Gas Chromatography.—The analyses were carried out on the Perkin-Elmer 226 fitted with a 150 ft × 0.01 in. Golay column. Authentic samples were utilized to identify the products.[13]

Epoxidation of Olefins.—The olefins were epoxidized with *m*-chloroperbenzoic acid in methylene chloride.[4]

Typical Procedure for the Lithium–Ethylenediamine Reduction of Epoxides.—To a 100-ml three-necked flask fitted with a septum outlet, thermometer, and magnetic stirring bar under nitrogen was added 10 mmol of norbornene oxide and 10 ml of anhydrous ethylenediamine. Then 0.21 g (30 mg-atoms) of lithium wire cut into 2-mm pieces and washed with pentane was added at room temperature with vigorous stirring. The reduction is exothermic above room temperature, but a water bath was necessary to keep the temperature at 50° for 1 hr. Many colors are observed during the reduction, but the reduction is complete when a blue-purple color persists. The reaction mixture was cooled and 10 ml of water was added to destroy excess reagent. Extraction with 20 ml of tetrahydrofuran, drying ($MgSO_4$), addition of a calibrated internal standard, and analysis by glpc indicated an 87% yield of 99.3% 2-norbornanol, 0.2% 7-norbornanol, and 0.5% nortricyclanol (Ucon LB 550X at 100°) in order of increasing retention time. No 2-norbornanone, norbornene oxide, or norbornene were detected.

Reduction of Norbornene Oxide with $LiAlH_4$.—To a flame-dried 50-ml round-bottomed flask was added 5 ml of a 1 *M* $LiAlH_4$ solution in diglyme, 15 ml of dry and peroxide-free diglyme, and 0.55 g (5 mmol) of norbornene oxide under nitrogen. After 67 hr at 100° there was obtained a 77% yield of 98.1% *exo*- and 1.9% *endo*-norbornanol, and a trace of 7-norbornanol. If the same reduction was run in the presence of air, the amount of *endo*-norbornanol increased to 7% in 24 hr.[14] Although no 7-norbornanol was detected, there was obtained 9% an unknown with a shorter retention time than *exo*-norbornanol (Ucon LB 550X at 100°).

Reduction of 7,7-Dimethylnorbornene Oxide with $LiAlH_4$.—The crude oxide was reduced at 100° in 24 hr with $LiAlH_4$ in diglyme in the presence of dry air. There was obtained 19% recovered oxide, 18% an unknown (alcohol), 6% 5,5-dimethyl-*exo*-2-norbornanol (?), 2.5% 7,7-dimethyl-2-*exo*-norbornanol, 1% 6,6-dimethyl-2-norbornanol, 47.2% 7,7-dimethyl-2-*endo*-norbornanol, and seven other minor peaks.

Reduction of Norbornene Oxide with Li in Ethylamine.—To a 50-ml flask fitted with a magnetic stirring bar, Dry Ice condenser, and a nitrogen inlet was added 1.1 g (10 mmol) of norbornene oxide and 20 ml of ethylamine *via* a syringe cooled with Dry Ice. The mixture was cooled to −20° and 0.21 g (30 mg-atoms) of Li wire cut in 2-mm pieces was added. The reduction was vigorous. In 5 min a persistent blue color appeared. The Dry Ice condenser was removed and the ethylamine swept out with nitrogen. Water (20 ml) was added; extraction with 20 ml of ether gave on evaporation an 89% yield of 2-norbornanol with only traces of other isomers.

Side Reactions in Reductions with Li in Ethylamine.—After a mixture of 10 ml of ethylamine and 0.21 g (30 mg-atoms) of Li at −20° remained blue for 5 min, a solution of 1.1 g (10 mmol) of norbornene oxide in 30 ml of petroleum ether (35–37°) was added. The blue color dissipated after only 1 mmol of the epoxide solution was added. After stirring the mixture for 15 min at −20°, the work-up indicated an 87% yield of unreacted epoxide, 10% 2-*exo*-norbornanol, and 3% nortricyclanol. In contrast, if the epoxide was added 1 min after the appearance of the blue color, 1% norbornene oxide, 64% 2-norbornanol, and 35% nortricyclanol were obtained.

Reduction of Nonhindered Epoxides.—The lithium–ethylenediamine reductions of nonhindered epoxides such as 1-butene oxide are quite exothermic. The reduction can be controlled with ice cooling.

Registry No.—Norbornene, 498-66-8; 7,7-dimethylnorbornene, 6541-60-2; 1-methyl-2-norbornene, 822-73-1; 2-methyl-2-norbornene, 694-92-8; 1,7,7-trimethylnorbornene, 464-17-5; 2-methylenenorbornene, 497-35-8; 2-methylene-7,7-dimethylnorbornane, 471-84-1; 1-methylcyclohexene, 591-49-1; 1-butene, 106-98-9; 2-methyl-2-butene, 513-35-9.

[13] H. C. Brown and J. H. Kawakami, *J. Amer. Chem. Soc.*, **92**, 1990 (1970).

