Appendix

The differential eq 1–3 were derived as follows. From Scheme I and entering the cycle at A· or B·

$$d[C]/d[A] = k_c[C\cdot]/k_a[A\cdot] \tag{12}$$

$$d[B]/d[A] = k_b[B\cdot]/k_a[A\cdot] \tag{13}$$

However, from the usual steady-state assumption

$$d[C\cdot]/dt = 0$$

$$k_{ac}[A\cdot] + k_{bc}[B\cdot] = k_{ca}[C\cdot] + k_{cb}[C\cdot] + k_c[S][C\cdot] \tag{14}$$

Eliminating radical concentrations by combination of eq 12–14 yields eq 1, and eq 2 and 3 follow by virtue of the symmetry of the system when it is entered at A· or C· or at B· or C·, respectively.

Pentachlorocyclopentadienide Anion[1]

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Abstract: Salts of the aromatic pentachlorocyclopentadienide anion, $C_5Cl_5^-$, with the large cations Tl^+, $Tl^+\cdot 2C_6H_5CH_3$, $(C_2H_5)_3NH^+$, 1-methylpyridinium, $(C_4H_9)_4P^+$, and quaternary ammonium, have been isolated and characterized spectroscopically. The results are consistent with a delocalized, fivefold symmetric structure. The anion shows only two absorptions in the near infrared at about 1415 and 679 cm^{-1}. The electronic spectrum of $C_5Cl_5^-$ shows a principal absorption at approximately 201 nm with several shoulders. The nqr spectra of the salts (except for the $Tl^+\cdot 2C_6H_5CH_3$ salt) show frequencies in the range 35.0–35.7 MHz. Charge distributions in $C_5Cl_5^-$, C_6Cl_6, and $C_3Cl_3^+$ are estimated from nqr data and compared with distributions in their hydrocarbon analogs. $Tl^+C_5Cl_5^-\cdot 2C_6H_5CH_3$ appears to be a ground-state charge transfer complex; the 1-methylpyridinium salt is an excited-state charge transfer complex. Nqr spectra are presented for decachlororuthenocene and 1,1′-dichloroferrocene and are interpreted in terms of repulsions between lone pairs on chlorine and electrons located on the metal atom. The salts of $C_5Cl_5^-$ are all unstable at room temperature. The $C_5Cl_5^-$ anion is weakly basic, easily oxidized, and appears to decompose *via* the pentachlorocyclopentadienyl radical, $C_5Cl_5\cdot$. A simple preparation of 5-bromopentachlorocyclopentadiene is reported. All attempts to date to react $C_5Cl_5^-$ with transition metal salts to give perchlorometallocenes have failed.

Four members of the family of monocyclic conjugated chlorocarbons[2] $(CCl)_n^{m\pm}$ have been well characterized: $C_3Cl_3^+$, C_6Cl_6, $C_7Cl_7^+$, and C_8Cl_8. There is evidence for the existence of C_4Cl_4, $C_5Cl_5^+$, $C_5Cl_5\cdot$,[3] and $C_5Cl_5^-$. Our interest in the chemistry of the members of this family led us to study more thoroughly the chemistry of the pentachlorocyclopentadienide anion, $C_5Cl_5^-$. Neglecting the chlorine atoms, this anion has six π electrons, and so should be aromatic.

Lithium pentachlorocyclopentadienide was first mentioned in 1955 as the probable product of $LiAlH_4$ reduction of hexachlorocyclopentadiene (C_5Cl_6) at low temperature.[4] This reaction produced, after hydrolysis, 1,2,3,4,5-pentachlorocyclopentadiene, C_5Cl_5H. The chemistry of LiC_5Cl_5 has been further investigated by McBee, Halling, and Morton,[5] who found that LiC_5Cl_5 solutions can also be prepared from C_5Cl_6 and lithium metal at low temperature. The anion has been generated by electroreduction of C_5Cl_6 or octachlorocyclopentene,[6] and mentioned as a possible intermediate in the reaction of trialkyl phosphites with C_5Cl_6.[7]

Despite its frequent mention, no salts of the $C_5Cl_5^-$ anion have been isolated, nor has the ion been characterized spectroscopically. We wish to report the preparation and characterization of a series of solid salts: $Tl^+C_5Cl_5^-$ (**1**), $Tl^+C_5Cl_5^-\cdot 2C_6H_5CH_3$ (**2**); $R_4N^+C_5Cl_5^-$, where R = n-C_3H_7 (**3a**), n-C_4H_9 (**3b**), or n-C_7H_{15} (**3c**); $(C_2H_5)_3NH^+C_5Cl_5^-$ (**4**); $(n$-$C_4H_9)_4P^+C_5Cl_5^-$ (**5**); and $C_5H_5NCH_3^+C_5Cl_5^-$ (**6**).

Preparation. The thallium(I) salt (**1**) may be prepared by the reduction of C_5Cl_6 in ether at −25° with thallium amalgam. However, this reaction is slow and decomposition of **1** reduces the yield. The preferred method is addition of thallium(I) ethoxide $(TlOC_2H_5)_4$ to C_5Cl_5H in pentane at −78°. If this reaction is carried out in toluene solution, the adduct **2** crystallizes rather than **1**.

The salts **3a**, **3b**, and **3c** may be precipitated at −78° from methanol by (a) adding a solution of the quaternary ammonium hydroxide to C_5Cl_5H or (b) adding lithium methoxide to a solution of the quaternary ammonium halide and C_5Cl_5H. **5** and **6** are prepared analogously. **4** may be precipitated from ether by adding triethylamine to C_5Cl_5H at −78°.

All of the compounds may be stored indefinitely at −80°, but none are thermally stable above −15°. Their rates of decomposition vary. **1** ignites spontaneously at −15° in air or in a nitrogen atmosphere with emission of orange light but without violence, yielding a deep blue ash. **4** also decomposes rapidly, but without light emission. **2**, **5**, and **6** can be handled

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(1) Some of this work has appeared in preliminary form; G. Wulfsberg and R. West, *J. Amer. Chem. Soc.*, **93**, 4085 (1971).

(2) Review by R. West, *Accounts Chem. Res.*, **3**, 130 (1970).

(3) F. Graf and Hs. H. Gunthard, *Chem. Phys. Lett.*, 7, 25 (1970).

(4) E. T. McBee and D. K. Smith, *J. Amer. Chem. Soc.*, 77, 389 (1955).

(5) E. T. McBee, R. A. Halling, and C. J. Morton, unpublished studies. R. A. Halling, Ph.D. Thesis, Purdue University, 1965; *Diss. Abstr. B*, 27 (2), 409 (1966).

(6) L. G. Feoktistov and A. S. Solonar, *J. Gen. Chem. USSR*, 37, 931 (1967).

(7) V. Mark, *Tetrahedron Lett.*, 295 (1961).

at −15° for 30 min, but decompose within minutes at +25° to deep blue ash. The tetraalkylammonium salts are the most stable and show increasing room temperature stability in air with increasing size of the alkyl group. **3c** can be kept at −15° for about 1 week and at +25° for 0.5 hr before decomposing to blue solids.

The solubilities of these salts show corresponding trends. **1** is soluble in ether, methanol, and chlorinated solvents ($CHCl_3$, CH_2Cl_2, and C_6H_5Cl). **4** is insoluble in ether but is soluble in the others; **3b** and **3c** are quite insoluble except in chlorinated solvents. Hence stability and insolubility are both favored by increasing cation size. In solution the anion is unstable above −30°, decomposing to yield deep blue and green solutions.

