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STABILIZATION OF NEGATIVE CHARGE BY THE COBALTICINIUM NUCLEUS*

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Summary

The acidity of alkylcobalticinium salts is greatly enhanced and the basicity of aminocobalticinium salts is greatly reduced in comparison to alkyl- and amino-benzenes and -ferrocenes. The methyl hydrogens of 1,1′-dimethylcobalticinium ion exchange in 0.91 *M* NaOD in D_2O with a rate constant of 1.40×10^{-2} min^{-1} at 70°C and an activation energy of 25.4 ± 1 kcal mol^{-1}. The pK_a of benzhydrylcobalticinium ion is 15-16 at 25°C, approximately 10^{11} times more acidic than triphenylmethane. The following basicities (pK_b) were observed: aminocobalticinium, 15.6 ± 0.1, 1,1′-diaminocobalticinium, 13.5 ± 0.1 and 18.1 ± 0.1, 1-amino-1′-carboxycobalticinium, 18.06 ± 0.05. These values are interpreted in terms of strong electron-withdrawing field, inductive and resonance effects exerted by the cobalticinium moiety.

Introduction

Stabilization of carbonium ions by the α-ferrocenyl moiety has been the subject of extensive research by Hill [1], Rosenblum [2], Traylor [3], Williams [4], and others. Stabilization of the positive charge is produced by conjugation of the vacant orbital with the cyclopentadienyl ring to form a fulvenoid structure or by overlap of the vacant orbital with filled *d* orbitals on the iron atom [3,4]. However, the ferrocenyl moiety offers little stabilization to carbanions.

The cobalticinium moiety, however, because of the field effect of the positive charge and the strong electron-withdrawing inductive effect of the tripositive cobalt, should interact strongly with a negative charge or a lone pair of electrons in the α-position, but offer little stabilization to a positive charge. Furthermore, resonance of the lone pair of electrons with the cyclopentadienyl ring can produce a fulvene structure which still retains 36 electrons about the cobalt

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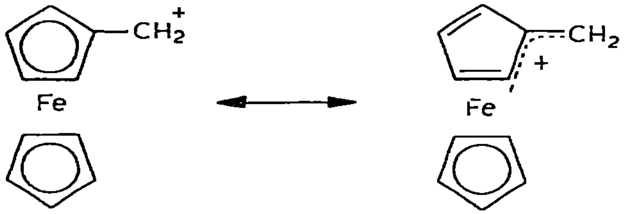
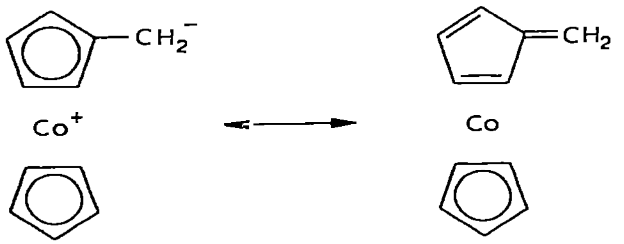
atom. The formal oxidation state of the cobalt atom in such a complex would be reduced from +3 to +1. Stable cyclopentadienylcobalt(I) diene complexes are well known, so resonance structures of this type are likely to have an important role in stabilization of adjacent negative charge.





The first evidence for resonance of this type was reported for hydroxycobalticinium complexes and the π-cyclopentadienylcyclopentadienonecobalt complexes produced from them [5], and will be discussed in greater detail in a companion paper in this series [6]. In this paper the acidity of alkylcobalticinium salts and the basicity of aminocobalticinium salts will be discussed, and an attempt will be made to assess the relative importance of field, inductive and resonance effects exerted by the cobalticinium moiety.

