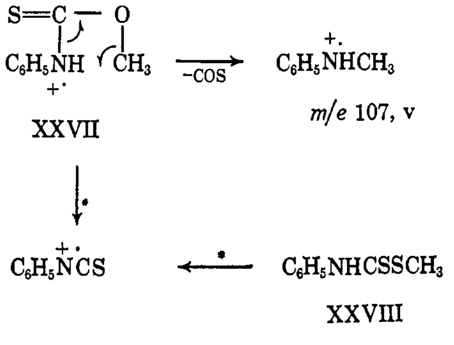
but no rearrangement peak is apparent. Phenyl methyldithiocarbamate (XXIX) shows the same behavior as its oxygen analog (XX) with $C_6H_6S\cdot^+$ (*m/e* 110) and CH_3N^+CS (*m/e* 73) abundant. A weak (1% relative intensity) rearrangement peak is observed at *m/e* 124 (M − HNCS).



In summary, the important conclusion can be drawn from the present study that substitution of one heteroatom by another, in otherwise identical substances, can profoundly modify the fragmentation pattern. This conclusion constitutes an important limitation to the *a priori* prediction of fragmentation modes as well as to the application of the "element mapping" technique[24] in such compounds.

Experimental Section

Low-resolution spectra were obtained, for liquid samples, by Dr. A. M. Duffield using an Atlas CH-4 mass spectrometer (ionizing voltage 70 ev, trap current 10 μa, reservoir temperature 70°, inlet temperature 150–160°, ion-source temperature 190°) and, for solid samples, by Mr. R. G. Ross using an AEI MS-9 instrument with direct insertion probe (ionizing voltage 70 ev, ion-source temperature 200°). High-resolution measurements were made with the MS-9 instrument (apparent resolution 1 part in 15,000).

Thiocarbonates. The thiocarbonates were prepared by reaction of the appropriate acid chloride with methanol or phenol in pyridine[12,25] or with a suspension of the sodium salt of methyl mercaptan, thiophenol, or naphthol in benzene.[26] The following compounds have not been described previously: methyl S-phenyl thiocarbonate (III), bp 86–88° (1.5 mm); methyl α-naphthyl thioncarbonate (V), mp 52–53° (hexane); methyl β-naphthyl thioncarbonate (VI), mp 50–51° (hexane); S-methyl phenyl dithiocarbonate (VIII), bp 108–109° (1.5 mm).

Carbamates and Thiocarbamates. Compounds XVIII and XXIX were prepared by the classical method[27] of shaking the anhydrous methanol, or thiophenol, with phenyl isocyanate, or methyl isothiocyanate, at room temperature. Compounds XXVII and XXVIII were prepared by shaking phenyl isothiocyanate with methanol or methyl mercaptan in 30% aqueous sodium hydroxide, followed by acidification of the solution.[28] Compound XXIII was obtained by rearrangement of the thioncarbamate XXVII in the presence of methyl iodide.[29] The remaining compounds were obtained by treatment of the appropriate amine with phenyl chloroformate or S-phenyl thiochloroformate.

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(24) K. Biemann, *Pure Appl. Chem.*, **9**, 95 (1964); K. Biemann, P. Bommer, and D. M. Desiderio, *Tetrahedron Letters*, 1725 (1964).

(25) K. Freudenberg and G. Dietrich, *Ann.*, **563**, 146 (1949).

(26) H. C. Godt and R. E. Wann, *J. Org. Chem.*, **26**, 4047 (1961).

(27) A. I. Vogel, "Textbook of Practical Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1962, p 264.

(28) M. Roshdestwenski, *J. Russ. Phys. Chem. Soc.*, **41**, 1438 (1909); *Chem. Zentr.*, **I**, 910 (1910).

(29) H. L. Wheeler and B. Barnes, *Am. Chem. J.*, **24**, 60 (1900).

Diazotetracyanocyclopentadiene[1]

O. W. Webster

Contribution No. 1197 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898. *Received May 31, 1966*

Abstract: In aqueous acid, hexacyanobutenediide cyclizes to 1-amino-2,3,4,5,5-pentacyanocyclopentadiene. Nucleophiles cause this labile compound to lose a cyano group giving aminotetracyanocyclopentadienide. This ion is readily converted to diazotetracyanocyclopentadiene by nitrous acid. The chemistry of diazotetracyanocyclopentadiene parallels that of aromatic diazonium compounds. Pentacyanocyclopentadienide, tetracyanocyclopentadienide, and chloro-, bromo-, iodo-, mercapto-, nitro-, phenyl-, *p*-hydroxyphenyl-, carboxy-, azido-, and azotetracyanocyclopentadienide resulted from substitution reactions. Coupling reactions gave 4-(dimethylamino)-phenyl- and 1-(2-hydroxynaphthyl)azotetracyanocyclopentadienide, while addition reactions produced triphenylphosphonium, sulfonato-, and cyanoazotetracyanocyclopentadienide.

As part of a broad study of polycyano compounds,[2] undertaken to determine the effect of a multitude of cyano groups on the chemical and physical properties of organic structures, we have synthesized diazotetracyanocyclopentadiene[3] (DTCC, **4**), a stable, light yellow solid which decomposes at about 200°. Its structure is supported by elemental analysis, infrared and ultraviolet spectral data, and its chemical properties. The stabilizing power of the four cyano groups coupled with that of the 6 π electron, cyclopentadienide system are likely the major factors in determining which resonance form (**4**), the diazonium or the diazo, will contribute

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[1] Part of this work has been published as a Communication to the Editor: O. W. Webster, *J. Am. Chem. Soc.*, **87**, 1820 (1965).

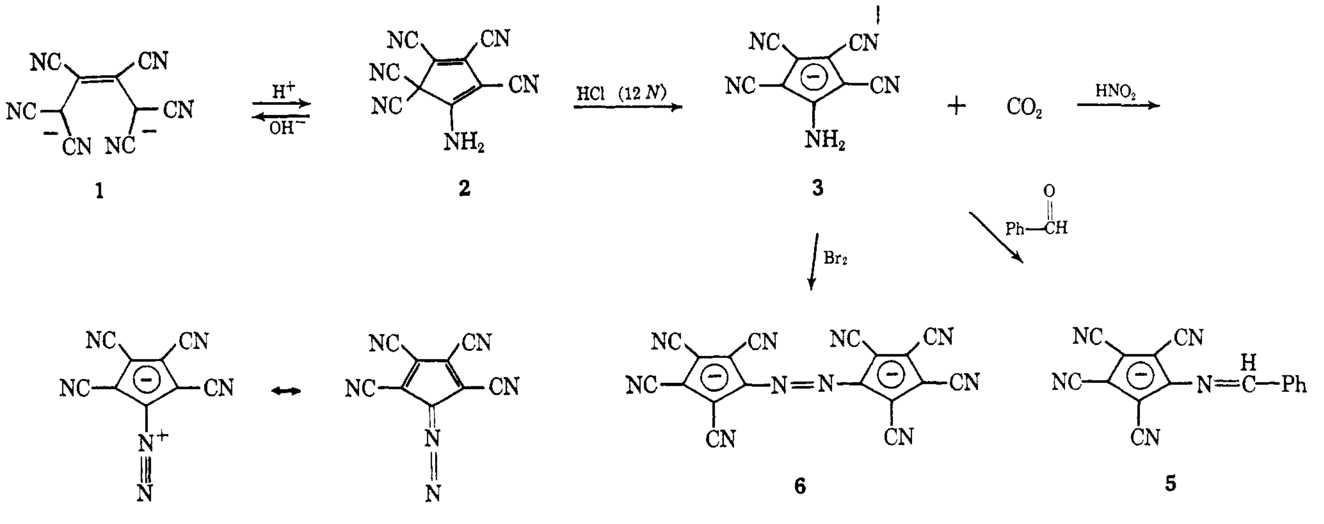
[2] For a review of cyanocarbon chemistry, see T. L. Cairns and B. C. McKusick, *Angew. Chem.*, **73**, 520 (1961); B. C. McKusick and T. L. Cairns, "Kirk-Othmer Encyclopedia of Chemical Technology," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1965, p 625.