[14] S. V. Vitt and N. S. Martinkova, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 524 (1964); *Chem. Abstr.*, **60**, 15696 (1964). These authors observed that when benzhydrol-1-*d* and its potassium salt are heated under nitrogen in diglyme and lithium aluminum hydride, benzhydrol loses some deuterium.

Synthesis and Properties of Cobalticinium Salts.
I. Synthesis of Monosubstituted Cobalticinium Salts[1]

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Procedures for synthesis of methyl (**2**, **3**), carboxy (**4**, **5**), chlorocarbonyl (**6**), carbalkoxy (**7**), amino (**9**), and nitro (**10**) cobalticinium salts are given. The amino derivative shows extremely low basicity ($pK_b = 15.6 \pm 0.1$) but, in marked contrast to the ferrocene analog, can be diazotized and coupled with phenol to form an azo dye **10**, $pK_a = 7.05 \pm 0.03$. The substituted cobalticinium salts show greater resistance toward oxidation than the corresponding ferrocene analogs and are not degraded by concentrated mineral acids or aqueous base. Hydroxy-2,3,4,5-tetraphenylcobalticinium ion, **15**, exists in proteolytic equilibrium with the stable π-cyclopentadienyltetraphenylcyclopentadienonecobalt complex, **14**, $pK_a = 2.3 \pm 0.1$ in 50% ethanol. Procedure for synthesis of salts of **15** and the acetoxy derivative **16** from **14** are given.

Cobalticinium salts, in contrast to the isoelectronic ferrocene analogs, show strong resistance to oxidation, even by strong oxidizing agents such as fuming nitric acid, potassium permanganate, and ozone.[3] Gill and Mann[4] have found that ferrocene derivatives act as potent haptens, greatly enhancing the ability of synthetic peptides to induce formation of antibodies, but these compounds are degraded by enzymes of the host organism. They proposed the use of the more stable cobalticinium salts as haptens, as tracers in biological systems, as electron dense markers in electron microscopy and X-ray crystallography, and as carriers of Co^{60} in radiotherapy. We have therefore undertaken a systematic study of the synthesis and chemical properties of cobalticinium salts and their rhodium and iridium analogs.

Results and Discussion

Since electrophilic substitution on the cobalticinium nucleus is yet to be accomplished, substituted derivatives must be prepared directly from substituted cy-

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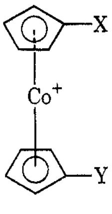
[1] Part II: J. E. Sheats, C. E. Whitten, and W. M. Minihane, paper in preparation.

[2] National Science Foundation Science Faculty Fellow, 1969. Chemistry Department, Rider College, Trenton, N. J. 08602.

[3] E. O. Fischer and G. E. Herberich, *Chem. Ber.*, **94**, 1517 (1961).

[4] T. J. Gill, III, and L. T. Mann, Jr., *J. Immunology*, **96**, 906 (1966).

clopentadienes. Methylcyclopentadiene, readily available commercially, was chosen as the starting material for the syntheses. A mixture of **1**, **2**, and **3** was prepared in 20–30% yield from equimolar amounts of cyclopentadiene, methylcyclopentadiene, and cobalt bromide by a modification of the amine method for preparing metallocenes.[5] Pyrrolidine, which is a stronger base and a better solvent for cobalt bromide, was used instead of diethylamine as the solvent for the reaction. Hexafluorophosphate was employed as the counterion in most of the subsequent syntheses, since the resulting salts crystallized readily, were not hygroscopic, and showed moderate solubility (1–10 g/l.) in both water and polar organic solvents. Elemental analyses of these compounds, however, usually showed a low phosphorus content, possibly because of partial degradation of the hexafluorophosphate ion. When analytical samples were required, the compounds were converted to the tetraphenylborates, which could be purified more readily.

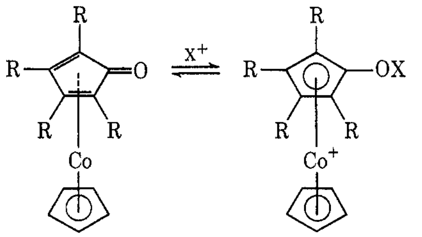


1, $X = H; Y = H$
2, $X = CH_3; Y = H$
3, $X = CH_3; Y = CH_3$
4, $X = CO_2H; Y = H$
5, $X = CO_2H; Y = CO_2H$
6, $X = COCl; Y = H$
7, $X = CO_2CH_3; Y = H$
8, $X = CON_3; Y = H$
9, $X = NH_2; Y = H$
10, $X = NO_2; Y = H$
11, $X = \text{-N=N-}p\text{-}C_6H_4OH; Y = H$

Attempts to separate the hexafluorophosphates of **1**, **2**, and **3** by fractional crystallization or column chromatography were unsuccessful. The methyl groups were therefore oxidized to carboxyls by treatment with basic aqueous potassium permanganate.[3] Addition of excess sodium hexafluorophosphate to the basic solution precipitated **1** quantitatively. After acidification, a mixture of the mono- and dicarboxylic acid derivatives, **4** and **5**, precipitated as hexafluorophosphate salts. Compound **4** dissolved readily in acetone, whereas **5** was virtually insoluble. The acyl chloride **6** was prepared from **4** and converted to the methyl ester **7** and the acyl azide **8**. Rearrangement of **8** in concentrated sulfuric acid at 130° produced a 60% yield of the amino derivative **9** and a 20% yield of **4**. No sulfonic acid derivatives of either **4** or **9** were obtained.