Results and discussion

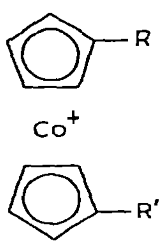
Kursanov [7] has reported that the ring hydrogens of the cobalticinium ion exchange in 10% sodium methoxide in methanol-*d* with a rate constant of 6.4×10^{-5} sec^{-1} at 50°C. The carbanion formed by removal of a proton from the ring of cobalticinium ion cannot be stabilized by resonance, but field and inductive effects enhance its stability. The carbanion formed by removal of a hydrogen α to the cobalticinium nucleus, however, can be stabilized by resonance. The rate of exchange of the α-hydrogens of 0.1 *M* 1,1′-dimethylcobalticinium bromide (I) in 1.00 *M* NaOD in D_2O (Table 1) is approximately 100 times as fast as

TABLE 1

RATE OF EXCHANGE OF METHYL HYDROGENS OF 0.1 *M* 1,1′-DIMETHYLCOBALTICINIUM BROMIDE IN DEUTERIUM OXIDE

NaOD (*M*)	*T* (°C)	$k \times 10^2$ (min^{-1})	$t_{1/2}$ (min)
0.91	70	1.40 ± 0.1	50
1.15	75	2.22 ± 0.1	31
1.02	80	3.91 ± 0.2	18
0.20	80	0.80 ± 0.05	89
		E_a = 25.4 ± 1 kcal mol^{-1}	

exchange of the ring hydrogens. In the more strongly basic solution employed by Kursanov [7] exchange of both the α-hydrogens and the ring hydrogens occurs readily and perdeuterated I can be prepared (see Experimental).



I: $R = CH_3, R' = CH_3$
II: $R = (C_6H_5)_2C^-, R' = H$
III: $R = (C_6H_5)_2\ CH, R' = H$
IV: $R = NH_2, R' = H$
V: $R = NH_2, R' = NH_2$
VI: $R = NH_2, R' = CO_2H$
VII: $R = CO_2H, R' = CO_2H$

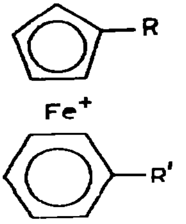
Benzhydrylcobalticinium salts (III) can be prepared from diphenylfulvene and cyclopentadienylcobalt dicarbonyl by protonation of the intermediate fulvene complex (II). When III is treated with 10% aqueous NaOH, II is regenerated and precipitates from solution. Compound II can be converted back to III by acidification. Compounds II and III exist in approximately equal amounts in a 1.8 *M* solution of KOH in 80% ethanol. The pK_a of III is therefore approximately 15-16, a factor of 10^{11} more acidic than triphenylmethane. This enhancement of acidity seems much too large to arise solely from inductive and field effects. Resonance, therefore, plays a major role. The large solubility of II in xylene and its insolubility in water indicate that II is primarily a fulvene complex rather than a cobalticinium carbanion.

The basicities of the amino groups of aniline, $C_5H_5FeC_5H_4NH_2$, $C_5H_5Co^+$-$C_5H_4NH_2$ (IV), $(C_5H_4NH_2)_2Co^+$ (V), $C_5H_4CO_2HCo^+C_5H_4NH_2$ (VI), $C_6H_6Fe^+C_5H_4NH_2$ (VIII) [8], $C_5H_5Fe^+C_6H_5NH_2$ (IX) [9], and $C_5H_4NH_2Mn$-$(CO)_3$ (XII) [10] are given in Table 2. The order of basicity predicted by field and inductive effects is the order observed: $C_6H_5NH_2 > C_5H_5Fe\ C_5H_4NH_2 >$ XII > IX ≈ VIII > IV > VI ≈ K_2 for V. Compound XII is a weaker base than aminoferrocene because of the strong electron-withdrawing effect of the carbonyl groups, but is stronger than IX, VIII, and IV because it lacks a positive charge. Although the field effects are comparable, IV should be less basic than IX and VIII because the tripositive cobalt exerts a stronger electron-attracting inductive effect than the dipositive iron atom.