[3] Other reported diazocyclopentadienes are the parent compound: W. von E. Doering and C. H. DePuy, *J. Am. Chem. Soc.*, **75**, 5955 (1953); tetrabromo-, 2-nitro-, 3-nitro- 2,5-diiodomercuri-, 2,5-diiodo-, and 2-tricyanovinyldiazocyclopentadiene: D. J. Cram and R. D. Partos, *ibid.*, **85**, 1273 (1963); 2,3,4-triphenyl- and 2,3,5-triphenyldiazocyclopentadiene: P. L. Paulson and B. J. Williams, *J. Chem. Soc.*, 4153 (1961).

the most to DTCC's structure. Its high dipole moment, 11.44 D., and stability to acid conditions (DTCC can be recovered from concentrated sulfuric acid solutions) leave little doubt that it is a diazonium rather than a diazo compound. The heat of combustion of DTCC is 5470 cal/g (1117 kcal/mole). This value compares with 5660 cal/g (722 kcal/mole) for tetracyanoethylene. Although we were unable to detonate DTCC, even with a blasting cap, only small amounts were prepared and used at a time because of its high energy and the well-known explosive properties of diazo and diazonium compounds.

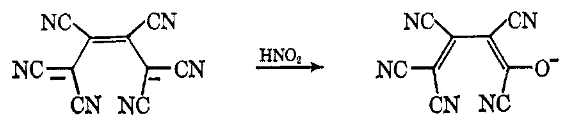
Synthesis

In dilute aqueous acid, disodium hexacyanobutenediide[4] (**1**) cyclizes to 1-amino-2,3,4,5,5-pentacyanocyclopentadiene (**2**), a bright yellow, unstable solid, $\lambda_{max}^{CH_3CN}$ 413 mμ (ε 7000). This amino compound reverts to butenediide **1** in aqueous base. Treatment of the amine **2** with concentrated hydrochloric acid, potassium iodide, hot methanol, or potassium cyanide in hydrogen cyanide gives the aminocyclopentadienide **3** isolated as its insoluble tetraethylammonium salt, mp 126–127°, $pK_a^{H_2O}$ = 2.0. Aminotetracyanocyclopentadienide reacts with benzaldehyde to form the anil **5** and with bromine to give the azo derivative[1] **6**. Diazotetracyanocyclopentadiene (**4**) results when aminotetracyanocyclopentadienide is diazotized under conditions ordinarily used to prepare aromatic diazonium compounds.



1 2 3 4 6 5

The entire sequence from the butenediide **1** to diazotetracyanocyclopentadiene (**4**) can be conducted without isolation of intermediates by treatment of butenediide first with concentrated hydrochloric acid and then with sodium nitrite. When the order of addition is reversed, pentacyanobutadienolate[4] (**7**), but no DTCC, is produced. This reaction is reminiscent of the action of sodium nitrite on tetracyanoquinodimethan to give the sodium salt of α,α-dicyano-*p*-toluoyl cyanide.[5]



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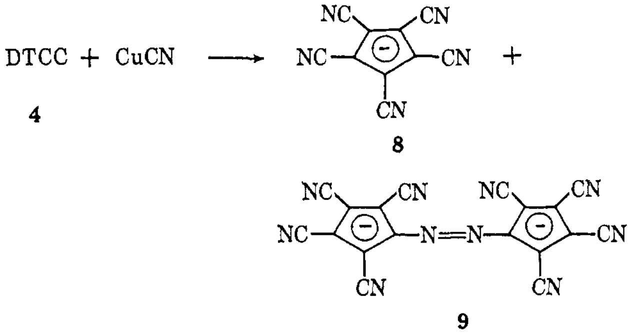
The chemistry of diazotetracyanocyclopentadiene is essentially that of a diazonium compound rather than that of a diazo compound.[6]

Elimination Reactions

DTCC and cuprous cyanide yield pentacyanocyclopentadienide (**8**) and azotetracyanocyclopentadienide (**9**), isolated as their tetraethylammonium salt. Pentacyanocyclopentadienide's ultraviolet spectrum, λ_{max} 255 mμ (ε 95,500) and 291 mμ (ε 10,250), compares well with that of penta(methoxycarbonyl)cyclopentadienide,[7] λ_{max} 265 mμ (ε 50,000) and 295 mμ (ε 15,000). Potassium pentacyanocyclopentadienide can be heated to its melting point, ~400°, in air without decomposition. It is not protonated by perchloric acid in acetonitrile, one of the strongest acid systems available.[8] Salts of the azo ion **9** are bright orange, λ_{max} 484 mμ (ε 21,800) but form blue solutions in strong acids.



Iodide or bromide reacts with DTCC to give halotetracyanocyclopentadienide[9] (**10**), while chloride requires copper as a catalyst. The mechanism of these substitutions is likely free radical, even in the iodide

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[4] O. W. Webster, *J. Am. Chem. Soc.*, **86**, 2898 (1964).

[5] W. R. Hertler, H. D. Hartzler, D. S. Acker, and R. E. Benson, *ibid.*, **84**, 3387 (1962).

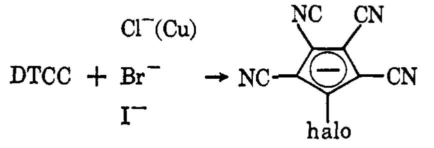
[6] For a comprehensive review of diazonium reactions, see H. Zollinger, "Azo and Diazo Chemistry," Interscience Publishers, Inc., New York, N. Y., 1961.

[7] R. C. Cookson, J. Hudec, and B. Whitear, *Proc. Chem. Soc.*, 117 (1961).