Aminocobalticinium ion **9**, $pK_b = 15.6 \pm 0.1$, exhibits the very low basicity expected for a highly deactivated aromatic amine bearing a positive charge. It is less basic than benzene–aminocyclopentadienyl iron(II) fluoroborate,[6] **12**, $pK_b = 14.6$, which also bears a positive charge and the neutral molecules aminocyclopentadienylmanganesetricarbonyl,[7] **13**, $pK_b = 11.79$, and aminoferrocene,[8] $pK_b = 10.35$. In contrast to aminoferrocene, which is destroyed rapidly by atmospheric oxygen, nitrous acid or other oxidizing agents, **9** can be oxidized by hydrogen peroxide to the nitro derivative **10** and can be diazotized in hydrochloric acid. Compounds **12** and **13**, although less stable toward oxidation than **9**, can also be diazotized.[6,7] Coupling of the diazonium salt formed from **9** with phenol in basic solution produced a brilliantly colored azo dye **11**. Compound **11** changes color from yellow in aqueous acid to red in aqueous base, $pK_a = 7.05 \pm 0.03$, and is blue in basic alcohol solutions. The structural changes accompanying the color changes are currently under investigation.

Hydroxycobalticinium salts have been prepared previously,[9] and exist in proteolytic equilibrium with stable π-cyclopentadienyl-π-cyclopentadienone–cobalt(I) complexes.[10,11] Because of the strong electron-withdrawing effect of the tripositive cobalt and the net positive charge, hydroxycobalticinium salts should be much stronger acids than phenol. We wished to determine the acidity constant of a hydroxycobalticinium salt and compare its ir and uv spectra with those of the other substituted cobalticinium salts. The bromide, perchlorate, and fluoroborate salts of **15** were prepared by shaking a chloroform solution of **14** with a concentrated aqueous solution of the appropriate acid.



14, $R = C_6H_5$

15, $R = C_6H_5; X = H$
16, $R = C_6H_5; X = COCH_3$

The C=O peak in the ir spectrum shifted from 1585 cm^{-1} in **14** to 1430 cm^{-1} in **15**, indicating a substantial decrease in bond order, and a broad O—H stretch appeared at 3200–3500 cm^{-1}. The π-cyclopentadienyl peak in the nmr spectrum shifted from δ 4.90 in **14** to δ 5.64 in **15** which is comparable to the value δ 5.53 for the unsubstituted ring of the amino derivative **9** (Table I). Thus, spectral evidence indicates that **15** is a hydroxycobalticinium ion, rather than the hydrogen-bonded complex previously postulated for solutions of the tetramethyl analog of **14** (**14**, $R = CH_3$) in aqueous perchloric acid.[11] The dissociation constant of **15** (chloride salt), $pK_a = 2.28 \pm 0.1$ in 50% ethanol, was determined spectrophotometrically. Thus **15** is approximately 10^7 times as acidic as phenol.

When **14** was heated with acetyl chloride, the acetoxy derivative **16** was obtained, which was isolated as the tetraphenylborate salt. Hydrolysis of **16** to regenerate **14** occurred rapidly in aqueous solution. An attempt to displace the acetoxy group with sodium iodide in acetone also regenerated **14**. Hopefully, with a more powerful leaving group attached to the oxygen, nucleophilic substitution on the ring can be accomplished.

Spectra of Cobalticinium Salts.—Monosubstituted cobalticinium salts show a sharp peak at 3120 cm^{-1} for the C–H stretch and a peak of medium intensity at 1412 cm^{-1} for the unsubstituted ring, but lack the sharp peaks at 1110 and 1000 cm^{-1} commonly observed in monosubstituted ferrocene derivatives. The spectra of

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[5] Norman Rabjohn, Ed., "Organic Syntheses," Coll. Vol. IV, Wiley, New York, N. Y., 1963, p 476.

[6] A. N. Nesmeyanov, N. A. Vol'kenau, and L. S. Isaeva, *Dokl. Akad. Nauk SSSR*, **183**, 606 (1968).

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[10] R. Markby, H. W. Sternberg, and I. Wender, *Chem. Ind. (London)*, 1381 (1959).

[11] G. N. Schrauzer and G. Kratel, *J. Organometal. Chem.*, **2**, 336 (1964).

