-cyclopentadienone cobalt or rhodium compounds (IIa-IIe) can be prepared by thermal or photochemical decomposition of cyclopentadienyl cobalt or rhodium dicarbonyl in the presence of di-substituted acetylenes (eqn. 1) [1-5]. A wide variety of other organometallic complexes including cyclobutadiene complexes and polynuclear species are also formed [3-5]. A simpler procedure which offers better yields is the thermal

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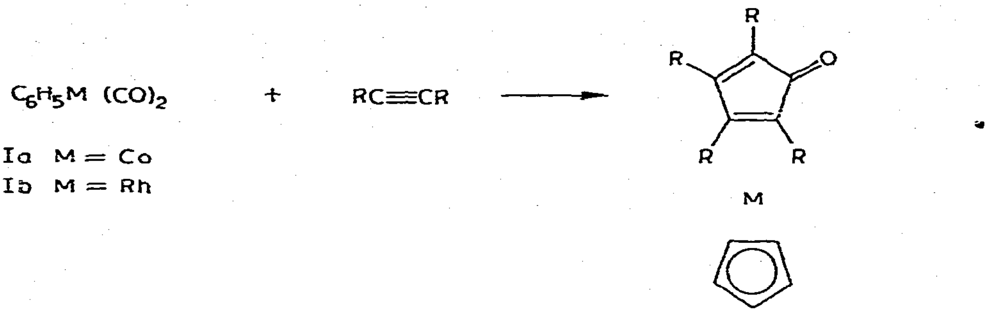
[*] For part I see ref. 7.

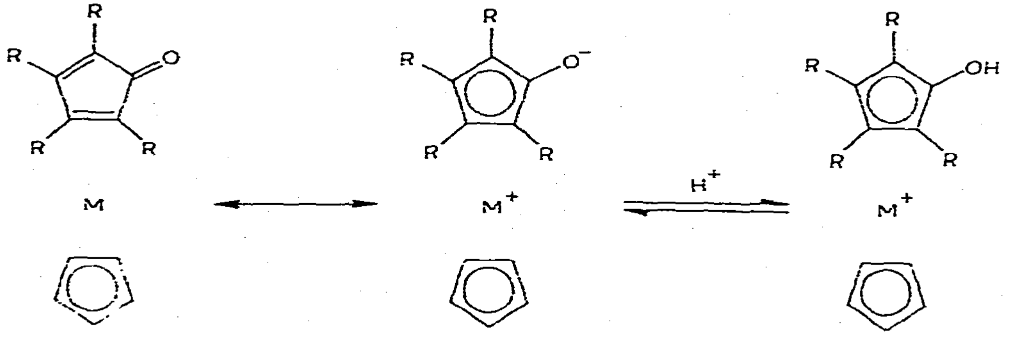
decomposition of Ia or Ib in the presence of the appropriate tetra-substituted cyclopentadienone in xylene [6,8].



Ia M = Co
Ib M = Rh

(1)

IIa R = CH_3, M = Co
IIb R = C_6H_5, M = Co
IIc R = C_6F_5, M = Co
IId R = C_6H_5, M = Rh
IIe R = C_6F_5, M = Rh



IIa-IIe IIIa-IIIe IVa-IVe

(2)

Previous investigators had proposed a strong resonance interaction between the metal atom and the carbonyl group, leading to a partial polarization of the carbonyl group [1]. The limiting cases of such resonance would be the dipolar structures IIIa-IIIe. Evidence given for single-bond character of the C—O bond was the reduction of the C=O absorption from 1710 cm^{-1} in tetraphenylcyclopentadienone to 1570 cm^{-1} in IIa. Marked changes in the ultraviolet spectrum of IIb in acidic media were attributed to interaction of the solvent with the carbonyl group [2]. In an earlier paper [6] we showed that protonation of IIb occurred in acidic solutions to produce stable hydroxycobalticinium salts IVb. In this paper we will study additional complexes of cobalt and rhodium, measure the acidity and note the changes in spectra observed.

Results and discussion

Compounds IIa-IIe were prepared as described previously [1-5,8]. The infrared spectra in chloroform and in KBr showed strong maxima in the region 1570-

TABLE 1

INFRARED SPECTRA OF THE C—O BONDS OF π-CYCLOPENTADIENONE COMPLEXES IIa-IIe AND HYDROXYMETALLOCENES IVa-IVe

Compound	ν_{max} (C=O) (cm^{-1})	Compound	ν_{max} (C—OH) (cm^{-1})
IIa	1570	IVa	1485[a]
IIb	1585	IVb	1430
IIc	1605	IVc	1467
IId	1582	IVd	1430
IIe	1615	IVe	1472
Tetraphenyl-cyclopentadienone	1710		

[a] Spectrum in KBr.