[8] I. M. Kolthoff, S. Bruckenstein, and M. K. Chantooni, Jr., *J. Am. Chem. Soc.*, **83**, 3921 (1961).

[9] K. Friedrich, *Angew. Chem.*, **78**, 449 (1966).

case, since sodium iodide in ethanol gave no **10**, only tetracyanocyclopentadienide (**11**). The tetracyanocyclopentadienidyl ion-radical (**12**) intermediate for these reactions is generated polarographically at 0.23 v *vs.* sce in acetonitrile or by mild reducing agents, such as copper powder, cuprous ion, or zinc powder. If methanol or ethanol is present, the only cyanocarbon product isolated is tetracyanocyclopentadienide (**11**). To show that the alcohol is oxidized by the radical, in one reaction with ethanol acetaldehyde was isolated as its 2,4-dinitrophenylhydrazone. In acetonitrile or water, the ion radical will attack benzene or phenol but not nitrobenzene.



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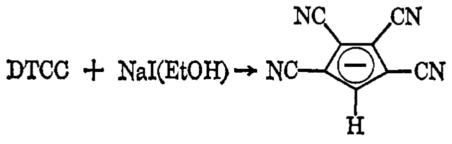

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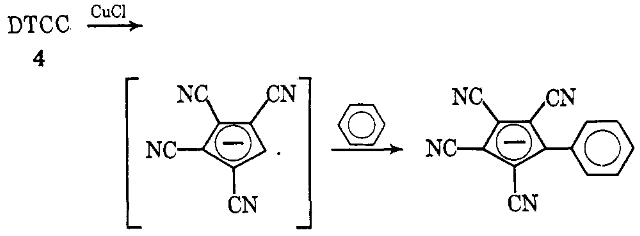

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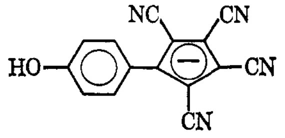
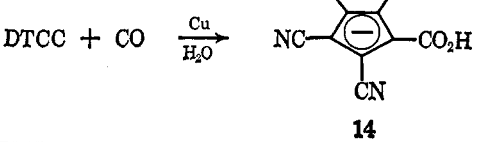
With phenol, a mixture of products (assumed to be the *ortho*, *meta*, and *para* isomers) was produced, but only the *para*-substituted ion **13** was isolated and characterized.



13

The pK_a[10] of the phenol (**13**) in water is 9.66. Based on a pK_a for phenol of 9.92 and a reaction constant, ρ, of 2.23, the Hammett σ_p for tetracyanocyclopentadienidyl is +0.12 (slightly electron withdrawing).

This electron-withdrawing ability of the tetracyanopentadienidyl group is borne out by a pK_a value of 2.0 for the ammonium tetracyanocyclopentadienidyl zwitterion (from the amine **2**) compared to anilinium, 4.6; and by the pK_a of carboxytetracyanocyclopentadienide (**14**) (from the copper-catalyzed reaction of DTCC, carbon monoxide, and water), 4.11 compared to benzoic acid, 4.20.



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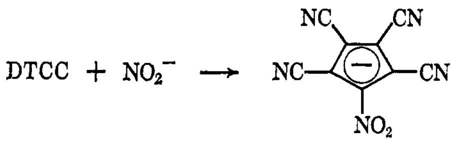
The action of nitrite on DTCC in water gives nitro tetracyanocyclopentadienide[9] (**15**).



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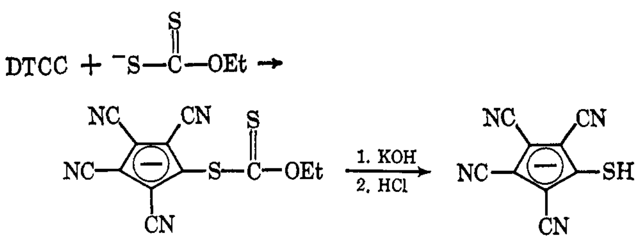
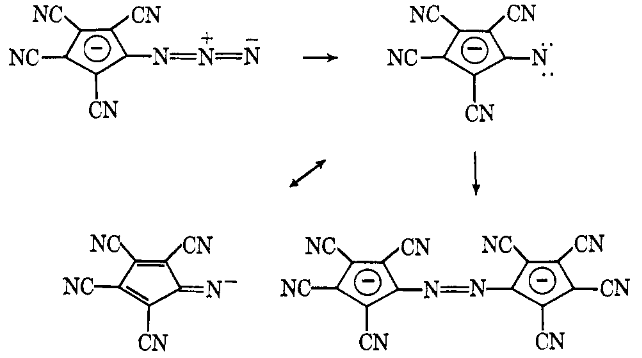
The thiol derivative **16** was made by reaction of DTCC with potassium xanthate followed by hydrolysis.



16

DTCC reacts with sodium azide to give sodium azidotetracyanocyclopentadienide (**17**), an unstable white compound which quickly turns orange on exposure to light or when warmed. Orange disodium azotetracyanocyclopentadienide (**9**) resulted (66% yield) when a solution of the azide in acetonitrile was refluxed 2 hr. Essentially the same yield of azo compound and none of the expected nitrene products were obtained on addition of norbornene or cyclohexene to the azide under the above pyrolysis conditions. We believe the nitrene is produced but is too stable to react with olefins.



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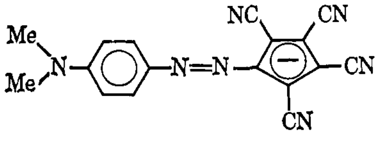
Coupling Reactions

DTCC coupled with N,N-dimethylaniline and with 2-naphthol to give the azo compounds **18** and **19**.



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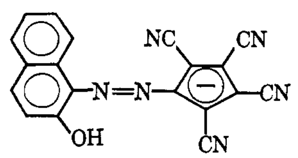

19

Salts of these ions are light stable, orange dyes, $\lambda_{\max}$ 472 mμ (ϵ 32,700) and 498 mμ (ϵ 22,800).

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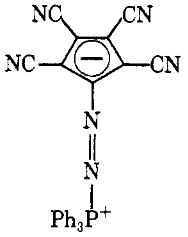
[10] The pK_a was determined spectroscopically by the method outlined in A. I. Biggs and R. A. Robinson, *J. Chem. Soc.*, 388 (1961).

Addition Reactions

As with diazonium compounds, some reagents add to the terminal nitrogen of DTCC. Triphenylphosphine gives the orange-red phosphazene (**20**); sodium cyanide, the azocyanide **21**; and sodium bisulfite, the adduct **22**.