TABLE I

NMR SPECTRA OF COBALTICINIUM HEXAFLUOROPHOSPHATES AND FERROCENE ANALOGS

	Cobalticinium, δ, ppm				Ferrocene,[c,j] δ, ppm			
Substituent	Unsubstituted ring	H_α	H_β	Other	Unsubstituted ring	H_α	H_β	Other
H	6.25[a]				4.05			
CH_3	6.13[b]	6.10	6.10	2.42[f]	3.99[k]	3.94	3.94	1.96
CO_2H	6.04[a]	6.33	6.09					
COCl	6.00[d]	6.41	6.10					
CO_2CH_3	6.00[b]	6.33	6.07	3.97[f]	4.12	4.27	4.09	
NH_2	5.53[a]	5.50	5.38	5.69[g]	3.95	3.80	3.70	
NO_2	6.23[a]	6.80	6.17		4.26	5.13	4.37	
N=N-*p*-C_6H_4OH	5.60[a]	6.19	5.67	6.96, 7.11[h] 7.80, 7.96				
OH, 2,3,4,5-$(C_6H_5)_4$[l]	5.64[e]			6.9–7.5[i]				
OAc, 2,3,4,5-$(C_6H_5)_4$	5.97[e]			2.25,[f] 6.7–6.9[i] 7.2–7.5				
O^-, 2,3,4,5-$(C_6H_5)_4$[m]	4.90[e]			7.1–7.3, 7.5–7.8[i]				

[a] Spectra in acetone. [b] Spectra in acetone-d_6. [c] Spectra in CCl_4. [d] Spectra in CF_3CO_2H. [e] Spectra in $CDCl_3$. [f] CH_3 group. [g] NH_2 group. [h] Phenol ring AB pattern. [i] C_6H_5 groups. [j] G. G. Dvoryantseva, S. L. Portnova, K. I. Grandberg, S. P. Gubin, and Y. N. Sheinker, *Dokl. Akad. Nauk SSSR.*, **160,** 1075 (1965). [k] Y. Nagai, J. Hooz, R. A. Benkeser, *Bull. Soc. Chem. Jap.*, **37,** 53 (1964). [l] Registry no., 12427-61-1. [m] Registry no., 12427-57-5.

TABLE II

UV SPECTRA OF COBALTICINIUM SALTS

Substituent	λ_{max}, mμ (ε)				
H[a]		264 (33,400)	300 sh (1200)	409 (200)	
1,1′-Di-CH_3[b]		267 (34,000)	308 sh (1200)	416 (255)	
CO_2H[a]	235 (4000)	272 (26,500)	315 (1700)	414 (246)	
1,1′-Di-CO_2H[b]	222 (7300)	271 (23,200)	323 sh (1400)	416 (263)	
NH_2[b]		275 (19,000)	355 (3450)	410 (980)	
NH_3^+[c,h]		268 (28,000)	305 sh (1200)	405 (230)	
N=N-*p*-C_6H_4OH[a]	210 (23,000)	268 (15,000)	358 sh (5800)	416 (7290) 395 (9600)[f]	
N=N-*p*-$C_6H_4O^-$[a,i]	211 (52,500)	265 (13,130)	296 sh (6260)	410 (6720) 395 (4500)	575 (18,700) 530 (13,700)[g]
O^-, 2,3,4,5-$(C_6H_5)_4$[d]	Strong end absorption		334 (15,000)	400 sh (2100)	510 sh (508)
OH, 2,3,4,5-$(C_6H_5)_4$[d]	Strong end absorption		334 (19,000)	400 sh (2000)	510 sh (10)
OAc, 2,3,4,5-$(C_6H_5)_4$[e]		230 (43,500)	335 (13,700)	395 sh (2700)	510 sh (70)

[a] Spectrum in 95% ethanol. [b] Spectrum in H_2O. [c] Spectrum in 10.8 *M* HCl. [d] Spectrum in 50% ethanol. [e] Spectrum in CH_3CN. [f] Spectrum in 0.100 *M* HCl. [g] Spectrum in 0.100 *M* NaOH. [h] Registry no., 12427-44-0. [i] Registry no., 12427-52-0.

the 1,1′ disubstituted derivatives lack the peak at 1412 cm^{-1} but are otherwise very similar to those of the monosubstituted derivatives.

The nmr spectrum of a monosubstituted cobalticinium salt (Table I) consists of a sharp singlet for the unsubstituted ring and an A_2B_2 pattern of two triplets with peak separation of ≃2 Hz for the substituted ring. The triplets are located upfield from the singlet in compounds with electron-releasing substituents and downfield in compounds with electron-withdrawing substituents. A tentative assignment of the downfield triplet to the hydrogens α to the substituent can be made by comparison with the ferrocene analogs.[12,13] Because of the strong electron-withdrawing effect of the tripositive cobalt, the peaks for the cobalticinium salts are shifted 1.5–2.0 ppm downfield from the peaks for the corresponding ferrocene derivatives.

The uv spectra of cobalticinium salts (Table II) show strong end absorption, a peak at 260–275 mμ, a shoulder at 300–325 mμ, and a peak at 400–415 mμ. Both electron-donating and electron-withdrawing substituents diminish the absorbance at 260–275 mμ. The corresponding ferrocene derivatives[14] show similar peaks with weaker absorbance at 20–30-mμ longer wavelengths.