1620 cm^{-1} characteristic of the C=O group (Table 1). When chloroform solutions of IIa-IIe were shaken with concentrated hydrochloric acid or fluoroboric acid, the infrared absorption at 1570-1620 cm^{-1} disappeared and a new peak appeared in the region 1430-1485 cm^{-1}. An OH stretch also appears in the region 3500-2500 cm^{-1} but is broad and poorly defined. Salts IVa-IVe could be isolated in quantitative yield by evaporation of the chloroform [6]. The absorption of the C—O bond of IVa-IVe is approximately 200 cm^{-1} higher than that of phenols, which usually absorb around 1250 cm^{-1}. (Phenols also exhibit an additional absorption in the region 1310-1410 cm^{-1} attributed to the OH bending modes.) The C—O bond therefore still possesses substantial double bond character. The higher electronegativity of the C_6F_5 group in IIc and IIe increases the resonance interaction between the OH group and the ring, and produces absorption approximately 20-40 cm^{-1} higher than the C_6H_5 compounds IIb and IId.

TABLE 2

UV SPECTRA OF COMPOUNDS IIa-IIe AND IVa-IVe

Compound	λ_{max} (nm)				Solvent
	ε	ε	ε		
IIa	286(22500)	358(1805)	400(sh)(864)		0.1 *M* NaOH
IVa	284(32600)	350(1654)			12 *M* HCl
IIb	strong end absorption	333(11510)	510(207)		50% dioxane
IVb	strong end absorption	334(20500)	516(16)		50% dioxane/ 6 *M* HCl
IIc	265(25100)	319(14150)	400(3180)	450(1590)	80% dioxane
IVc	250(35000)	322(30000)	370(3500)	430(1400)	80% dioxane/ 14% H_2SO_4
IId	289(20200)	354(sh)(3200)	410(sh)(956)		50% dioxane
IVd	290(23100)				50% dioxane/ 6 *M* HCl
IIe	276(27600)	365(4830)			80% dioxane
IVe	277(26200)				80% dioxane/ 14% H_2SO_4

TABLE 3

NMR SPECTRA OF UNSUBSTITUTED CYCLOPENTADIENYL RINGS OF IIa-IIe AND IVa-IVe

Compound	Chemical shift δ (ppm)	Compound	Chemical shift δ (ppm)
IIa	4.62 (1.75, 1.95)[a]	IVa	5.07 (1.99, 2.05)[a]
IIb	4.90	IVb	5.64
IIc	5.33	IVc	5.80
IId	5.35, 5.37 ($J \approx 1$ Hz)	IVd	5.93
IIe	5.67	IVe	6.17

[a] CH_3 groups.

The UV spectra of compounds IIa-IIe (Table 2) exhibits strong absorption in the region 260-290 nm ($\epsilon > 20000$), a maximum at 320-350 nm (ϵ 5000-10000) and shoulders in the region 400-500 nm. In acidic media of sufficient strength compounds IIa-IIe are protonated to form the hydroxymetallocenes IVa-IVe which show greatly diminished absorption in the region 400-500 but similar absorption below 400. It is this decrease in absorption in the region 400-500 upon protonation which enables us to measure the equilibrium constants, K_a, for the dissociation of IVa-IVe.

The NMR absorption of the unsubstituted cyclopentadienyl ring of IIa-IIe (Table 3) undergoes a downfield shift of 0.4-0.7 ppm upon protonation. The methyl groups in IIa are also shifted downfield 0.1-0.2 ppm upon protonation. A small splitting ($J \approx 1$ Hz) is observed in the case of IId which is caused by coupling with the ^{103}Rh nucleus. The peaks in IVd, IVe and IIe are somewhat broader than for the Co analogs but do not show a definite splitting pattern. Increasing electronegativity of R produces a downfield shift $CH_3 < C_6H_5 < C_6F_5$. of the same magnitude in IIa-IIc and IVa-IVc. The positions of the absorptions for IVa-IVe are consistent with the hydroxymetallocene structure proposed.

The acidity constants (pK_a) for compounds IIa-IIe are given in Table 4. An effort was made to use the most polar solvents possible which would dissolve both IIa-IIe and IVa-IVe. The low solubility of compounds IIc and IIe caused particular difficulty.