The analysis of these salts was complicated by their ease of decomposition; however, it proved possible to determine equivalent weights by neutralization with trichloroacetic acid in chlorobenzene, and to determine the cations gravimetrically as the tetraphenylborates (thallium as the chromate). For salts with large alkyl groups (**3b** and **5**) this method was not successful. The successful analyses are reported in Table I.

Table I. Analytical Data for $C_5Cl_5^-$ Salts

	Equiv wt		% cation	
Compd	Calcd	Found	Calcd	Found
1	441.7	466.7	46.3	44.9
2	626.0	630.9	32.6	32.4
3a	423.7	424.8	44.0	43.6
4	339.5	339.3	30.1	29.9
6	331.4	327.4	28.4	28.7

Infrared Spectra. Spectra of the more stable salts were obtained as mineral oil mulls at room temperature. The known spectra of the cations were then subtracted to give the results presented in Table II.[8–10] The spectra of the less stable salts were obtained in chloroform solution at −55°. Again, deletion of cation and solvent spectra was necessary.

Table II. Infrared Spectra of $C_5Cl_5^-$ and Other Cyclic Species

		Frequencies, cm^{-1}		
Compd	Ref	C–C	C–C	C–Cl
		(a) D_{nh} Symmetry		
3a	*a*	1415 (s)		670 (s)
3b	*a*	1414 (s)		679 (s)
3c	*a*	1415 (s)		681 (s)
5	*a*	1410 (s)		678 (m)
6	*b*			657 (m)
C_6Cl_6	*c*	1345		694
$C_3Cl_3^+$	*d*	1312 (vs)		735 (s)
$C_5H_5^-$	*e*	1435–1499		
		(b) C_{5v} Symmetry		
1	*b*	1407 (m)	1190 (m)	657 (s)
2	*b*	1408 (m)	1191 (vw)	659 (m)
$Tl^+C_5H_5^-$	*e*	1423	1121	

[a] This work, mineral oil mull, +26°. [b] This work, saturated $CHCl_3$ solution, −55°. [c] Reference 8. [d] Reference 9. [e] Reference 10.

The infrared spectra are clearly consistent with formulation of $C_5Cl_5^-$ as a symmetrical ionic species. If the $C_5Cl_5^-$ group was σ bonded to the cation, its infrared spectrum (above 250 cm^{-1}) would be expected to show nine absorptions due to the ring and five C–Cl stretching absorptions. (C–Cl bending modes are expected to fall below 250 cm^{-1}.) In contrast, the free anion (symmetry group D_{5h}) is expected to show only one ring absorption and one C–Cl stretching absorption. The anion may also have a metallic cation centered above the ring on one side lowering its symmetry from D_{5h} to C_{5v}. In this case two ring modes and two C–Cl stretching modes are expected to be infrared active. Salts **3**, **5**, and **6** show the simple spectra to be expected from an ion of D_{5h} symmetry. The thallium salt **1**, like its analog TlC_5H_5, shows enough interaction of the cation with the anion to lower the symmetry to C_{5v}.

The solution infrared spectrum of **2** contrasts with that of **1** in that the second ring stretching absorption, while present, is very weak. This probably reflects a decrease in interaction of the Tl^+ cation with the anion which would result if the predominant species in solution were the bis(toluene)thallium(I) cation. Although arene–silver(I) complexes are well known, only two arene–thallium(I) complexes have been reported,[11] $Tl^+AlCl_4^- \cdot 2C_6H_6$ and $2Tl^+AlCl_4^- \cdot C_6H_6$. **2** may represent a third example of this type of complex.

Nuclear Quadrupole Resonance (Nqr) Spectra. In Table III[12–15] are given the nqr spectra of **2**, **3a**, **5**, and **6** as recorded at 77°K on a Decca Radar nqr spectrometer. Also shown for comparison are data from related compounds.

Table III. ^{35}Cl Nqr Spectra of $C_5Cl_5^-$ and Related Species

Compd	Frequency, MHz[a]	Average frequency
2	At least 17 lines between 35.95 and 36.71	36.36
3a	35.08 (2.3), 35.37 (1.7), 35.52 (2.3)	35.31
5	35.20 (10), 35.28 (10), 35.33 (10), 35.50 (7), 35.68 (8)	35.40
6	35.02 (9), 35.59 (5)	35.25
C_5Cl_6[b]	36.95 (9), 37.27 (6), 37.28 (10), 37.45 (10), 38.81 (7), 39.08 (10)	
$Ru(C_5Cl_5)_2$[c]	38.61 (5), 38.66 (5), 38.74 (2)	
C_6Cl_6[d]	38.38, 38.45, 38.49	
$Fe(C_5H_4Cl)_2$[e]	35.48 (>50)	

[a] Resonant frequencies are accurate to ±0.01 MHz. Numbers in parentheses indicate signal-to-noise ratios. [b] Hexachlorocyclopentadiene, α phase.[13] [c] Perchlororuthenocene[12] sample kindly lent by H. Rosenberg. [d] Hexachlorobenzene.[14] [e] 1,1′-Dichloroferrocene[15] sample kindly lent by J. Stenson.

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(8) P. Delorme, V. Lorenzelli, and M. Fournier, *C. R. Acad. Sci.*, **259**, 751 (1964).

(9) R. West, A. Sadô, and S. W. Tobey, *J. Amer. Chem. Soc.*, **88**, 2488 (1966).

(10) H. P. Fritz, *Advan. Organometal. Chem.*, 1, 254 (1964).

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(12) F. L. Hedberg and H. Rosenberg, *ibid.*, **92**, 3239 (1970).

(13) M. Hayek, D. Gill, I. Agranat, and M. Rabinovitz, *J. Chem. Phys.*, 47, 3680 (1967).

(14) T. L. Weatherly, E. H. Davidson, and Q. Williams, *ibid.*, **21**, 761 (1953).

(15) Since submission of this paper, this frequency has been reported at 35.47 MHz (A. N. Nesmeyanov, G. K. Semin, T. L. Khopyanova, E. V. Bryukhova, N. A. Vol'kenau, and E. I. Sirotkina, *Dokl. Akad. Nauk SSSR*, 202, 854 (1972).

The frequencies of **2**, **3a**, **5**, and **6** are consistent with the expectations for an ionic $C_5Cl_5^-$ species. In such a species all chlorines would be chemically equivalent; however, in a lattice they could not be crystallographically equivalent since a crystal lattice cannot have a fivefold axis of symmetry. Hence the nqr spectrum of $C_5Cl_5^-$ must show splitting. This splitting will produce either three signals of intensity 2:2:1, or five signals of intensity 1:1:1:1:1. It is generally observed[16] that, in a molecular solid, crystallographic splitting is about 2% of the frequency, or 0.7 MHz in the present case. The compounds under discussion are ionic not molecular solids so that larger electric field gradient variations are possible; nevertheless, in the spectra reported, the largest splitting is 0.76 MHz in **2**. In contrast, the spectrum of C_5Cl_6, which has *chemically* different chlorines, shows splittings of as much as 2.23 MHz.

Compound **5** shows the five-line pattern, of intensities 1:1:1:1:1, and **3a** shows a 2:2:1 triplet. Compound **6** shows a 3:2 doublet which is *not* expected for $C_5Cl_5^-$ but is probably due to the accidental coincidence of two lines of a 2:2:1 triplet. (It is often impossible to distinguish lines falling within 0.010 MHz of each other.) Compound **2** shows a very complicated pattern due to the presence of at least four crystallographically nonequivalent $C_5Cl_5^-$ ions (each with nonequivalent atoms) per unit cell.