Experimental Section

All chemicals were reagent grade unless otherwise specified. Melting points and boiling points are uncorrected. Ir spectra were measured on a Beckman IR-10 spectrophotometer; uv spectra on a Perkin-Elmer 202 spectrophotometer; nmr spectra on a Varian A-60 spectrometer. The extinction coefficients used for the determination of values of pK_a and pK_b were measured on a Zeiss PMQ-II spectrophotometer. Elemental analyses were performed by C. F. Meade of the Microanalytical Laboratory of the University of Massachusetts.[15]

Synthesis of Cobalticinium (1), Methylcobalticinium (2), and 1,1′-Dimethylcobalticinium (3) Salts.—Methylcyclopentadiene and cyclopentadiene were prepared from the dimers by the procedure of Reynolds and Wilkinson.[16] Pyrrolidine (technical grade) was dried ($CaSO_4$) and distilled, bp 86–87°. Anhydrous cobalt(II) bromide, 83 g (0.4 mol), was added in small portions with continuous stirring to a solution of 80 g (1.0 mol) methylcyclopentadiene and 65 g (1.0 mol) cyclopentadiene in 360 ml of pyrrolidine at 0° in a nitrogen atmosphere. The solution was

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[12] D. W. Slocum, T. R. Englemann, R. Lewis, and R. J. Kurland, *J. Chem. Eng. Data*, **13,** 378 (1968).

[13] D. W. Slocum, P. S. Shenkin, and T. R. Engelmann, "Proceedings of the Fourth International Conference on Organometallic Chemistry," Bristol, U. K., July 27–Aug 1, 1969, p G-5.

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[15] Oxygen analyses were performed by the procedure of C. F. Meade, D. A. Keyworth, V. T. Brand, and J. R. Deering, *Anal. Chem.*, **39,** 512 (1967). The procedure for degradation of cobalticinium salts for cobalt analysis will be described by C. F. Meade in a future publication.

[16] L. T. Reynolds and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **9,** 86 (1959).

allowed to warm to room temperature and the stirring continued for 12 hr. The solvent was evaporated on a rotary evaporator and the purple residue dissolved in 1–2 l. of hot water. A green residue containing cobalt(II) oxide remained. The aqueous solution was extracted with ether to remove unreacted cyclopentadiene and clarified with charcoal. The mixture of **1**, **2**, and **3** was precipitated as the hexafluorophosphate salts by dropwise addition of a solution of 40–50 g of sodium hexafluorophosphate in 150 ml of water: yield 34 g (25%); ir (KBr) 3120, 2920, 2860, 1478, 1465, 1415, 1385, 900–800 (vs) (PF_6^-), 550 and 440 cm^{-1}. The nmr spectrum in trifluoroacetic acid showed sharp singlets for **1** at δ 6.23; **2** at 6.13 (5), 6.10 (4), and 2.42 (3); and **3** at 5.98 (8), and 2.39 (6). The assignments were confirmed by addition of authentic samples of **1** and **3** to the mixture. Integration of the spectrum showed a composition of 5% **1**, 65% **2**, and 30% **3**. Proportions of the three components varied when the synthesis was repeated, but the yield of **2** was usually at least 50%. An attempt to prepare **1**, **2** and **3** from a mixture of sodium cyclopentadienide and sodium methylcyclopentadienide in THF produced a 30% yield of **1** with only traces of **2** and **3** and large amounts of tarry byproducts.

Preparation of Carboxycobalticinium (4) and 1,1′-Dicarboxycobalticinium (5) Salts.—A solution of 26 g (0.17 mol) of potassium permanganate, 3.6 g (0.09 mol) of sodium hydroxide, and 18 g ($\simeq$0.05 mol) of the mixture of **1**, **2**, and **3** in 400 ml of water was heated at 95° for 3 hr. The hot solution was filtered through asbestos to remove the manganese dioxide. Sodium hexafluorophosphate, 10 g, was added and the solution chilled. Approximately 1 g of **1**, identified by its nmr spectrum, was obtained. Dropwise addition of 6 *M* HCl produced a curdy yellow precipitate of the carboxylic acids **4** and **5**, yield 14 g (70%). The nmr spectrum in 96% sulfuric acid gave clearly resolved signals for **4** at δ 6.28 (t, 2, J = 2 Hz), 5.93 (t, 2, J = 2 Hz), 5.86 (s, 5), and **5** at 6.36 (t, 4, J = 2 Hz), 6.10 (t, 4, J = 2 Hz), corresponding to a mixture of 75% **4** and 25% **5**.

The precipitate was washed repeatedly with hot acetone. Compound **4** dissolved readily (solubility 10 g/l.), whereas **5** was virtually insoluble (<0.1 g/l.). The acetone solution was evaporated and 10 g of **4** obtained as yellow flakes: ir (KBr) 3120, 3000–2500 (O–H stretch), 1710 (s), 1490, 1410, 1395, 1295, 1170, 1030 (s), 820 (s), 552, 490 (w), 468 and 440 (w) cm^{-1}.

A 378-mg (1 mmol) sample of **4** was dissolved in 100 ml of water and precipitated by dropwise addition of a solution of 342 mg of sodium tetraphenylborate in 50 ml of water. The precipitate was crystallized twice from acetone–chloroform and dried overnight at 80° *in vacuo*, mp 234–235° dec.

Anal. Calcd for $C_{35}H_{30}BCoO_2$: C, 76.11; H, 5.47; O, 5.79; Co, 10.67. Found: C, 75.90; H, 5.42; O, 5.80; Co, 10.73.