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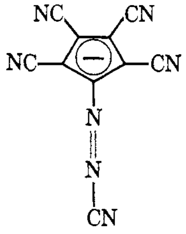

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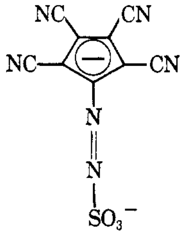

22

Physical Properties of Substituted Tetracyanocyclopentadiene Salts

For convenience, most of the substituted tetracyanocyclopentadienes described here were isolated as their water-insoluble tetraethylammonium salts. These derivatives generally recrystallize readily and melt at moderately low temperatures without decomposition. In cases where water solubility was desired, the tetraethylammonium salt was converted to the insoluble silver salt with excess silver nitrate and then to the potassium salt by potassium chloride. In no case was the parent-substituted tetracyanocyclopentadiene isolated (the $\mathrm{p}K_a^{\mathrm{H_2O}}$ of tetracyanocyclopentadiene is estimated to be -8). Although solutions of the acids could be made by ion exchange when the solvent was evaporated, extensive decomposition occurred. Tetracyanocyclopentadiene metal salts are surprisingly soluble in organic solvents (potassium tetracyanocyclopentadienide is soluble in ethyl acetate). This may be due to the formation of an ion pair with the metal atom over the center of the cyclopentadienide ion. The ferrous salt of pentacyanocyclopentadiene, however, was nonvolatile and extremely air sensitive, properties indicative of an ionic ferrous compound rather than a ferrocene.

Experimental Section

1-Amino-2,3,4,5,5-pentacyanocyclopentadiene (2). A mixture of disodium hexacyanobutenediide (15 g, 0.10 mole), water (15 ml), Amberlite IR 120 ion-exchange resin (acid form, 50 g), and ether (500 ml) was stirred for 0.5 hr. The ether layer was collected, dried with calcium chloride, and clarified with carbon black. Evaporation gave 1-amino-2,3,4,5,5-pentacyanocyclopentadiene (10.0 g, 82% yield). An analytical sample (dec pt 215–230°) was prepared by recrystallization from ether: $\lambda_{\max}^{\text{Nujol}}$ 2.96, 3.22, 4.53, 5.99, 6.25, 6.41, and 7.45 μ; $\lambda_{\max}^{\mathrm{CH_3CN}}$ 413 mμ (ϵ 7000).

Anal. Calcd for $C_{10}H_2N_6$: C, 58.3; H, 0.98; N, 40.8. Found: C, 58.5; H, 1.13; N, 40.6.

Reaction of 1-Amino-2,3,4,5,5-pentacyanocyclopentadiene with KOH. To an ice-cold solution of KOH (5.0 g, 89.2 mmoles) in water (20 ml) was added 1-amino-2,3,4,5,5-pentacyanocyclopentadiene (1.00 g, 4.85 mmoles). In a few seconds, yellow *cis*-dipotassium hexacyanobutenediide (1.35 g, 98% yield) precipitated, was collected on a filter, and was dried. The product was identified by its infrared spectrum.[5]

Aminotetracyanocyclopentadienide (3). Concentrated hydrochloric acid (10 ml) was cooled to 5°, and 1-amino-2,3,4,5,5-pentacyanocyclopentadiene (2.0 g, 9.7 mmoles) was added. The mixture was allowed to warm slowly. At about 15°, gas evolution occurred, and cooling was necessary to hold the temperature between 15 and 20°. After gas evolution had ceased (about 10 min), the solution was poured into ice-water (100 ml) containing sodium bicarbonate (20 g). The resulting mixture was filtered, and the filtrate was treated with tetraethylammonium bromide (4.0 g). Tetraethylammonium 1-amino-2,3,4,5,5-pentacyanocyclopentadiene (2.0 g, 68% yield) precipitated. An analytical sample (mp 126–127°) was prepared by recrystallization from water.

Anal. Calcd for $C_{17}H_{22}N_6$: C, 65.3; H, 7.25; N, 27.6. Found: C, 65.5; H, 7.11; N, 27.4.

In a subsequent experiment, the gas evolved was trapped in an aqueous solution of $Ba(OH)_2$. $BaCO_3$ was isolated in 54% yield and identified by its infrared spectrum.

Aminotetracyanocyclopentadienide was also produced from the aminopentacyano compound by refluxing in methanol 16 hr, by refluxing in acetonitrile with KI for 24 hr, or by stirring in liquid hydrogen cyanide at 0° with KCN. Potassium aminotetracyanocyclopentadienide absorbed at: $\lambda_{\max}^{\text{KBr}}$ 3.00 μ, 4.52, 4.57, 6.15, 6.61, 6.74, 6.82, 7.13, 7.38, 9.05, and 14.41; $\lambda_{\max}$ 237 mμ (ϵ 39,000), 262 (15,760), 296 (10,420), and 340 (9600).

Diazotetracyanocyclopentadiene (4). A suspension of tetraethylammonium aminotetracyanocyclopentadienide (6.08 g, 19.7 mmoles) in water (200 ml) and hydrochloric acid (10 ml) was cooled to 0°, and a solution of $NaNO_2$ (0.60 g, 8.7 mmoles) in water (10 ml) was added slowly over 0.5 hr. The reaction mixture was allowed to warm to room temperature over 0.5 hr. The insoluble portion was collected on a filter. This product in water (200 ml) was again treated with HCl (10 ml) and $NaNO_2$ (0.60 g) and was allowed to stand at room temperature 2 hr. The product was again collected on a filter and dried under reduced pressure. The dry diazotetracyanocyclopentadiene weighed 3.37 g (88% yield). An analytical sample (dec pt 200–225°) was prepared by recrystallization from ethylene dichloride and then from acetonitrile: $\lambda_{\max}^{\text{Nujol}}$ 4.44 μ, 4.51, 6.60, 6.94, and 7.65; $\lambda_{\max}^{\mathrm{CH_3CN}}$ 331 mμ (ϵ 14,950), 261.5 (26,800), and 252 (29,400).

Anal. Calcd for C_9N_6: C, 56.3; N, 43.8. Found: C, 56.2; N, 43.2.

The Preparation of Diazotetracyanocyclopentadiene from Disodium Hexacyanobutenediide without Isolation of Intermediates. To ice-cold, concentrated HCl (250 ml) was added disodium hexacyanobutenediide (25 g, 0.10 mole). The solution was stirred 0.5 hr, and sodium nitrite (15 g, 0.217 mole) in water (15 ml) was added slowly with stirring over 15 min. The solution was then diluted with water (250 ml), and the insoluble product was collected on a filter and dried. The yield of diazotetracyanocyclopentadiene (identified by its infrared spectrum) was 11.0 g (61%).