The series $C_3Cl_3^+$, C_6Cl_6, and $C_5Cl_5^-$ affords an opportunity to study the interaction of electronic charge in aromatic rings with carbon–chlorine bonds. If we consider only the π electrons, it is apparent that a cationic system such as $C_3Cl_3^+$ can be stabilized by π donation of $3p_y$ electrons of the chlorine atoms. Some such stabilization can be expected in neutral species but, in an anionic species such as $C_5Cl_5^-$, π donation would only intensify the negative charge already present in the ring; hence no π bonding is expected. $C_3Cl_3^+$ has in fact a much higher carbon–chlorine π bond order (0.16) than do the chlorobenzenes (0.03–0.08).[17a] (The π bond order in $C_5Cl_5^-$ cannot be determined from our measurements.)

This analysis, however, ignores the possible role of the carbon–chlorine σ bond, which, although inherently polarized with a partial negative charge at chlorine, may be altered considerably by the ring charge. Calculations performed by Del Bene and Jaffe[18] on the $C_5H_5^-$ anion which explicitly treated all σ and π electrons in the ion showed that the C–H σ bond is affected by the negative charge. A net population of 1.05 electrons on each hydrogen atom was calculated which indicated that one fourth of the anionic charge is delocalized onto the hydrogens by a σ mechanism. Experimental confirmation is available; measurement of the ^{19}F nmr of *m*- and *p*-$FC_6H_4C_5H_4^-$ indicates that the $C_5H_4^-$ group is a powerful inductive donor, far exceeding trimethylsilyl in electron-donating abilities.[19] Similar effects certainly ought to be present in chlorocarbons.

The nqr data for these systems can be analyzed by the usual Townes and Dailey theory to reveal the approximate charge distributions in the chlorocarbon molecules and ions.[17b] We can find the population $N_{Cl,\sigma}$ of the σ-bonding orbital at chlorine from the equation[20]

$$N_{Cl,\sigma} = 2 - \pi/2 + e^2Qq_{mol}/e^2Qq_0 \qquad (1)$$

where e^2Qq_{mol} is the quadrupole coupling constant of the molecule or ion[21] and e^2Qq_0 is the quadrupole coupling due to a single electron in the $3p_z$ orbital of chlorine (+109.746 MHz). Using known or assumed values of the π bond order we obtain the values of $N_{Cl,\sigma}$ which are given in Table IV. Adding this to the populations of the chlorine p_y, p_x, and 3s orbitals and subtracting 7, we obtain the net electronic charge on each chlorine atom. From this we can deduce the net charge on each ring carbon atom.

Table IV. Charge Distributions in $C_nCl_n^{m\pm}$ Species

Species[a]	π	e^2Qq_{mol}, MHz	$N_{Cl,\sigma}$	Charge[g] on each Cl(H)	Charge[g] on each C
$C_3Cl_3^+$	0.16[b]	−78.8	1.20	−0.04	+0.37
C_6Cl_6	0.08[c]	−76.5	1.26	−0.18	+0.18
$C_5Cl_5^-$	0.08[d]	−70.2	1.32	−0.24	+0.04
	0.00[d]	−70.6	1.36	−0.36	+0.16
2	0.08[d]	−72.3	1.30	−0.22	?
C_6H_6[e]	0			+0.03	−0.03
$C_5H_5^-$[f]	0			−0.05	−0.15

[a] Column headings are explained in text. [b] Data from ref 22. [c] Estimated from data on C_6Cl_5OH in ref 17a. [d] True value unknown. These are plausible postulated values. See text. [e] Calculated in J. Del Bene and H. H. Jaffé, *J. Chem. Phys.*, **48**, 1807 (1968). [f] Calculated in ref 18. [g] The approximations involved in the Townes–Dailey theory may not cancel out when comparing chlorocarbon to hydrocarbon species or when comparing chlorocarbon species of widely varying nature. Hence the values of charges given in this table are only semiquantitative. See also footnote 20.

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(16) T. A. Babushkina, V. I. Robas, and G. K. Semin, "Transactions of the All-Union Conference on Magnetic Resonance in Solids" (in Russian), Krasnoyarsk, 1964; as reported in T. A. Babushkina, E. V. Bryukhova, F. K. Velichko, V. I. Pakhomov, and G. K. Semin, *J. Struct. Chem.*, **9**, 153 (1968).

(17) E. A. C. Lucken, "Nuclear Quadrupole Coupling Constants," Academic Press, London, 1969, (a) Chapter 10; (b) Chapter 7.

(18) J. Del Bene and H. H. Jaffe, *J. Chem. Phys.*, **48**, 4050 (1968).

(19) A. A. Koridze, S. P. Gubin, A. A. Lubovich, B. A. Kvasov, and N. A. Ogorodnikova, *J. Organometal. Chem.*, **32**, 273 (1971).

(20) ^{35}Cl quadrupole coupling constants are functions of the electric field gradients at ^{35}Cl nuclei. The contribution to the electric field gradient from the counter cation or anion is thought to be small, on the order of 0.3–0.8 MHz (M. Kubo and D. Nakamura, *Advan. Inorg. Chem. Radiochem.*, **8**, 287 (1966)). There is no contribution from the chlorine core electrons or 3s electrons which are spherically symmetric. The 3d orbitals are not likely to be important in bonding. Hence e^2Qq_{mol} can be expressed in terms of e^2Qq_0 and the populations N_z, N_y, and N_x of the $3p_z$, $3p_y$, and $3p_x$ orbitals of the Cl atom

$$e^2Qq_{mol} = e^2Qq_0(N_z - (N_x + N_y)/2). \qquad (1a)$$

If we assume that there is no hybridization of the chlorine 3s orbital into the orbital, then $N_z = N_{Cl,\sigma}$. Fragmentary evidence[17b] suggests 3–10% s participation in C–Cl covalent bonds; allowing 10% s participation would require the Cl charge distributions to be adjusted by +0.07 to +0.08; the C charge distributions would be adjusted by −0.07 to −0.08. Hence there *would* be a small delocalization of positive charge (+0.04 charge per Cl) in $C_3Cl_3^+$; and there could be a small amount of carbanionic character (−0.03 charge per C) in $C_5Cl_5^-$ (π = 0.08).

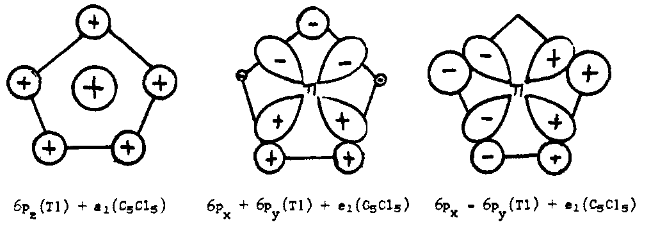
Equation 1 is then derived by fixing N_x at 2.00, setting N_y equal to $2 - \pi$, and substituting into eq 1a.

(21) Calculated from the assumed π bond order and the observed nqr frequencies according to the equations (ref 17)

$$\eta = \frac{3}{2}\left|\frac{e^2Qq_{atom}}{e^2Qq_{mol}}\right|\pi$$

$$e^2Qq_{mol} = -2\nu/\sqrt{1 + \eta^2/3}$$

e^2Qq_{mol} is very nearly equal to −2 times the average nqr frequency.