Chlorocarbonylcobalticinium Hexafluorophosphate (6).—A 10-g sample of **4** (hexafluorophosphate salt) was refluxed in 500 ml of thionyl chloride for 24–48 hr. As the reaction progressed, the peaks in the ir (KBr) at 1710, 1490, 1395, and 1295 cm^{-1} disappeared and the carbonyl chloride doublet at 1770 and 1740 cm^{-1} appeared. When the reaction was complete, the solution was concentrated to 150 ml, chilled, and filtered. Approximately 8 g of **6** (probably a mixture of chloride and PF_6^- salts) was obtained as yellow crystals: ir (KBr) 3120, 1770 (s), 1740 (s), 1445, 1420, 1404, 1373, 1240 (s), 1048, 945, 830 (s), 560, and 460 cm^{-1}. Compound **6** hydrolyzed rapidly in a moist atmosphere but could be stored almost indefinitely in a desiccator.

Carbomethoxycobalticinium Salts (7).—A 367-mg sample of **6** was refluxed 30 min in 40 ml of absolute methanol. The ester was precipitated by dropwise addition of 5 ml of a saturated solution of sodium hexafluorophosphate in methanol: yield 192 mg (50%); ir (KBr) 3120, 1725 (s), 1472, 1435, 1418, 1398, 1370, 1285 (s), 1205, 1160 (s), 1030, 965, 830 (s), 560 (s), 510, 475, and 278 cm^{-1}. The tetraphenylborate of **7**, precipitated by the same procedure, was recrystallized twice from acetone–chloroform, mp 215° dec.

Anal. Calcd for $C_{36}H_{32}BCoO_2$: C, 76.34; H, 5.69; O, 5.65; Co, 10.41. Found: C, 76.24; H, 5.80; O, 5.64; Co, 10.40.

Carbonylazidocobalticinium Salts. (8).—An 8.5-g sample of **6** was stirred with 100 ml of 30% aqueous sodium azide at 0° for 30–60 min until the carbonyl chloride peaks in the ir at 1780 and 1745 cm^{-1} disappeared and a carbonyl peak appeared at 1704 cm^{-1}. No hydrolysis to the carboxylic acid, which would also absorb at 1490, 1395, and 1295 cm^{-1} was observed. When the reaction was complete, the yellow precipitate was collected and dried by suction filtration: yield 7 g (probably a mixture of azide and hexafluorophosphate salts); ir (KBr) 3120, 2230, 2190, 2140 (s) (N_3 group), 1690 (s), 1460, 1418, 1400, 1375, 1270 (s), 1180 (s), 1060 (w), 1045 (w), 1000 (w), 950, 830 (s), 560, 500, 450, and 275 cm^{-1}.

Aminocobalticinium Salts (9).—The crude azide **9** (7 g) was dissolved in a solution of 34 ml of 96% sulfuric acid and 7 ml of fuming sulfuric acid. Sodium azide, 1 g, was added and the solution heated on a steam bath for 1 hr, then on a hot plate at 110–130° for an additional 1 hr. Gas evolution was initially rapid but gradually subsided. The solution was poured over 100 g of ice, neutralized by addition of 200 ml of 6 *M* sodium hydroxide in small portions, and diluted with 800 ml of 95% ethanol. A semisolid mass of sodium sulfate precipitated. The alcohol layer was decanted and the solid washed repeatedly with ethanol. The ethanol solutions were combined and concentrated to 50–100 ml on a rotary evaporator. (If the solution were evaporated to dryness, a black residue formed and the yield was reduced.) After treatment with charcoal, the amino derivative **9** was precipitated as the hexafluorophosphate salt, yield 3.6 g (57%). Acidification of the mother liquor produced 1.7 g of **4** (24%). Since the mother liquor was only faintly colored, sulfonation of either **8** or **9** must be only a minor side reaction. The crude amine was recrystallized from acetone–chloroform: mp 324–325° dec; ir (KBr) 3500, 3400, 3240, 3120, 1630 (s), 1530 (s), 1410, 1380, 1050 (w), 1030 (w), 1010 (w), 830 (s), 560 and 440 cm^{-1}. The extinction coefficients of the amine **9** in water [uv max 275 mμ (ϵ 19,000), 355 (3450), 410 (980)]; the protonated amine in 10.8 *M* HCl [uv max 267 mμ (ϵ 28,000), 305 (1200), 405 (230)]; and a mixture of the two in 6.08 *M* HCl were measured over the 300–410-mμ region on a Zeiss PMQ-II spectrophotometer. The amine was calculated to be 77% protonated in 6.08 *M* HCl. Substituting an effective pH of −2.12 for 6.0 *M* HCl given by the Hammett acidity funtion[17] into the Henderson–Hasselbalch equation gave $pK_a = -1.60 \pm 0.1$ for the protonated amine.

The tetraphenylborate of **9** was also prepared and recrystallized from acetone–chloroform, mp 241–243° dec.

Anal. Calcd for $C_{34}H_{31}BCoN$: C, 78.03; H, 5.97; N, 2.68; Co, 11.26. Found: C, 77.80; H, 6.04; N, 2.82; Co. 11.00.