Disodium Azotetracyanocyclopentadienide (6). To a solution of sodium aminotetracyanocyclopentadienide (1.00 g, 4.93 mmoles) in water (50 ml) was added sodium hydroxide (0.40 g) and bromine (0.50 ml, 9.4 mmoles). Disodium azotetracyanocyclopentadienide (0.44 g, 45% yield) precipitated and after 10 min was collected and dried. It was identified by its characteristic visible spectrum.[4]

Benzylidenaminotetracyanocyclopentadienide (5). A solution of tetraethylammonium aminotetracyanocyclopentadienide (2.00 g, 6.44 mmoles) in benzaldehyde (20 ml) was heated at 150° for 0.5 hr. The light yellow solution was then cooled and diluted with ether (500 ml). Tetraethylammonium benzylidenaminotetracyanocyclopentadienide (2.4 g, 93% yield) was collected on a filter and dried. An analytical sample (mp 155–157°) was prepared by recrystallization from ethylene chloride: $\lambda_{\max}^{\text{KBr}}$ 3.35 μ, 4.56, 6.20, 6.26, 6.35, 6.75, 6.85, 6.90, 7.20, 8.55, 12.79, 13.14, 14.10, 14.42, and 14.95; $\lambda_{\max}^{\mathrm{CH_3CN}}$ 365 mμ (ϵ 13,400), 280 (37,400), 222 (24,100), and 212 (22,100).

Anal. Calcd for $C_{24}H_{26}N_6$: C, 72.3; H, 6.57; N, 21.1. Found: C, 72.3; H, 6.33; N, 21.3.

Tetraethylammonium 1,2,3,4,4-Pentacyanobutadien-1-olate (7). Disodium hexacyanobutenediide (2.50 g, 10.0 mmoles) and sodium nitrite (5.0 g, 72 mmoles) were dissolved in water (100 ml), and the solution was acidified with 6 *N* HCl. After 10 min, excess tetraethylammonium chloride was added, and the precipitate of tetraethylammonium 1,2,3,4,4-pentacyanobutadien-1-olate (1.50 g, 46% yield) was collected and dried. It was identified by comparison of its infrared spectrum with that of a sample prepared from hexacyanobutadiene and water.[5]

Pentacyanocyclopentadienide (8) and Azotetracyanocyclopentadienide (9). A suspension of 1.00 g (5.6 mmoles) of cuprous cyanide in 50 ml of acetonitrile was refluxed under nitrogen. A solution of 0.96 g (5.00 mmoles) of DTCC in 20 ml of acetonitrile was added dropwise over 15 min. Gas (86 cc, 3.6 mmoles) was evolved. An orange precipitate was separated from the reaction mixture by filtration. The filtrate was concentrated to dryness, and the residue was dissolved in a solution of 2 g of sodium cyanide in 200 ml of water. Tetraethylammonium pentacyanocyclopentadiene (1.11 g, 69% yield) precipitated on addition of 2 g of tetraethylammonium chloride. An analytical sample, mp 357–362°, was prepared by recrystallization from water: $\lambda_{\max}^{\mathrm{CH_3CN}}$ 291 mμ (ϵ 10,250), 281 (10,850), 255 (95,500), and 246 (59,600); $\lambda_{\max}^{\mathrm{KBr}}$ (potassium salt) 4.47 μ and 6.79 μ.

Anal. Calcd for $C_{18}H_{20}N_6$: C, 67.5; H, 6.29; N, 26.2. Found: C, 67.3; H, 6.21; N, 26.4.

The orange product insoluble in the reaction mixture above was washed with 2 g of sodium cyanide in 100 ml of water. The insoluble material remaining was then dissolved in 50 ml of acetonitrile containing 2 g of tetraethylammonium chloride. The orange solution was then chromatographed on aluminum (Woelm, acid, activity 1). The first band to appear was collected and recrystallized from water to give 0.24 g (15% yield) of tetraethylammonium azotetracyanocyclopentadienide, mp 350°: $\lambda_{\max}^{\mathrm{CH_3CN}}$ 484 mμ (ϵ 21,800), 455 (23,500), 428 (23,400), 300 (23,700), 282 (53,300), 272 (39,700), 256 (24,600), and 217 (52,100); $\lambda_{\max}^{\mathrm{KBr}}$ (in addition to Et_4N^+ bands) 4.48 μ.

Anal. Calcd for $C_{34}H_{40}N_{12}$: C, 66.2; H, 6.54; N, 27.3. Found: C, 66.0; H, 6.38; N, 26.6.

Chlorotetracyanocyclopentadienide (10). A mixture of 2.82 g (17.1 mmoles) of tetraethylammonium chloride, 1.00 g of copper powder, and 50 ml of acetonitrile was heated under reflux, and 2.02 g (10.6 mmoles) of DTCC in 30 ml of acetonitrile was added dropwise over 1 hr. Gas (223 cc, 9.3 mmoles) was evolved. The reaction mixture was cooled and filtered, and the filtrate concentrated to approximately 20 ml. The concentrate was diluted with 100 ml of water, and the precipitate which formed was collected on a filter and dried. The crude product weighed 2.99 g (86% yield). An analytical sample of tetraethylammonium chlorotetracyanocyclopentadienide (mp 243–246°) was prepared by recrystallization from ethylene chloride three times.

Anal. Calcd for $C_{17}H_{20}N_5Cl$: C, 61.9; H, 6.11; N, 21.2; Cl, 10.8. Found: C, 61.5; H, 5.91; N, 21.3; Cl, 10.6.

Bromotetracyanocyclopentadienide (10). A solution of 0.96 g (5.00 mmoles) of DTCC, 3.19 g (15.2 mmoles) of tetraethylammonium bromide, and 50 ml of acetonitrile was warmed to 50°. In the course of 0.5 hr, 103 cc (4.3 mmoles) of gas was evolved. The reaction solution was concentrated and was diluted with water. Tetraethylammonium bromotetracyanocyclopentadienide (1.47 g, 78% yield) was collected on a filter and dried. An analytical sample, mp 226–228°, was prepared by recrystallization from ethylene chloride three times and once from water.

Anal. Calcd for $C_{17}H_{20}N_5Br$: C, 54.6; H, 5.39; N, 18.7. Found: C, 54.8; H, 5.44; N, 19.1.

Iodotetracyanocyclopentadienide (10). A solution of 5.00 g (33.3 mmoles) of sodium iodide in 70 ml of acetonitrile was stirred at room temperature, and a solution of 5.00 g (26.0 mmoles) of DTCC in 100 ml of acetonitrile was added dropwise over 0.5 hr. Nitrogen (608 cc, 25.4 mmoles) was evolved. The solution was evaporated to dryness, and the residue was dissolved in 100 ml of water. The aqueous solution was treated with 5.00 g of tetraethylammonium chloride. Tetraethylammonium iodotetracyanocyclopentadienide (9.1 g, 86% yield) precipitated, was collected on a filter, and was dried. An analytical sample, mp 194.5–195.5°, was prepared by recrystallization three times from ethylene dichloride and once from water: $\lambda_{\max}^{\mathrm{CH_3CN}}$ 300 mμ (ϵ 10,100), 290 (9700), 250 (40,400), and 243 (42,800).

Anal. Calcd for $C_{17}H_{20}N_5I$: C, 48.5; H, 4.79; N, 16.6; I, 30.2. Found: C, 48.7; H, 4.69; N, 16.5; I, 29.9.