$6p_z(Tl) + a_1(C_5Cl_5)$ $6p_x + 6p_y(Tl) + e_1(C_5Cl_5)$ $6p_x - 6p_y(Tl) + e_1(C_5Cl_5)$

Figure 1. Electron donation from ring orbitals to Tl 6p orbitals.

In his paper on the nqr of $C_3Cl_3^+$ and C_3Cl_4, Lucken[22] concluded that the stability of $C_3Cl_3^+$ relative to C_3Cl_4 was largely due to the transfer of half to three-quarters of the ring positive charge to chlorine relative[23] to the transfer present in C_3Cl_4. From the data in Table IV we can see that there is actually little[20] or *no* delocalization of the positive charge of $C_3Cl_3^+$ onto chlorine.

We do not know the degree of π bonding in $C_5Cl_5^-$. It seems unlikely that it would exceed that found in C_6Cl_6, so we can set estimated bounds on its value as 0.00 (the π-only theoretical value) and 0.08, the largest value found in halobenzenes. The charge distributions calculated for these extreme values are listed in Table IV. Provided that $0.00 \leq \pi \leq 0.10$, we estimate that *all*[20] the negative charge in $C_5Cl_5^-$ is delocalized onto chlorine *via* a σ mechanism.

This allows us to predict that $C_5Cl_5^-$ will be a weak base and a very poor nucleophile. As we shall see in the Experimental Section, these predictions are verified. If the value of π is appreciable, indicating overlap between the filled chlorine $3p_y$ orbitals and the filled ring π orbitals, then we would expect substantial destabilization of the ring π orbitals, with consequent easy loss of an electron to give the $C_5Cl_5\cdot$ radical. As we shall see, this seems to be the characteristic reaction of $C_5Cl_5^-$.

The nqr frequency of **2** is substantially higher than the frequencies of the other salts. We would explain this by proposing that, in the solid state, the Tl^+ cation nestles in the $C_5Cl_5^-$ anion with some ground-state charge transfer going from the anion to the empty 6p orbitals of thallium. Figure 1 diagrams the symmetry-allowed overlap between the filled a_1 and e_1 orbitals of the anion and combinations of the Tl 6p orbitals. As we have previously indicated, the anion π electrons (particularly the e_1) may be rather high in energy in the free anion and thus rather easily donated. With some charge removed from the anion, the excess polarization of the C–Cl bond can be reduced giving a higher nqr frequency. (The value of π for **2** is also unknown; the value of 0.08 is assumed in Table IV for purposes of comparison.)

Table III also contains the first measurements of ^{35}Cl nqr frequencies in halogen-substituted metallocenes. The spectrum for decachlororuthenocene[12] shows the expected three-line pattern of intensity 2:2:1. The frequencies are quite similar to those of C_6Cl_6 and are more than 3 MHz higher than those of $C_5Cl_5^-$.

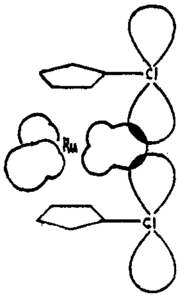


Figure 2. Repulsion of girdle and chlorine $3p_y$ orbitals.

However, it is generally felt that in a metallocene a partial positive charge resides on the metal and a corresponding negative charge on the ring.[24] The substitution of electron-withdrawing chlorines is not likely to reduce this effect. Hence, in a simple model, the nqr frequency of $Ru(C_5Cl_5)_2$ should *not* be like that of C_6Cl_6, but should be intermediate between $C_5Cl_5^-$ and C_6Cl_6.

The raising of the frequency of $Ru(C_5Cl_5)_2$ is probably caused by a Stark-effect repulsion of the p_z lone pairs on chlorine by filled girdle d orbitals around the metal atom (Figure 2). This repulsion would be expected to cause the chlorine atoms to be bent away from the metal atom; the X-ray crystal study[25] shows that this is the case and that the bending cannot be caused by interring Cl–Cl repulsion. The single nqr frequency of 1,1′-dichloroferrocene shows the repulsion due to girdle orbitals even more clearly. Its frequency is 0.70 MHz higher than that of *p*-dichlorobenzene. Direct repulsion between the 1 and the 1′ chlorine is again not likely to be the cause in this molecule since this repulsion could be avoided by rotation of the rings.

Ultraviolet Spectra. The solution uv spectra of some $C_5Cl_5^-$ salts are reported in Table V. Difficulties were experienced in obtaining these spectra due to decomposition at room temperature and weighing, mixing, and baseline problems at reduced temperature. Hence the values (especially of ϵ) in Table V are subject to uncertainty (such as has plagued the measurement of the spectrum of $C_5H_5^-$).[26]

In $C_5H_5^-$ the first $\pi \rightarrow \pi^*$ electronic transition gives rise to two bands: the lowest energy transition, $A_1' \rightarrow E_2'$, is symmetry forbidden and has been calculated to occur at 5.79–6.10 eV. This has been observed at 5.64 eV in the K^+ salt and 5.94 eV in the Li^+ salt.[26] The second transition, $A_1 \rightarrow E_1$, is calculated to occur at 7.10–7.27 eV and to be highly symmetry allowed. Only the tailing of this band, which is not to be expected in the accessible ultraviolet, has been observed.

In the spectrum of $C_5Cl_5^-$, it seems likely that the very intense absorption at 201 nm corresponds to the allowed $A_1 \rightarrow E_1$ transition. This represents a bathochromic shift of 1.0 eV from the value calculated for $C_5H_5^-$. By comparison, the highest intensity band of benzene is shifted by 1.05 eV in C_6Cl_6.[27]

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[22] E. A. C. Lucken and C. Mazeline, *J. Chem. Soc. A*, 153 (1968).

[23] One should not misinterpret this as applying in comparing the stability of $C_3Cl_3^+$ to $C_3H_3^+$; however, the +0.37 charge per carbon in $C_3Cl_3^+$ is *greater* than we would expect in $C_3H_3^+$ (+0.33 or less).

[24] G. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds," Vol. 2, 34th ed, Methuen, London, 1968, p 102.

[25] G. M. Brown, F. L. Hedberg, and H. Rosenberg, *J. Chem. Soc., Chem. Commun.*, 5 (1972).

[26] B. O. Wagner and H. F. Ebel, *Tetrahedron*, **26**, 5155 (1970).

[27] Comparison of data for C_6H_6 ("Uv Atlas of Organic Compounds," Butterworths, London, 1966, D1/1) and C_6Cl_6 (M. Ballester and J. Castañer, *J. Amer. Chem. Soc.*, **82**, 4259 (1960)).

Table V. Ultraviolet Spectra of $C_5Cl_5^-$

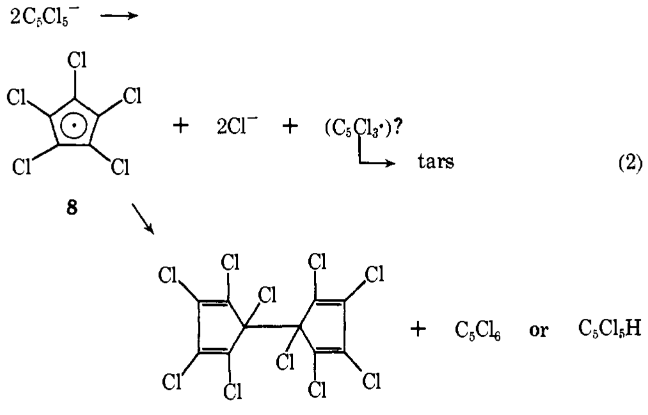
Compd	Conditions	Absorption maxima, nm 1	2	3	4	5
$Na^+C_5Cl_5^-$	95% C_2H_5OH, 25°	201	230 sh	253 sh		307
$Na^+C_5Cl_5^-$	95% C_2H_5OH, <0°	201	226 sh	253 sh		311
$Na^+C_5Cl_5^-$	CH_3OH, 25°	*a*	*a*	252 sh		318
3a	CH_3CN, −30°	<202	218 sh	250	271 sh	325
3b	CH_2Cl_2, −60°	*a*	*a*	252 sh		325
Energy of bands, eV		6.2	5.4–5.7	4.9		3.8–4.0
Estimated log ε of bands		4.3–4.6	3.6–4.0	3.2–3.3		2.8–3.0

[a] Not observed (too intense or obscured by solvent).