The activity of the hydrogen ion in these solutions is assumed to be equal to

TABLE 4

ACIDITY OF HYDROXYCOBALTICINIUM AND RHODICINIUM SALTS

Compound	pK_a	Solvent
IIa	4.30 ± 0.07	H_2O
IIb	2.42 ± 0.05 2.28 ± 0.10	50% dioxane H_2O 50% C_2H_5OH H_2O[a]
IIc	−0.60 ± 0.10	80% dioxane H_2O
IId	2.54 ± 0.03	50% dioxane H_2O
IIe	−0.41 ± 0.10	80% dioxane H_2O

[a] Ref. 6.

its concentration. This assumption is particularly questionable in 80% dioxane, where the dielectric constant of the medium is substantially lower than that of water. The amount of data available is inadequate for a Hammett correlation, but the relationship between the acidity of compounds IVa-IVe and the electronegativity of R is clear. Compound IVa is a weak acid, approximately three times as strong as acetic acid and 10^5 times as strong as phenol. The strong electron withdrawing field, inductive and resonance effects of the cobalticinium nucleus previously demonstrated in the case of alkyl and aminocobalticinium salts [7] are here reflected in the acidity of hydroxycobalticinium salts. Increasing the electronegativity of R results in a substantial enhancement of the acidity, so that IVc and IVe are comparable in strength to the mineral acids. The decrease in electronegativity as one moves down the periodic table, is suggested by the slightly lower acidity of the rhodium compounds IVd-IVe as compared to the cobalt analogs IVb-IVc.

Experimental

Compounds IIa [1] and IIb [1,6,8] were prepared and characterized as published previously. Samples of compounds IIc [5], IId [3] and IIe [4] were obtained from the authors cited. Analytical data for all of the compounds are given in Table 5. IR spectra were measured in chloroform solution and as KBr pellets on a Perkin—Elmer 237-B Spectrophotometer. Complete spectra are available upon request. The NMR spectra were measured in chloroform-*d* with TMS internal standard on a Varian A 60-A Spectrometer.

Determination of the pK_a *of IIa-IIe*

A 1.00×10^{-2} *M* solution of IIa in water was prepared and 1 ml aliquots diluted to 10 ml with 0.1 *M* NaOH, water, pH 5, pH 4 and pH 3 potassium acid phthalate buffers and 12 *M* HCl. The solution in NaOH was taken as the spectrum of IIa and the solution in HCl as the protonated form IVa. The absorption of the solutions was measured at 10 nm intervals over the range 370-450 nm on a Zeiss PMQ-2 spectrophotometer and the relative amounts of IIa and IVa in each of the three buffer solutions calculated. From these data the pK_a was calculated.

Solutions 1.00×10^{-3} *M* in compounds IIb and 4×10^{-3} *M* in IId were prepared in dioxane and 1 ml aliquots were diluted with 4 ml of dioxane and 5 ml of the following: water, pH 3 buffer, 0.008 *M* HCl, 0.01 *M* HCl and 0.02 *M* HCl and 12.0 *M* HCl. The resulting solutions were 1.00×10^{-4} *M* IIb or 4.00×10^{-4} *M* IId in 50% dioxane containing 0-6.0 *M* HCl. The solutions containing no HCl were taken as the standards for IIb and IId and solutions containing 6 *M* HCl as standards for IVb and IVd. Spectra and pK_a values were calculated as described previously.

Solutions 10^{-3} *M* in IIc and IIe were prepared in dioxane and 1 ml aliquots diluted with 7 ml of dioxane and 2 ml of the following: water, 1.0 *M* HCl, 3.0 *M* HCl, and 70% sulfuric acid. The solutions with water gave the spectra for IIc and IIe, the solution with sulfuric acid gave the spectra for IVc and IVe, and the 3.0 *M* HCl gave the spectra of a mixture of IIc and IVc or IIe and IVe. Compounds IIc and IIe were approximately 20% protonated in the solution made

TABLE 5

ANALYTICAL DATA FOR COMPOUNDS IIa-IIe AND COMPOUND IVb

Compound	Molecular formula	M.p.	Mol. wt. (mass spec) found (calcd.)	Analysis found (calcd.)							Ref.
				C	H	Co	Br	F	O	Rh	
IIa	$C_{14}H_{17}CoO$	178-180		64.62 (64.61)	6.95 (6.86)	22.65 (22.42)					1
IIb	$C_{34}H_{25}CoO$	327-329	508 (508)	80.18 (80.31)	(4.96) (4.96)	(11.62) (11.59)					1,8
IVb (Br^- salt)	$C_{34}H_{26}BrCoO$	289-290		69.00 (69.28)	(4.70) (4.45)	9.98 (10.00)	14.00 (13.56)		2.70 (2.71)		6
IIc	$C_{34}H_5CoF_{20}O$	311-311.5	868 (868)	47.30 (47.03)	0.60 (0.58)			43.90 (43.76)			5
IId	$C_{34}H_{25}ORh$	334-336	552 (552)	73.90 (73.91)	4.57 (4.56)				2.82 (2.90)	18.65 (18.63)	3
IIe	$C_{34}H_5F_{20}ORh$	328-329	912 (912)	44.56 (44.76)	0.75 (0.55)			41.66 (41.55)	1.85 (1.75)	11.18 (11.28)	4

from 6.0 *M* HCl. More concentrated HCl solutions were immiscible with the dioxane solutions.

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