TABLE 2

BASICITY OF AMINOCOBALTICINIUM SALTS AND THEIR ANALOGS

Compound	pK_b	Ref.
Aniline	9.38	
Aminoferrocene	10.35	8,11
Aminocyclopentadienylmanganese tricarbonyl	11.79	10
Benzeneaminocyclopentadienyliron(II)	13.80	8
Aminobenzenecyclopentadienyliron(II)	15.07	8
Aminocobalticinium	15.6 ± 0.1	12
1,1'-Diaminocobalticinium	13.5 ± 0.1	this work
	18.1 ± 0.1	this work
1-Amino-1'-carboxycobalticinium	18.06 ± 0.05	this work



VIII: $R = NH_2$, $R' = H$
IX: $R = H$, $R' = NH_2$
X: $R = CO_2H$, $R' = H$
XI: $R = H$, $R' = CO_2H$

Substituents in the 1′ position affect the basicity of IV markedly. An amino group enhances the basicity by a factor of 30 (actually 60, but this must be divided by 2, since there are 2 amino groups in V); whereas a protonated amino group (NH_3^+) reduces the basicity by a factor of 250. The carboxyl group in VI, which may be protonated in 50-70% sulfuric acid ($CO_2H_2^+$) also reduces the basicity by a factor of 250.

Separation of field effects (the influence of a charge as transmitted through space), inductive effects (the influence of charge as transmitted through the σ bond framework) and resonance effects (the influence of charge as transmitted through the π bonds) has always proved difficult, particularly when all three effects operate in the same direction. The data available, while not wholly adequate, allow us to draw a few conclusions:

Since an amino group when bound to an aromatic ring acts as an electron-donating group primarily through resonance, much of the enhancement of the basicity of V in comparison to IV can be attributed to resonance. The NH_3^+ group can not exert a resonance effect and the reduction of basicity must therefore be attributed to field and inductive effects. The carboxyl and protonated carboxyl groups exert field, inductive and resonance effects to reduce the basicity of VI.

Field and inductive effects apparently work in opposite directions in the case of VIII and IX. Compound IX would be more basic than VIII if field effects were more important, since the amino group on the six-membered ring is farther removed from the positive charge than the amino group on the five-membered ring. However, the cyclopentadienyl ring has a higher π-electron density than the benzene ring and exerts a greater electron-releasing inductive effect. Inductive effects are apparently more important, since VIII is more basic than IX by a factor of 20. A similar greater electron-releasing inductive effect for the cyclopentadienyl ring is observed for the carboxylic acids X and XI, where XI is a factor of 3 stronger than X [9]. These effects, however, might also be explained by differing degrees of resonance interaction between the amino group and the benzene or cyclopentadienyl rings.

A final indication of the strength of the electron-withdrawing resonance of the cobalticinium moiety is that *p*-cobalticiniumazophenol ($C_5H_5Co^+C_5H_4N_2C_6H_4OH$) shows approximately the same acidity as *p*-nitrophenol [12]. Since the cobalticinium group is much too far away from the hydroxyl to exert an inductive effect, the resonance effect of the cobalticinium azo group must be comparable to that of the nitro group. Further experimental work, such as studies of hindered rotation about the cobalticinium—substituent bond or steric inhibition of resonance, is needed to determine quantitatively the resonance effects exerted by the cobalticinium moiety.

TABLE 3

ULTRAVIOLET SPECTRA OF COBALTICINIUM SALTS

Compound							Solvent
I			267 (43000)	308 (sh) (1200)		416 (255)	H_2O
II			268 (36000)	325 (10000)		510 (8000)	4 *M* KOH in 80% EtOH
III			266 (34000)	320 (1800)		404 (400)	H_2O
IV			275 (19000)		355 (3450)	410 (980)	H_2O
IV	monoprotonated		268 (18000)	305 (3380)		405 (230)	10.8 *M* HCl
V			269 (9900)	306 (13450)	365 (3300)	420 (sh) (1690)	H_2O
V	monoprotonated		276 (16180)		358 (3720)	406 (1280)	1.5 *M* HCl
V	diprotonated		267 (39400)	310 (1120)		400 (260)	18 *M* H_2SO_4
VI			279 (16810)		360 (13140)	414 (912)	H_2O
VI	monoprotonated		273 (30000)	308 (sh) (1473)		408 (282)	18 *M* H_2SO_4
VII		222 (7300)	271 (23200)	323 (sh) (1400)		416 (263)	H_2O