The forbidden transition, then, is likely to be the one at 253 nm which is shifted to the red by 0.7–1.0 eV from the 209–220-nm band in $C_5H_5^-$. The weak 307–325-cm^{-1} band may be due to the excitation of a chlorine nonbonding electron to a π^* orbital ($n \rightarrow \pi^*$). This band has the characteristic usually observed for $n \rightarrow \pi^*$ transitions,[28] that is, a blue shift with increasing hydrogen-bonding capacity of the solvent. The nature of the remaining shoulders is unclear.

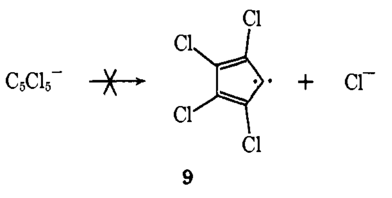
Reactions of the $C_5Cl_5^-$ Ion. The principal reactions of $C_5Cl_5^-$ investigated previously have been with alkyl halides.[5,29] The anion is a remarkably weak nucleophile. McBee, *et al.*, report[5] that it will not react with methyl bromide in 12 hr at −15° unless Lewis acids such as $ZnCl_2$ or aluminum chlorohydrides are present. Reactions above this temperature are hindered by the decomposition of the anion.

A cold solution of **3b** in CH_2Cl_2 was warmed in an esr spectrometer up to 0° without giving a signal or any discoloration; at 0° a signal and a blue color developed. The products observed from the decomposition include decachlorobis(cyclopentadienyl) (**7**), C_5Cl_6 or C_5Cl_5H, a trace of H^+, and blue or green tars.[30] Consequently it is believed that the decomposition proceeds through the pentachlorocyclopentadienyl radical[3] (**8**). The products **7**, C_5Cl_6, and C_5Cl_5H, would be expected from dimerization of **8**, capture of Cl from solvent, and capture of H from solvent, respectively. Another plausible intermediate, the known carbene tetrachlorocyclopentadienylide[31] (**9**), would not be expected to give these products.



(2)

7



(3)

9

Feoktistor and Solonar[6] have noted from their polarographic studies of $C_5Cl_5^-$ that it is weakly basic. The ultraviolet spectrum of $Na^+C_5Cl_5^-$ in 95% ethanol shows little or no hydrolysis; in contrast, $Na^+C_5Cl_4H^-$ was about 85% hydrolyzed to $C_5Cl_4H_2$. The conjugate acid, C_5Cl_5H, should then be at least a moderately strong acid: although we do not observe its ionization in solvents normally, it is observed to decompose to blue and green tars in CH_2Cl_2 solutions when ammonium (or similar) salts are added. Perhaps the formation of an ion pair with the bulky cation stabilizes the anion enough to allow reaction 4 to go appreciably to the right.

$$C_5Cl_5H + R_4N^+ \rightleftharpoons C_5Cl_5^- \cdot R_4N^+ + H^+ \qquad (4)$$

C_5Cl_5H in ethanol is acidic enough to produce colors with thallous acetate. C_5Cl_5H reacts with the weakly basic methoxides of mercury,[1] whereas $C_5Cl_4H_2$ seems to be unable to do this.

The anion $C_5Cl_5^-$ also acts as a reducing agent. It has been reported to be oxidized to **7** by iodine and 1,2-dibromoethane.[5] We have observed that it will reduce the weakly oxidizing hexamminecobalt(III) ion to cobalt(II). It reacts very readily with Br_2 to give bromopentachlorocyclopentadiene.

The anion also reacts readily with bubbling O_2 at −78° in CH_2Cl_2 solution; a complex mixture results which shows carbonyl absorptions in the infrared.

$C_5Cl_5^-$ is capable of acting as a charge transfer donor as is witnessed by the yellow color of **6**. The development of colors in CH_2Cl_2 solution was observed with trinitrobenzene (red-violet), *p*-chloranil (blue-green), and *p*-benzoquinone (navy blue).

Much effort was made to find a way of reacting $C_5Cl_5^-$ with transition metal salts to produce perchlorometallocenes. These experiments have not been successful. Thus, reaction of $C_5H_5Fe(CO)_2I$ and $C_5Cl_5^-$ or C_5Cl_5HgCl[1] gave an unstable oil which decomposed to $C_5H_5Fe(CO)_2Cl$ and C_5Cl_5H. Reaction of **1** with $(C_4H_9)_3PCuI$ in ether at −78° produced a clear solution which may contain the chlorocarbon analog of the known π-$C_5H_5CuPR_3$.[32] However, warming to <0°

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(28) H. H. Jaffe and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1962, p 186.

(29) R. Riemschneider and R. Nehring, *Monatsh. Chem.*, **94**, 74 (1963).

(30) Little is known of the tars. They are soluble in many organic solvents, and absorb over the full visible range. They have a characteristic strong, broad infrared absorption at 975 cm^{-1}.

(31) E. T. McBee, J. A. Bosoms, and C. J. Morton, *J. Org. Chem.*, **31**, 768 (1966); E. T. McBee, G. W. Calundann, and T. Hodgins, *ibid.*, **31**, 4260 (1966).

(32) F. A. Cotton and J. Takats, *J. Amer. Chem. Soc.*, **92**, 2353 (1970).

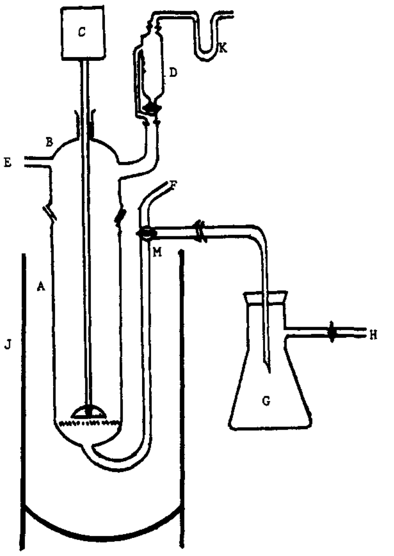

Figure 3. Low-temperature reaction apparatus.

produced decomposition giving many colors and leading to precipitation of copper metal.

The reaction of **1** with FeX_2 or NiX_2 at -78° gives pale yellow solutions which, on slight warming, develop the blue and green colors characteristic of the decomposing anion. Unstable organometallic compounds can be precipitated by the addition of heptane, but these do not show the properties of metallocenes.