Tetracyanocyclopentadienide (11). A mixture of 0.96 g (5.0 mmoles) of DTCC and 0.50 g (2.8 mmoles) of CuCN in 100 ml of methanol was heated under reflux for 0.5 hr. The reaction mixture was filtered, and the filtrate was concentrated to dryness. The residue was treated with a solution of 2 g of sodium cyanide and 2 g of tetraethylammonium chloride in water. The precipitate of tetraethylammonium tetracyanocyclopentadienide which formed was collected on a filter, washed with water, and dried to give 1.11 g, 75% yield. An analytical sample, mp 129–130°, was obtained by recrystallization from water: $\lambda_{\max}^{\mathrm{CH_3CN}}$ 298 mμ (ϵ 14,500), 287 (13,500), 244 (56,800), and 237 (42,400); $\lambda_{\max}^{\mathrm{KBr}}$ (other than Et_4N^+ bands) 4.55 μ, 8.75, and 12.53.

Anal. Calcd for $C_{17}H_{21}N_5$: C, 69.1; H, 7.17; N, 23.7. Found: C, 69.2; H, 7.26; N, 23.2.

A suspension of 1 g of copper powder in 250 ml of methanol was heated to reflux, and a solution of 2.22 g (11.5 mmoles) of DTCC in 30 ml of acetonitrile was added dropwise over 0.5 hr. Gas (179 cc, 7.5 mmoles) evolved. The reaction mixture was filtered and evaporated to dryness. The residue was taken up in water and filtered into 2.00 g of tetraethylammonium chloride in 100 ml of water. Tetraethylammonium tetracyanocyclopentadienide (2.06 g, 60% yield) was collected on a filter and dried. Its identity was confirmed by its infrared spectrum.

A solution of 1.00 g (6.67 mmoles) of sodium iodide in 50 ml of ethanol was heated under reflux, and a solution of 0.96 g (5.0 mmoles) of DTCC in 70 ml of ethanol was added dropwise over 15 min. Gas (106 cc, 4.4 mmoles) was evolved. The reaction mixture was concentrated to dryness, and the residue was dissolved in 70 ml of water. Tetraethylammonium chloride (1.00 g) was added, and the precipitate which formed was collected and recrystallized from water to give 0.96 g (65% yield) of tetraethylammonium tetracyanocyclopentadienide (mp 126–128°), further identified by its infrared spectrum.

Phenyltetracyanocyclopentadienide. A mixture of 10.0 g (51.0 mmoles) of DTCC, 10 g of benzene, 5 g of copper powder, and 300 ml of water was stirred overnight at 20–40°. The reaction mixture was filtered, and excess tetramethylammonium chloride was added to the filtrate. The precipitate which formed was air dried and was then extracted with 300 ml of hot ethylene chloride. The extract was concentrated to dryness to give tetramethylammonium phenyltetracyanocyclopentadienide (1.5 g, 9% yield). It was purified by chromatography on Woelm alumina (acid, activity 1) with ethylene chloride–ethyl acetate wash. The chromatographed product was recrystallized from ethyl acetate. The purified product (mp 252–254°) weighed 0.3 g: $\lambda_{\max}^{\mathrm{CH_3CN}}$ 300 mμ (ϵ 12,600) and 262 mμ (ϵ 45,800); $\lambda_{\max}^{\mathrm{KBr}}$ 4.55 μ, 6.25, 5.74, 6.85, 6.95, 7.00, 7.25, 9.32, 9.72, 10.58, 12.58, 13.25, and 14.21.

Anal. Calcd for $C_{19}H_{17}N_5$: C, 72.36; H, 5.43; N, 22.21. Found: C, 72.51; H, 5.44; N, 22.07.

A solution of 5.00 g of DTCC, 2.50 g of $CuCl_2$, 25 ml of benzene, 350 ml of acetone, and 150 ml of water was allowed to stand at room temperature 15 min and was then refluxed 15 min. The reaction mixture was concentrated to approximately 100 ml, and a solution of 10 g of tetramethylammonium chloride in 200 ml of water was added. The precipitate which formed was collected on a filter and dried. The dry precipitate (9.0 g) was extracted with acetone, and the acetone-soluble product was then extracted with hot water. The material insoluble in the hot water (2.25 g, 28% yield) was pure tetramethylammonium phenyltetracyanocyclopentadienide. Its identity was confirmed by its infrared spectrum.

4-Hydroxyphenyltetracyanocyclopentadienide (13). To a mixture of 10 g (107 mmoles) of phenol, 5 g of zinc powder, and 500 ml of water was added 10 g (51.0 mmoles) of DTCC in approximately 1-g portions. After gas evolution had ceased (approximately 1 hr), the mixture was filtered, and the filtrate was treated with 20 g of tetramethylammonium chloride. The gummy precipitate which formed was crystallized from hot water. The crystallized product was extracted with ethyl acetate, and the ethyl acetate soluble portion was recrystallized from water to give tetramethylammonium 4-hydroxyphenyltetracyanocyclopentadienide (0.5 g, 3% yield, mp 260–265° dec). In another run, the crude product was purified by chromatography on Woelm alumina (acid, activity 1) with ethyl acetate and acetonitrile wash to give tetramethylammonium 4-hydroxyphenyltetracyanocyclopentadienide (2.25 g, 13% yield): $\lambda_{\max}^{\mathrm{CH_3CN}}$ 264 mμ (ϵ 37,600); $\lambda_{\max}^{\mathrm{KBr}}$ 3.02 μ, 4.53, 6.16, 6.53, 6.72, 6.82, 6.92, 7.00, 7.26, 7.87, 8.12, 8.42, 10.53, and 11.95.

Anal. Calcd for $C_{19}H_{17}N_5O$: C, 68.86; H, 5.17; N, 21.14. Found: C, 68.79; H, 5.05; N, 21.00.

A solution of 2.0 g of Me_4N^+ 4-hydroxyphenyltetracyanocyclopentadienide and 2.0 g of $AgNO_3$ in 100 ml of acetonitrile was concentrated to dryness, and the residue was washed with water. The insoluble silver salt was then suspended in 100 ml of acetonitrile and was stirred with 4 g of KCl in 10 ml of water for 1 hr. The reaction mixture was filtered, and the filtrate was concentrated to dryness. The residue was dissolved in water, and KCl was added to precipitate potassium 4-hydroxyphenyltetracyanocyclopentadienide (0.5 g). This product was recrystallized from acetonitrile and used for determination of its pK_a spectroscopically in water at 24°: $\lambda_{\max}^{\mathrm{H_2O}}$ (acid) 310 mμ (ϵ 11,650) and 263 mμ (ϵ 39,600); $\lambda_{\max}^{\mathrm{H_2O}}$ (base) 320 mμ (ϵ 14,900), 285 (29,100), 270 (sh) (25,420), 246 (30,150); pK_a = 9.66. The nmr spectrum (CH_3CN) a weak–strong–strong–weak pattern centered at δ 6.98 with a separation of 0.43 ppm between the strong peaks and 0.73 ppm between the weak.