The UV spectra of the cobalticinium salts I-VII are shown in Table 3. Compounds I and III show three peaks at 265-275, 310-320, and 405-415 nm typical for cobalticinium salts [12]. Introduction of the amino groups enhances absorption at 410 and 365 and in V a strong new peak appears at 306 nm. Protonation destroys the interaction between the amino group and the ring so that the spectra of monoprotonated IV and diprotonated V closely resemble the spectrum of I and monoprotonated V resembles IV. Protonation of VI produces a spectrum similar to that of VII and the monocarboxylic acid. The carboxyl group exerts little influence on the UV spectra of cobalticinium salts. Removal of the α-proton of III produces II, which shows intense absorption at 325 and 510 nm, so that even small amounts of II can be detected in the presence of III.

Experimental

Compounds I, IV and VII were prepared as described previously [12,13].

Preparation of III

Cyclopentadienylcobalt dicarbonyl, 10 g (0.056 mol) (Strem Chemical Company), diphenylfulvene, 12.8 g (0.056 mol) and 100 ml of xylene were refluxed for 12 h under nitrogen. The xylene solution was shaken with three 300 ml portions of 3 *M* HCl. The aqueous layer was extracted with xylene, clarified with charcoal and allowed to stand. A small amount of III precipitated as the chloride in fine needles. Dropwise addition of an aqueous solution of NH_4PF_6 precipitated III as the PF_6 salt (yield 15 g, 30%) which was purified by crystallization from acetone—chloroform.

Characteristic infrared absorption bands for the PF_6 salt (KBr pellet) were 3130, 3050 w, 3030 w, 1600, 1585, 1490, 1450, 1420, 1400, 1150, 1089, 1030, 1010, 935, 830 s, 740, 708, 693, 630, 553, 508 and 459 cm^{-1}. The NMR spectrum in acetone-d_6 showed δ 5.57 s (1), 5.63 s (5), 5.86 m (4), 7.37 s (4), 7.37 s (10). (Found: C, 55.06; H, 4.19; F, 22.58. Calcd.: C, 55.22; H, 4.03; F, 22.79%.)

Preparation of V and VI [14]

Cobalticinium 1,1'-dicarboxylic acid (VII) was converted to the diacyl halide by refluxing 6 h in excess thionyl chloride. The acyl chloride was converted to the azide by treatment with excess 30% aqueous sodium azide, and rearranged in concentrated sulfuric acid at 100°C. After neutralization with potassium hydroxide, precipitation of the potassium sulfate with ethanol and stripping of excess solvent, V was precipitated by dropwise addition of aqueous NH_4PF_6 and recrystallized from acetone—chloroform, (20-40% yield) m.p. 275°C (dec.). Characteristic infrared absorption bands (KBr pellet) were 3480, 3380, 3110, 1630, 1515, 1360, 1280 w, 1065 w, 1048 w, 1030 w, 830 vs and 560 cm^{-1}. The NMR spectrum in actone-d_6 showed δ 4.76 broad (2), 5.04 t (4) (J = 1 Hz), 5.22 t (4) (J = 1 Hz). (Found: C, 33.20; H, 3.52; N, 7.56; Co, 16.35; P, 8.43. Calcd.: C, 32.98; H, 3.32; N, 7.69; Co, 16.16; P, 8.52%.)

Upon acidification VI precipitated and was recrystallized from acetone—chloroform (20-30% yield). Characteristic infrared absorption bands (KBr pellet) were 3495, 3395, 3125 (C—H stretch), 3500-2300 (CO_2H group), 1695, 1630, 1533, 1485, 1410, 1360, 1292, 1170, 1050, 1030, 820 (PF_6 ion), 745, 630.

558 and 450 cm^{-1}. The NMR spectrum in acetone-d_6 showed δ 5.43 t (J = 1 Hz) (2), 5.71 m (4), 6.08 t (J = 1 Hz) (2). (Found: C, 33.82; H, 2.70; N, 3.26. Calcd.: C, 33.61; H, 2.82; N, 3.56%.)