It seems likely that the THF solution resulting from the reaction of **1** and MX_2 at -78° contains an ionized and solvated $Ni(THF)_n{}^{2+}$, $2C_5Cl_5{}^-$ or $Fe(THF)_n{}^{2+}$, $2C_5Cl_5{}^-$. That the compound could be ionic seems plausible in view of the low basicity and nucleophilicity of $C_5Cl_5{}^-$. It has been proposed[33] that ferrocene is formed from $FeCl_2$ and NaC_5H_5 *via* a σ-bonded intermediate. The basicity and nucleophilicity of $C_5Cl_5{}^-$ may be so low that the anion cannot displace THF from the $Fe(THF)_n{}^{2+}$ to form a σ-bonded intermediate. Experiments to be reported[34] also suggest that σ-bonded MC_5Cl_5 derivatives are not stable at room temperature unless the Pauling electronegativity of M exceeds about 2.0. Finally, the paramagnetic transition metal ion may hasten the decomposition of $C_5Cl_5{}^-$ to $C_5Cl_5\cdot$ in a manner similar to the activity of such metal ions in promoting the radical coupling of Grignard reagents.[35]

Experimental Section

Reagents. 1,2,3,4,5-Pentachlorocyclopentadiene was prepared by the reduction of hexachlorocyclopentadiene with stannous chloride dihydrate.[4] To retard dimerization it was stored in the solid state at -15°. Thallous ethoxide and Gold Label grade sodium tetraphenylboron were purchased from Aldrich Chemical Co. *N*-Methylpyridinium iodide was prepared according to Bergmann, *et al.*[36] Lithium methoxide (1.00 *M*) was prepared by dissolving lithium wire of known weight/unit length in methanol which had been treated with magnesium, and then distilled. Solvents were dried in the usual manner.

Thallium(I) Pentachlorocyclopentadienide (1). Recommended Synthesis. The apparatus used for low-temperature manipulations is illustrated in Figure 3. Reactor A is constructed from a 60-ml fritted-glass filtering funnel, a ₮ 45/50 ground glass joint, and a three-way stopcock (M). The reactor head B is provided with a nitrogen inlet (E), mechanical stirring (C), and a pressure-equalized addition funnel (D) topped with a nitrogen outlet (K). F is an inlet for nitrogen which is slightly pressurized by means of a needle valve. An erlenmeyer flask (G) receives waste mother liquors and is connected to a water aspirator (H). A cooling bath is put in a dewar flask (J).

The apparatus is purged with nitrogen. A positive pressure of nitrogen is maintained on the underside of the frit with stopcock M. A solution of 2.38 g (10 mmol) of C_5Cl_5H in 50 ml of pentane is put into the reactor which is then cooled to -80°.

Mechanical stirring is commenced and thallous ethoxide (2.50 g, 10 mequiv) in pentane is slowly added to the cold solution before the C_5Cl_5H can crystallize. The solution initially turns maroon, but then deposits a white precipitate of **1**. After allowing the solution to stir for 15 min, the stopcocks M and H are turned so that the frit is now under aspiration, and the mother liquor is sucked into flask G. The precipitate is rinsed twice with 20-ml portions of precooled Skelly A. The yield is quantitative.

For analysis, the precipitate is dried by replacing the Dry Ice bath with a chlorobenzene slush bath (-45°) and aspirating precooled nitrogen through the frit for 1 hr. For further reactions, the reactor is kept at -78°, the underside of the frit is repressurized, and the precipitate is dissolved in precooled solvent.

Alternate Preparation of 1. Thallium amalgam (5.5 *M*, 26 mmol of Tl), 12 mmol of C_5Cl_6, and 50 ml of diethyl ether are placed in a three-necked 250-ml, round-bottomed flask with mechanical stirring, which is purged with N_2, cooled to 0°, and stirred for 1–7 hr. The solution is removed by syringe and filtered rapidly by aspiration under N_2 into a receiver cooled in Dry Ice. A white or Prussian blue solid crystallizes. It is likely to inflame on warming. The ethereal solution was analyzed by filtering onto HCl and weighing the TlCl produced. The yield of **1** is 15–34%. After hydrolysis, the ether contains C_5Cl_6 and C_5Cl_5H.

Tetra-*n*-butylammonium Pentachlorocyclopentadienide (3b). Procedure A. In the apparatus of Figure 3 a solution of 2.38 g (10 mmol) of C_5Cl_5H in 25 ml of methanol and 5 ml of 2,2-dimethoxypropane is treated at -78° with 10 g (10 mmol) of 25% tetrabutylammonium hydroxide titrant. A white milky suspension results which is quite viscous and is filtered with great difficulty. The white solid is rinsed twice with 20-ml portions of methanol and twice with ether and then dried at -25° (CCl_4 slush bath) for 1 hr.

***N*-Methylpyridinium Pentachlorocyclopentadienide (6). Procedure B.** In the apparatus of Figure 3 is placed a solution of 3.31 g (15 mmol) of *N*-methylpyridinium iodide and 3.57 g (15 mmol) of C_5Cl_5H in 75 ml of methanol. It is cooled to -78° (if this is not done quickly, the solution will turn green due to reaction 4). $LiOCH_3$-methanol (15 ml, 1.0 *M*) is added with stirring. Yellow crystals form, are filtered, rinsed three times with methanol and twice with ether, and dried at -25° for 1 hr. Yield is 4.19 g (84%).

Triethylammonium Pentachlorocyclopentadienide (4). A solution of 4.77 g (20 mmol) of C_5Cl_5H in 25 ml of diethyl ether is added to a cooled (-78°) solution of 2.23 g (22 mmol) of triethylamine in ether. The precipitate is filtered, rinsed twice with precooled ether, and dried 1 hr at -45°.

Other Salts. **2** was prepared in the same manner as **1** using toluene as a solvent. The yield of colorless crystals is 91%. **3a**, **3c**, and **5** have been prepared by procedures A and B. **3a** and **5** have been recrystallized by dissolving the crystals in a minimum of CH_2Cl_2 at -10°, adding an equal volume of ethanol, and cooling to -78°. The crystals are filtered after 1 hr, rinsed with 4:1 ethanol-CH_2Cl_2 and pentane, and dried. Although some decomposition occurs at -10°, larger crystals are produced. A melting point was obtained on **3c**: 60–62° dec.

Analysis of Salts. A protonating solution, 1 *M* trichloroacetic acid in chlorobenzene, was prepared and standardized against aqueous NaOH. Weighed, stoppered erlenmeyer flasks containing 5.00 ml of the hydrolyzing solution were cooled in a cold room (-15°), charged with 1-g samples of the salt being analyzed, and then shaken to dissolve and protonate the salt. The flasks were then allowed to warm to room temperature and reweighed giving the accurate sample weight by difference.

The solutions were extracted with 15-ml portions of deionized water. Each portion of water was decanted, filtered, and titrated

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[33] M. Tsutsui, M. Hancock, J. Ariyoshi, and M. N. Levy, *J. Amer. Chem. Soc.*, **91**, 5233 (1969).

[34] G. Wulfsberg and R. West, manuscript in preparation.

[35] F. Hedberg and H. Rosenberg report (private communication) that numerous attempts on their part to react $C_5Cl_5{}^-$ with transition metal systems have also been unsuccessful.

[36] E. D. Bergmann, F. E. Crane, Jr., and R. M. Fuoss, *J. Amer. Chem. Soc.*, 74, 5979 (1952).

with standard NaOH to a Phenolphthalein end point (Methyl Orange in the case of **4**). Extraction was repeated until no more NaOH was required. From these data the milliequivalent weight of the salt was determined.

The titrated aqueous extract was then treated with an excess of sodium tetraphenylboron to precipitate the cation. The precipitate was filtered, washed, dried *in vacuo* over P_2O_5, and weighed. Thallium was determined gravimetrically as the chromate.[37] As a check on the accuracy, the number of milliequivalents of cation so determined was compared to the milliequivalents of anion found previously on the same sample. Results are given in Table I.