Preparation of Nitrocobalticinium Salts (10).—A 200-mg sample of **9** (0.6 mmol) was added to a solution of 5 ml of 30% hydrogen peroxide and 5 ml of trifluoroacetic acid. The solution was heated at 50–70° for 30 min and allowed to cool, and **10** precipitated as the hexafluorophosphate salt. The crude material was recrystallized from hot water: yield 84 mg (40%); ir (KBr) 3140, 1550 (s), 1420, 1375 (s), 1345, 1020 (w), 830 (s), 720, 555, 495, 472, and 275 cm^{-1}. A portion of **10** was precipitated as the tetraphenylborate, and recrystallized from acetone–chloroform, mp 199–202° dec.

Anal. Calcd for $C_{34}H_{29}BCoNO_2$: C, 73.80; H, 5.28; N, 2.53; O, 5.78. Found: C, 74.00; H, 5.50; N, 2.29; O, 5.48.

Diazotization of Aminocobalticinium Salts.—Aminocobalticinium hexafluorophosphate, 0.700 g (2 mmol), was diazotized in 50 ml of 6 *M* hydrochloric acid at 0° by dropwise addition of 138 mg (2 mmol) of sodium nitrite in 2 ml of water. The solution was stirred for 5 min and then poured into a solution of 1.0 g of phenol (fivefold excess) and 12.5 g of sodium hydroxide (5% excess) in 100 ml of water. A deep purple color formed immediately. After 10 min, the solution was acidified with 3 *M* HCl, extracted repeatedly with ether to remove unreacted phenol, and heated briefly with 1 g of charcoal. The azo dye **11** was precipitated by dropwise addition of 686 mg (2 mmol) of sodium tetraphenylborate in 10 ml of water. After 10% of the solution had been added, the mixture was allowed to stand for 10 min and filtered. The brownish residue was discarded. The rest of the solution was added and the curdy orange precipitate collected, yield 700 mg (40%). A 200-mg portion of the crude material was dissolved in 25 ml of acetone; 10 ml of chloroform and 15 ml of ether were added and the solution chilled at −20° overnight. The dye was obtained as dark orange crystals: mp 175–176°; ir (KBr) 3100 (cyclopentadienyl C–H), 3050 (aromatic C–H), 1585 (s), 1500, 1475, 1412 (s), 1395, 1268, 1220, 1180, 1135 (s), 1060 (w), 1035 (w), 1000 (w), 940, 835, 730 (s), 700 (s), 610, 500, and 450 cm^{-1}.

Anal. Calcd for $C_{40}H_{34}BCoN_2O$: C, 76.45; H, 5.45; N, 4.46; Co, 9.38. Found: 76.01; H, 5.89; N, 4.55; Co, 9.00.

A 1.2 × 10^{-3} *M* solution of **11** in ethanol was prepared and diluted 1:25 with 0.100 *M* HCl, pH 7 standard buffer (Beckman

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[17] A review of the Hammett and other acidity functions for concentrated acid solutions is given in M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957).

Instrument Co.), pH 10 standard buffer (Fisher Chemical Co.), and 0.100 *M* NaOH. From the spectra of the dye in acidic, neutral, and basic solutions [uv max (0.100 *M* HCl) 395 mu (ϵ 9600) and 530 (400); uv max (pH 7 buffer) 530 mμ (ϵ 6850); uv max (0.100 *M* NaOH) 395 mμ (ϵ 4500) and 530 (13,700)], the dye was calculated to be 53% protonated at pH 7.00. The pK_a is therefore 7.05 ± 0.03.

π-Cyclopentadienyltetraphenylcyclopentadienone Cobalt (14).[18]—π-Cyclopentadienylcobaltdicarbonyl (6.0 g, 0.35 mol), tetracyclone (13.6 g, 0.35 mol), and 50 ml of xylene were refluxed overnight in a nitrogen atmosphere. The solution was cooled to room temperature and 15.4 g of purple crystals collected. The solid was chromatographed in 3-g portions on a 10 cm × 30 cm column of alumina. A purple band of tetracyclone was eluted with xylene and an orange band of **14** with chloroform. The crude **14** was recrystallized from chloroform–ligroin: yield 11.0 g (62%); mp 325–326° (lit.[10] 327–329°).

Hydroxy-2,3,4,5-tetraphenylcobalticinium Bromide (15).—A 254-mg sample of **14** (0.5 mmol) was suspended in 30 ml of 48% hydrobromic acid and heated for 30 min at 80–100°, with constant stirring. A gummy oil formed which solidified to a yellow powder. The solution was diluted with 50 ml water and the precipitate collected, yield 244 mg (83%). The crude material was recrystallized from acetone–ether: mp 289–290° dec; ir max (KBr) 3060, 2900–2400 (broad peak possibly due to H–Br bonding), 1600 (w), 1578 (w), 1470, 1430 (C–O stretch), 1410, 1400, 1240, 1170 (s), 1110, 1082, 1030, 1008, 850, 800, 753 (s), 697 (s), 640, 620, 582, 558, 500, 420 cm^{-1}.