Carboxytetracyanocyclopentadienide (14). A mixture of 2.00 g (10.4 mmoles) of DTCC, 1.00 g of copper powder, and 30 ml of water was heated at 70° for 1 hr under 1000 atm of carbon monoxide. The reaction mixture was filtered, and the filtrate was treated with 5 g of tetraethylammonium chloride. On dilution with water, 2.5 g (71% yield) of tetraethylammonium carboxytetracyanocyclopentadienide precipitated. An analytical sample, mp 273.5–275°, was prepared by recrystallization once from ethylene chloride and twice from water: $\lambda_{\max}^{\mathrm{CH_3CN}}$ 295 mμ (ε 10,450), 285 (10,500), 258 (79,800), and 250 (51,000); $\lambda_{\max}^{\mathrm{KBr}}$ 2.80 μ, 2.92, 3.35, 3.50, 3.60, 3.82, 3.96, 4.53, 6.00, 6.75, 6.82, 7.19, 7.32, 7.80, 8.46, 8.55, 8.84, 8.93, 10.00, 11.05, 11.76, 12.75, and 14.16.

Anal. Calcd for $C_{18}H_{21}N_5O_2$: C, 63.7; H, 6.24; N, 20.6. Found: C, 64.5, 64.3; H, 6.12, 6.08; N, 20.7, 20.7.

Nitrotetracyanocyclopentadienide (15). A mixture of 4.00 g (20.4 mmoles) of DTCC, 2.80 g (40.5 mmoles) of $NaNO_2$, and 100 ml of water was heated at 80° for 0.5 hr. Nitrogen evolved, and the DTCC dissolved. To the hot solution was added 5.0 g of tetraethylammonium chloride, and the precipitate of tetraethylammonium nitrotetracyanocyclopentadienide (3.5 g, 50% yield) was collected on a filter and dried. It was purified by chromatography on Woelm alumina (neutral, activity 1) with ethyl acetate–acetonitrile eluent followed by recrystallization from ethanol, mp 370° dec: $\lambda_{\max}^{\mathrm{CH_3CN}}$ 349 mμ (ε 3650), 273 (31,200), 265 (29,050), and 211 (25,250); $\lambda_{\max}^{\mathrm{KBr}}$ 4.48 μ, 6.54, 6.72, 7.46, 11.32, 13.18, and 13.50.

Anal. Calcd for $C_{17}H_{20}O_2N_6$: C, 60.0; H, 5.92; N, 24.7. Found: C, 60.2; H, 6.37; N, 24.5.

Decacyanoferrocene. To a stirred solution of 3.75 g (12.6 mmoles) of silver pentacyanocyclopentadienide in 60 ml of acetonitrile was added 1.60 g (12.5 mmoles) of $FeCl_2$ under nitrogen. After 0.5 hr, the white precipitate of silver chloride which had formed was removed by filtration under nitrogen, and the filtrate was concentrated to about 10 ml. On standing 2 hr, light green crystals of decacyanoferrocene slowly formed. The ferrocene was collected on a filter under nitrogen and was washed with a small amount of acetonitrile. The sample was dried at 112° (0.3 mm). (Although an effort was made to keep the system anhydrous, a small amount of water may have been present in the acetonitrile or $FeCl_2$.)

Anal. Calcd for $C_{20}N_{10}Fe \cdot H_2O$: C, 52.9; H, 0.44, N, 30.9. Found: C, 53.0; H, 0.57; N, 31.2.

Mercaptotetracyanocyclopentadienide (16). A solution of 2.00 g (10.2 mmoles) of DTCC and 1.65 g (10 mmoles) of ethyl potassium xanthate in 100 ml of acetonitrile was slowly warmed to reflux. At about 50°, nitrogen evolution became vigorous. The reaction solution was heated under reflux 0.5 hr and was then cooled and concentrated to dryness. The residue was dissolved in a warm solution of 20 g of KOH in 150 ml of water and was allowed to stand 0.5 hr. The basic solution was then acidified with dilute hydrochloric acid.

The acid solution was treated with 10 g of tetraethylammonium chloride, and the crude tetraethylammonium mercaptotetracyanocyclopentadienide which precipitated (2.25 g, 67% yield) was collected and dried. After two recrystallizations from ethanol, the product weighed 1.7 g, mp 275–280° dec: $\lambda_{\max}^{\mathrm{CH_3CN}}$ 340 mμ (ε 4000), 271 (22,200), and 233 (22,700); $\lambda_{\max}^{\mathrm{KBr}}$ 3.70 μ and 4.50 μ (Et_4N^+ bands not given).

Anal. Calcd for $C_{17}H_{21}N_5S$: C, 62.3; H, 6.41; N, 21.4; S, 9.80. Found: C, 61.9; H, 6.04; N, 21.7; S, 10.03.

Azidotetracyanocyclopentadienide (17). To a solution of 0.65 g (10 mmoles) of NaN_3 in 20 ml of water was slowly added 1.96 g (10 mmoles) of DTCC. Gas was evolved smoothly at room temperature. After 0.5 hr, 2.0 g of Et_4NCl was added, and the nearly white tetraethylammonium azidotetracyanocyclopentadienide (3.00 g, 90% yield) was collected on a filter and dried. The product was light orange after air drying overnight. An analytical sample (mp 120–125° dec) was prepared by recrystallization from ethanol: $\lambda_{\max}^{\mathrm{CH_3CN}}$ 300 mμ (ε 9560), 270 (34,500), and 257 (39,400); $\lambda_{\max}^{\mathrm{Nujol}}$ 4.52 μ, 4.60, 4.75, 7.88, and 11.18 (Et_4N^+ bands not given).

Anal. Calcd for $C_{17}H_{20}N_8$: C, 60.7; H, 5.99; N, 33.3. Found: C, 61.6; H, 6.11; N, 33.4.

The above precedure was repeated, and 5.0 g of $NaNO_3$ was added to the aqueous reaction solution. Sodium azidotetracyanocyclopentadienide precipitated, was collected on a filter, and was dried. The dried azide was then chromatographed on Woelm alumina (acid, activity 1) with acetonitrile wash. The purified sodium azidotetracyanocyclopentadienide (1.12 g, 42% yield) was identified by its infrared spectrum.

Anal. Calcd for $C_9N_7Na \cdot 2H_2O$: C, 40.7; H, 1.51; N, 37.0. Found: C, 40.2; H, 1.33; N, 35.2.

A solution of 0.60 g (2.26 mmoles) of sodium azidotetracyanocyclopentadienide dihydrate in 50 ml of acetonitrile was refluxed 2 hr. Disodium azotetracyanocyclopentadienide (0.35 g, 66% yield) precipitated, was collected on a filter, and was dried. The identity of the product was confirmed by its ultraviolet and infrared spectra.