Special analytical problems were presented by **3a** and **3b**. $(C_4H_9)_4N^+CCl_3COO^-$ could not be extracted completely. Reaction 4 caused a shifting end point with **3b**. Several samples of **3a** underwent protonation, but after several hours induction time suddenly decomposed to blue tar. No analysis was attempted on **3c**. The analysis of **1** is of low precision due to difficulty in drying.

Infrared Spectra. Spectra of **3a**, **3b**, **3c**, and **5** were measured on a Perkin-Elmer IR-457 instrument over the range 2000–250 cm^{-1} as mineral oil mulls between CsI plates. Bands due to the cations were deleted. As a check, the spectra of **3b** and **3c** were scanned up to four times, by which time the absorptions listed had disappeared.

Spectra of **1**, **2**, and **6** were measured at −55° using an RIIC variable-temperature apparatus with NaCl outer windows. The apparatus was modified by the addition of stainless steel needle tubing leading from the top of the apparatus to the 0.1-mm KBr liquid cell inside. After the apparatus was cooled, the solution of the salt was injected (with a cold syringe) into the cell. Salts were run as saturated solutions. The sample of **1** was prepared by mixing chloroform solutions of C_5Cl_5H and $TlOC_2H_5$; the bands due to ethanol were deleted. Toluene was observed in the spectrum of **2** and in the residues from the decomposition of **2**. Due to the expected interference of the $(C_2H_5)_3NH^+$ cation, **4** was not examined.

Nqr Spectra. Samples were put in vials in a cold room (−15°) using tools precooled to −78°. Spectra were recorded on a Decca Radar nqr spectrometer at 77°K using Zeeman modulation and (for resolution of adjacent frequencies) frequency modulation with side band suppression. No spectra were observed for **1**, **3b**, and **4**. (The failure to observe spectra for **4** means that this compound is uncharacterized except for analysis, and thus could have a non-salt-like structure such as $C_5Cl_5H \cdot (C_2H_5)_3N$.)

Uv Spectra. In an attempt to obtain spectra which were free from interference by decomposition products and which would give ϵ's, several experiments were tried. None was entirely satisfactory. Spectra were run on a Cary Model 14 recording spectrophotometer.

(1) $NaOCH_3$ was added to a solution of C_5Cl_5H in methanol in a quartz cell at 25° and the spectrum scanned immediately.

(2) Solutions of $NaOCH_3$ and of C_5Cl_5H in 95% ethanol were mixed in an ice bath and then run at 25°. A second sample, run 15 min later, showed an 18% loss of intensity in the 201-nm band.

(3) Using a Varian V-4540 variable-temperature controller, an excess of $NaOCH_3$ was injected into a solution of C_5Cl_5H in 95% ethanol in a thin quartz tube at low temperature. Quantitative mixing was difficult in this tube.

(4) In the cold room a sample of **3b** was put in a quartz tube; dry CH_2Cl_2 was distilled onto it. The solution was diluted several times to give the full spectrum. Some decomposition may have occurred during dissolution.

(5) Solutions of 1,2,3,4-tetrachlorocyclopentadiene[4] and $NaOCH_3$ were mixed in the manner of experiment 2. The resulting solution showed the 271-nm band of $C_5Cl_4H_2$ with 85% of full intensity. Hence the solution was about 85% hydrolyzed. Subtraction of the spectrum of $C_5Cl_4H_2$ left a spectrum of $C_5Cl_4H^-$ which resembled that of $C_5Cl_5^-$.

Esr Spectrum. **5** was put in a cold quartz tube and dry CH_2Cl_2 was distilled onto it from a vacuum line. The solution was degassed and then examined at −50° in a Varian epr spectrometer. No signal was observed from the colorless solution. The solution was warmed in 10° increments without change until 0° was reached. During this scan a signal developed suddenly enough to throw the instrument out of balance. The signal was a singlet with no visible fine structure. The solution had turned pale blue.

Decomposition of $C_5Cl_5^-$. A sample of 1.12 mmol of **3a** was allowed to decompose in the solid state. The blue product was extracted with water. Titration of the water showed the presence of 0.06 mmol of H^+. Sodium tetraphenylboron precipitated 0.91 mmol of $(C_3H_7)_4N^+(C_6H_5)_4B^-$.

The water-insoluble portion was extracted with pentane to give a brownish solution. Evaporation of solvent gave an oil which by ir contained **7** (major component), C_5Cl_6, some carbonyl compound, and possibly some C_5Cl_5H. The weight of the oil indicated the presence of about 0.45 mmol of $C_5Cl_5\cdot$. The remaining solid (0.100 g) was pentane insoluble.

From these data the approximate stoichiometry of the decomposition was deduced: $2C_5Cl_5^- \rightarrow C_5Cl_5\cdot + C_5Cl_3\cdot + 2Cl^-$.

Reaction of $C_5Cl_5^-$ with $Co(NH_3)_6^{3+}$. Hexamminecobalt(III) sulfate (2 mmol) was treated with excess $Ba(OH)_2$ (6 mmol) in water. $BaSO_4$ was filtered off, the solution was reduced in volume, and C_5Cl_5H (9 mmol) in methanol was added. An immediate green color and precipitate resulted. The solution was filtered to give an orange solution which continued to decompose. After allowing to react overnight and being filtered, the solution had a pale orange color and a strong ammoniacal odor. Only 4% of the $Co(NH_3)_6^{3+}$ ion remained (determined gravimetrically as the oxalate).

From the precipitate there was isolated **7** (2.2 mmol, 4.3 mequiv) and a solid soluble only in concentrated HCl (blue solution, pink on dilution, hence likely a cobalt(II) oxide). Hence the $C_5Cl_5^-$ anion reduced the cobalt: $2Co(NH_3)_6^{3+} + 2C_5Cl_5^- + 4OH^- = 2CoO + 12NH_3 + (C_5Cl_5)_2 + 2H_2O$.

Reaction of $C_5Cl_5^-$ with Br_2. A solution of C_5Cl_5H (11.92 g, 50 mmol) in 50 ml of CH_3OH at −78° was treated with 0.9 *N* $NaOCH_3$–CH_3OH (56 ml, 50 mmol). A solution of Br_2 (7.84 g, 49 mmol) in CH_3OH was slowly added. Near the end of the addition, the color of the solution changed from pale green to orange. The solution was warmed, and the methanol evaporated. The product was washed away from NaBr with pentane which was evaporated to give crude C_5Cl_5Br (13.7 g, 43 mmol). The product was distilled at 65–69° (0.06 mm). Its infrared spectrum compares with that reported for the authentic material.[38] This synthetic route is much simpler than the method in the literature.[38]

Reaction of $C_5Cl_5^-$ with O_2. Two flasks, each containing 100 ml of CH_2Cl_2, 2 mmol of $(C_2H_5)_3N$, and 2 mmol of C_5Cl_5H, were immersed in a −78° bath. Through one was bubbled N_2, through the other O_2, for 90 min. The N_2 solution did not change; the O_2 solution became orange. Evaporation of the solvent from the O_2 reaction left an oil, which after several days deposited a low yield of red-orange crystals. The ir spectrum was recorded (cm^{-1}, KBr pellet): 1752 s, 1601 m, 1589 s, 1565 w, 1231 m, 1200 m, 1162 m, 1134 w, 1114 m, 1075 m, 1009 m, 967 w, 930 m, 880 w, 774 s, 740 s, 729 m, 683 m, 669 m, 620 s. The identity of the compound is not known.