Rate of exchange of hydrogens of dimethylcobalticinium salts (I)

For each kinetic measurement, a 1.0 g sample of I was dissolved in 100 ml of water and passed through a 30 cm column of Amberlite IRA-400 resin which had been converted to the bromide form. The solution of I bromide was evaporated to dryness and the residue dissolved in D_2O. Sufficient concentrated NaOD was added to make the solution 1.00 *M*. Approximately 0.02 *M* tetramethylammonium chloride was added as an internal standard. The solutions were heated at 70, 75 or 80°C under nitrogen and samples withdrawn every 5-10 min until 20 samples had been taken. An infinity point was taken after 24 h. The NMR spectrum of each sample was scanned on a Varian A60A NMR spectrometer. The methyl region at δ 2.0 was integrated and compared with the rings at δ 5.9 and the internal standard at δ 3.5. Rate constants and half lives were calculated by the method of least-squares. A sample of α-deuterated I was collected after several half-lives by addition of NH_4PF_6. Characteristic IR peaks (KBr pellet) 3120, 2315, 1482, 1470, 1400, 1342, 1375, 1275, 1070, 1045, 1020, 940, 825 vs and 700 cm^{-1}. Fully deuterated material was prepared by the procedure of Kursanov [7]. Characteristic IR peaks (KBr pellet) 2330, 1445, 1405 w, 1305, 1067, 1047, 850 vs, 755 and 680 cm^{-1}.

Acidity of benzhydrylcobalticinium ion

A 10^{-3} *M* stock solution of III in 80% ethanol was diluted with 4.4 *M* KOH in ethanol to prepare solutions 10^{-4} *M* in III and 0, 1.0, 1.8, 2.7 and 4.0 *M* in KOH. Because of the extreme air sensitivity of II all solutions were flushed with nitrogen and all operations conducted under nitrogen.

The cuvette was sealed with a ground glass stopper prior to scanning. Visible spectra from 400 to 650 nm were scanned on a Beckman DB recording spectrophotometer. Compound II shows a strong maximum at 515 nm (ϵ 24000) while III is essentially transparent at that wavelength. Approximately equal amounts of II and III were present in 1.8 *M* KOH. The absolute basicity of this medium is difficult to measure but a pH of 15-16 is a reasonable estimate. The pK_a of III is therefore 15-16.

Basicity of aminocobalticinium salts

The UV spectra of IV, V and VI and their protonated forms are given in Table 3. A 1.00×10^{-3} *M* stock solution of V was prepared in distilled water and used to prepare 1.00×10^{-4} *M* solutions of V in pH 7 buffer and 0.10, 0.20, 0.30, 0.50, 1.0, 1.5, 2.0, 6.0 and 12.0 *M* HCl. Little change was observed in the spectrum from 1.0 to 2.0 *M* HCl. The spectrum in 1.5 *M* HCl was chosen as the spectrum of the monoprotonated form. Absorption at 300, 306 and 310 nm was used to calculate pK_a. The halfway point of the first neutralization occurred at approximately 0.3 *M* HCl. Since concentrated HCl was not sufficiently acidic to protonate both amino groups, 1.00×10^{-4} *M* solutions of V were prepared in 20, 30, 50, 55, 60, 65, 70, 75, 85 and 96% sulfuric acid. The spectrum in 20% sulfuric acid resembled that in 1.5 *M* HCl and the spectra in 75-96% sulfuric acid were identical. The halfway point of the second neutralization occurred in approximately 60% sulfuric acid. From the known Hammett acidities [15] of sulfuric acid solutions, the basicity constant for the second protonation was determined.

The basicity constant for VI in sulfuric acid was determined by the same procedure as for V. The amino group in VI is approximately half protonated in 60% sulfuric acid. Protonation of the carboxyl of VI may also occur but cannot be detected spectrophotometrically.

Acknowledgements

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