A solution of 10 ml of cyclohexene in 50 ml of acetonitrile was refluxed under nitrogen, and a solution of 0.49 g (1.85 mmoles) of sodium azidotetracyanocyclopentadienide dihydrate in 20 ml of acetonitrile was added dropwise over 15 min. The mixture was then refluxed 2 hr. The reaction mixture was cooled, and the disodium azotetracyanocyclopentadienide (0.19 g, 51% yield) was collected by filtration. Its identity was established by its ultraviolet spectrum. The residue which remained on evaporation of the acetonitrile and cyclohexene weighed 0.15 g. Its infrared spectrum was essentially the same as that of the corresponding residue produced by pyrolysis of sodium azidotetracyanocyclopentadienide with no cyclohexene present.

***p*-(Dimethylamino)phenylazotetracyanocyclopentadienide (18).** To a solution of 0.96 g (5.00 mmoles) of diazotetracyanocyclopentadiene in 20 ml of acetonitrile was slowly added 2.0 ml of N,N-dimethylaniline. The resulting orange solution was allowed to stand overnight. The solution was diluted with 200 ml of ether, and the precipitate which formed (1.8 g) was collected and dried. The precipitate was stirred 1 hr with 1 g of KOH and 58 ml of water. The precipitate was then collected on a filter and dissolved in hot water. The hot aqueous solution was treated with 1.0 g of tetraethylammonium chloride. Tetraethylammonium *p*-(dimethylamino)phenylazotetracyanocyclopentadienide (0.95 g, 43% yield) precipitated. An analytical sample (mp 173–175°) was prepared by two recrystallizations from ethylene chloride: $\lambda_{\max}^{\mathrm{CH_3CN}}$ 472 mμ (ε 32,700), 318 (11,170), 278 (27,100), and 218 (23,000); $\lambda_{\max}^{\mathrm{KBr}}$ 3.34 μ, 3.42, 3.55, 4.52, 6.24, 6.41, 6.57, 7.34, 8.75, 10.00, 10.57, 12.00, and 12.75.

Anal. Calcd for $C_{25}H_{30}N_8$: C, 67.9; H, 6.83; N, 25.3. Found: C, 68.0; H, 6.71; N, 25.5.

α-(β-Hydroxynaphthyl)azotetracyanocyclopentadienide (19). To a solution of 1.44 g (10.0 mmoles) of β-naphthol in 50 ml of acetonitrile at room temperature was added 1.96 g (10.0 mmoles) of DTCC. Potassium acetate (1.0 g) was then added, and the bright orange solution which resulted was allowed to stand overnight. Sufficient water was added to the reaction mixture to dissolve the suspended solids, and the resulting solution was filtered and added to a solution of 4.0 g of tetraethylammonium chloride in 100 ml of water. The precipitate of tetraethylammonium α-(β-hydroxynaphthyl)azotetracyanocyclopentadienide (3.50 g, 75% yield) was collected and was recrystallized from ethanol three times, mp 208–213°: $\lambda_{\max}^{\mathrm{CH_3CN}}$ 498 mμ (ε 22,800), 476 (22,400), 313 (9650), 283 (24,350), and 275 (24,750); $\lambda_{\max}^{\mathrm{Nujol}}$ 4.52 μ, 6.15, 6.25, 6.35, 6.60, 6.72, 7.70, 8.01, 8.54, 10.00, 10.50, 12.25, 12.80, 13.28, 13.32, and 13.83.

Anal. Calcd for $C_{27}H_{27}N_7O$: C, 69.5; H, 5.85; N, 22.0. Found: C, 69.7; H, 5.93; N, 22.0.

Triphenylphosphazinotetracyanocyclopentadienide (20). A solution of 0.96 g (5.00 mmoles) of DTCC in 20 ml of acetonitrile was treated with 1.41 g (5.38 mmoles) of $(C_6H_5)_3P$ at room temperature. A red solution resulted, and, in a few minutes, red crystals of the triphenylphosphazinotetracyanocyclopentadienide (2.1 g, 92% yield) formed. An analytical sample (mp 212–214° dec) was prepared by recrystallization from acetonitrile: $\lambda_{\max}^{\mathrm{CH_3CN}}$ 412 mμ (ε 29,600) and 273 mμ (ε 26,700); $\lambda_{\max}^{\mathrm{KBr}}$ 3.27 μ, 4.52, 6.31, 6.68, 6.75, 6.96, 7.24, 7.63, and 8.37.

Anal. Calcd for $C_{27}H_{15}N_6P$: C, 71.4; H, 3.33; N, 18.5. Found: C, 71.5; H, 3.65; N, 18.2.

Cyanoazotetracyanocyclopentadienide (21). To a solution of 0.33 g (5.1 mmoles) of dry KCN in 100 ml of methanol was added 0.96 g (5.0 mmoles) of DTCC. The deep yellow solution was poured into a solution of 5 g of tetraethylammonium chloride in 200 ml of water. Tetraethylammonium cyanoazotetracyanocyclopentadienide (0.93 g, 53% yield) was collected on a filter and dried. An analytical sample (dec pt 250°) was recrystallized from ethylene chloride: $\lambda_{\max}^{\mathrm{CH_3CN}}$ 405 mμ (ε 21,400), 276 (19,600), and 254 (13,230); $\lambda_{\max}^{\mathrm{KBr}}$ 4.52 μ, 4.60, 6.95, 7.55, 8.30, 9.75, and 10.80 (Et_4N^+ absorption not given).

Anal. Calcd for $C_{18}H_{20}N_8$: C, 62.1; H, 5.79; N, 32.2. Found: C, 62.1; H, 5.50; N, 32.3.

Sulfonatoazotetracyanocyclopentadienediide (22). To a solution of 2.14 g (23.2 mmoles) of sodium bisulfite in 50 ml of water was added 1.96 g (10.0 mmoles) of DTCC. The mixture was stirred 0.5 hr at room temperature and was filtered. To the yellow filtrate was added a solution of 5.0 g of tetraethylammonium chloride in 10 ml of water. Light yellow bis(tetraethylammonium) sulfonatoazotetracyanocyclopentadienediide (3.0 g, 56% yield) was collected on a filter and was dried. An analytical sample (mp 214–217° dec) was prepared by recrystallization three times from water: $\lambda_{\max}^{\mathrm{CH_3CN}}$ 436 mμ (ε 247), 342 (10,570), 279 (34,300), 271 (32,300), and 210 (9060); $\lambda_{\max}^{\mathrm{Nujol}}$ 4.54 μ, 7.95, 8.10, 8.50, 9.64, 10.05, 10.66, 12.28, 12.70, and 13.59.

Anal. Calcd for $C_{25}H_{40}N_8SO_3$: C, 56.4; H, 7.54; N, 21.1; S, 6.02. Found: C, 56.3; H, 7.54; N, 20.9; S, 6.00.