Charge Transfer Complexes. In three test tubes small amounts of (1) trinitrobenzene, (2) *p*-chloranil, and (3) *p*-benzoquinone were placed. To each was added 5 drops of C_5Cl_5H. Three other test tubes were run as controls with the C_5Cl_5H omitted. The tubes were treated with 3 ml of CH_2Cl_2, capped, and cooled to −78°. All tubes were treated with triethylamine in CH_2Cl_2. The control solutions became only faintly colored, but 1 became intensely red-violet, 2 became a less-intense bluish-green, and 3 became an intense navy blue.

Attempted Preparation of Perchloronickelocene. (a). $NiCl_2 \cdot 6H_2O$ (0.75 g, 3.2 mmol), C_5Cl_5H (1.43 g, 6.0 mmol), 2,2-dimethoxypropane (3 ml), and CH_3OH (30 ml) were stirred, then put in the apparatus of Figure 3, and cooled to −78°. Thallous ethoxide (6.0 mmol in 16 ml of CH_3OH) was added. After filtration the solution was amber yellow, but on warming it became navy blue and then purple. Removal of solvent left a red-purple solid. This was dissolved in CH_2Cl_2, but yellow nickel-containing solid began to precipitate. The solution was filtered into heptane which precipitated a red-violet solid. The red-violet solid gave an infrared spectrum with broad lines which could be assigned to **7** + C_5Cl_5H.

(b). **1** (4.0 mmol) was prepared in the usual way. To it was added a solution of 0.62 g (2.0 mmol) of NiI_2 in 60 ml of acetone. The pale-green solution was filtered, but on slight warming became intensely green. Methylcyclohexane was added and acetone was distilled off to leave a blue solid which was filtered off and dried *in*

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[37] I. M. Korenman, "Analytical Chemistry of Thallium," Israel Program for Scientific Translations Ltd., Jerusalem, 1963, p 70.

[38] V. Mark, U. S. Patent 3,420,900 (1969); *Chem. Abstr.*, 70, 677655 (1969).

vacuo. A weighed sample was refluxed with CH_2Cl_2, H_2O, and HCl for 4 hr, and the aqueous phase treated with excess NH_4OH and dimethylglyoxine. *Anal.* Calcd for $NiC_{10}Cl_{10}$: Ni, 11.01%. Found: Ni, 11.22%.

Reaction of C_5Cl_5HgCl with $C_5H_5Fe(CO)_2I$. C_5Cl_5HgCl[1] (0.95 g, 2 mmol), $C_5H_5Fe(CO)_2I$[39] (0.61 g, 2 mmol), and $CHCl_3$ (30 ml) were stirred overnight under N_2. The solution was filtered, mixed with heptane, and reduced in volume. A noncrystallizable oil settled out. Chromatography on alumina decomposed the oil immediately giving a blue color. Decomposition products C_5Cl_5H and $C_5H_5Fe(CO)_2Cl$ were identified by ir.

Reaction of 1 with Tributylphosphinecopper(I) Iodide. Thallous ethoxide (2.71 g, 10.9 mequiv) was dissolved in 10 ml of ether and cooled to −78° under N_2. C_5Cl_5H (2.59 g, 10.9 mmol) in 25 ml of ether was added, followed by $(C_4H_9)_3PCuI$[40] (4.21 g, 11.0 mmol) in 25 ml of ether. A clear colorless solution and yellow precipitate resulted. On warming to less than 0° the solution became multicolored and then deposited copper metal.

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[39] G. B. Kauffman and L. A. Teter, *Inorg. Syn.*, 7, 10 (1963).

[40] R. B. King and F. G. A. Stone, *ibid.*, 7, 110 (1963).

Reactions of Aromatic Radical Anions. VII.[1] Kinetic Study of the Reaction of Sodium Anthracene with Water[2a]

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Abstract: The kinetics of the reaction of sodium anthracene with water has been studied. The rate law is $-d[Anth\cdot^-]/dt = 2k_1[Anth\cdot^-][H_2O]$, with a value of k_1 at 20° of 664 M^{-1} sec^{-1} in tetrahydrofuran. The dihydroanthracenyl anion intermediate is more reactive than the radical anion. Activation parameters, the deuterium kinetic isotope effect, and the effect of ion pairing are included in the study. The mechanisms of protonation of sodium anthracene and sodium naphthalene are directly analogous; however, contrary to molecular orbital localization energy calculations, sodium anthracene is considerably less reactive than sodium naphthalene. The state of ion pairing of the radical anion has a marked effect upon reactivity. Finally, water bound to solvent-separated or free sodium ion is postulated to be the kinetically active proton donor. The discussion includes comparison of this system with other related work.

Our previous kinetic study of the reaction of sodium naphthalene with water verified the Paul, Lipkin, and Weissman mechanism.[3] Since the reactivity of sodium naphthalene toward a proton source is significantly less than that of a structurally related anion, the dihydronaphthyl anion, the likely intermediate, could not be detected. Most unexpectedly, the reactivity of tight ion pairs was found to be greater than solvent-separated ion pairs. Similar findings in other systems have since been reported by others.[4,5] A comparable kinetic study of the reaction of sodium anthracene with water would help to answer two fundamental questions about the relationship between structure and reactivity: can the relative reactivities be accounted for on the basis of a simple molecular orbital treatment, and what is the complex role of solvent and aggregation state in these reactions?

Results and Discussion

In contrast to naphthalene, reduction of anthracene by sodium metal proceeds to the dianion metal adduct in the ethereal solvents used. Since what is sought is the kinetic behavior of the monometal adduct, this presents a possible ambiguity. The problem was solved by taking advantage of the fast electron transfer reaction of sodium naphthalene and of the equilibrium constant (calculated from the known reduction potentials[6a,b]) for the reaction

$$2Anth\cdot^- \rightleftharpoons Anth^{2-} + Anth \qquad (1)$$

Two stock solutions were prepared, one of sodium naphthalene and the other of anthracene (in excess based on sodium naphthalene) and water in the appropriate ether solvent. On mixing in the stopped-flow device, rapid electron transfer from sodium naphthalene provides solely the monometal adduct of sodium anthracene and the subsequent protonation is then followed.

The validity of this method rests on three assumptions. First, the electron transfer to anthracene is kinetically faster than the protonation of sodium naphthalene. Second, the concentration of sodium naphthalene in equilibrium with sodium anthracene is ki-

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[1] Previous paper in this series: S. Bank and B. Bockrath, *J. Amer. Chem. Soc.*, **93**, 430 (1971).

[2] (a) Abstracted in part from the Ph.D. Thesis of B. Bockrath, State University of New York at Albany, Albany, N. Y., Aug 1971; (b) NDEA Title IV Fellow.

[3] D. E. Paul, P. Lipkin, and S. I. Weissman, *J. Amer. Chem. Soc.*, **78**, 116 (1956).

[4] E. S. Petrov, M. I. Terekhova, and A. I. Shatenshtein, *Dokl. Akad. Nauk SSSR*, **192**, 422 (1970).

[5] (a) E. R. Minnich and J. L. Dye, Abstracts of Papers, 161st National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1971; (b) J. L. Dye, private communication; we are grateful to Professor Dye for supplying us with this information prior to publication.

[6] (a) E. deBoer, *Advan. Organometal. Chem.*, **2**, 115 (1964), and references cited therein; (b) J. Jagur-Grodzinski, M. Feld, S. Yangand, and M. Szwarc, *J. Phys. Chem.*, **69**, 628 (1965).