Anal. Calcd for $C_{34}H_{26}BrCoO$: C, 69.28; H, 4.45; Br, 13.56; Co, 10.00; O, 2.71. Found: C, 69.00; H, 4.70; Br, 14.00; Co, 9.98; O, 2.70.

Hydroxy-2,3,4,5-tetraphenylcobalticinium Fluoroborate and Perchlorate.—A 508-mg sample of **14** (1 mmol) was dissolved in 25 ml of chloroform and shaken with 10 ml of 37% fluoroboric acid. The chloroform layer was dried over calcium sulfate. Dropwise addition of ligroin precipitated the product as a fine yellow powder, yield 517 mg (87%). The crude product was recrystallized from acetone–ether, mp 245–250° dec. The ir spectrum of the fluoroborate corresponded to the ir of the bromide except that the broad peak at 2900–2400 cm^{-1} was shifted to 3500–3200 cm^{-1}, and a broad peak for the BF_4^- anion appeared at 1130–950 cm^{-1}.

Anal. Calcd for $C_{34}H_{26}BCoF_4O$: C, 68.48; H, 4.40; Co, 9.88; O, 2.68. Found: C, 68.72; H, 4.65; Co, 9.80; O, 2.70.

The perchlorate salt, mp 253–255° dec, was prepared from 60% perchloric acid by the same procedure.

Anal. Calcd for $C_{34}H_{26}ClCoO_5$: C, 67.06; H, 4.30; O, 13.14. Found: C, 67.02; H, 4.45; O, 13.10.

Acetoxy-2,3,4,5-tetraphenylcobalticinium Salts (16).—A 152-mg portion of **14** (0.3 mmol) was dissolved in 10 ml of acetyl chloride. The acetyl chloride was evaporated and the residue was dissolved in 30 ml of water and filtered. The acetoxy derivative **16** was precipitated as the hexafluorophosphate salt: ir (KBr) 3120 (cobalticinium C–H), 3060 (phenyl C–H), 2920, 2860, 1785 (s), 1312 (w), 1275 (w), 1600 (w), 1580 (w), 1500 (w), 1450, 1418 (s), 1400, 1370, 1170 (s), 1100, 1085, 1010, 830 (s), 755 (s), 699 (s), 580 (w), 560 (s), 510, 415, and 278 cm^{-1}. The tetraphenylborate was also prepared and recrystallized twice from acetone–ether, mp 235°.

Anal. Calcd for $C_{60}H_{48}BCoO_2$: C, 82.75; H, 5.56; O, 3.68; Co, 6.77. Found: C, 82.80; H, 5.60; O, 3.68; Co, 6.76.

Registry No.—**1,** 12427-42-8; **2,** 12427-48-4; **3,** 12427-51-9; **4,** 12427-47-3; **5,** 12427-49-5; **6,** 12427-45-1; **7,** 12427-50-8; **8,** 12427-46-2; **9,** 12427-43-9; **9** (tetraphenylborate), 12427-55-3; **9** (diazo derivative), 12427-56-4; **10,** 12427-41-7; **11,** 12427-53-1; **15,** 12427-59-7: **16,** 12427-63-3; **16** (tetraphenylborate), 12427-62-2; **10** (tetraphenylborate), 12427-54-2; hydroxy-2,3,4,5-tetraphenylcobalticinum (BF_4), 12427-58-6; hydroxy-2,3,4,5-tetraphenylcobalticinium (perchlorate), 12427-60-0.

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Intermolecular Hydrogen Bonding between Nitriles and Methanol. A Nuclear Magnetic Resonance Study

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The addition of alkyl- and arylnitriles to methanol, with or without CCl_4 dilution, prolongs the residence time for exchange of the –OH proton. The inhibition of –OH exchange is sufficient to allow detection of J_{HCOH}. Studies of binary and ternary (CCl_4) mixtures of acetonitrile and methanol showed a marked variability in the –OH resonance position with increasing CH_3CN concentration. The observed spectral changes support prior postulations of a strong –CN—HO– hydrogen-bonding interaction, and appear to indicate changes in the equilibrium concentration of CH_3OH–CH_3CN associates over a broad range of binary and ternary (CCl_4) solution concentrations.

Studies of intermolecular –CN—HO– hydrogen bonding have been centered primarily on the elucidation of infrared hydroxyl frequency shifts ($\Delta\nu_{OH}$) for binary and ternary (CCl_4) mixtures of nitriles with alcohols and phenols.[1] The $\Delta\nu_{OH}$'s observed for methanol or phenol interacting with a wide variety of nitriles correlated well with Taft σ^* parameters,[2] however, even under carefully controlled experimental conditions it is evident that the magnitude of $\Delta\nu_{OH}$ is not necessarily a measure of hydrogen-bonding acceptor strength.[2,3] Consequently, no definite conclusions could be reached regarding the acceptor strengths of nitriles relative to other known hydrogen-bonding bases.

Recently, we have been concerned with solvent–solute interactions traceable through changes in the –OH and –CH_3 resonances of methanol,[4] *e.g.*, suppression of –OH exchange and the concentration dependence of the –OH resonance for both binary and ternary

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