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Alkylation of Tetracyanoethylene. Reaction with Grignard Reagents

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Abstract: The alkylation of tetracyanoethylene has been achieved by the slow addition of 1 equiv of Grignard reagent at low temperatures to produce a series of 1:1 adducts, which on neutralization with trifluoroacetic acid afford a variety of alkyltetracyanoethanes in excellent yields. The reaction of primary alkyl Grignard reagents with 2 equiv of TCNE produces the 1:2 adducts, 3-alkylhexacyanopentadienide salts, with the loss of 2 equiv of HCN. An x-ray crystal structure of the 3-isopropyl analog shows it to be in a twisted U conformation in contrast to a planar W form previously established for the parent 1,1,2,4,5,5-hexacyanopentadienide ion. A mechanistic scheme is presented for the addition of Grignard reagent to TCNE via nucleophilic and electron transfer routes. The metastability of the initial 1:1 adducts due to loss of HCN leads to tricyanoallyl carbanions, which can be exploited in the preparation of a variety of 3-alkyl-1,1,2,4,5,5-hexacyanopentadienide ions in high yields. The latter are electrochemically readily reduced to poly anions, and they undergo an irreversible rearrangement to a new series of 4-alkyl-2,3,5,6-tetracyanoanilines.

Polycyanoolefins such as tetracyanoethylene (TCNE) are highly electrophilic due to the delocalization of the π-electron density into the cyano substituents. Alkylation reactions of TCNE represent a limiting case of the attack of a nucleophile on such an activated olefin.[1]

The chemistry of polycyanocarbons has been actively investigated for the past 15 years,[2,3] and research has recently gained added impetus from their use in organic metals.[4] The unusual reactivity of TCNE is shown by its high reactivity toward many nucleophiles and rapid formation of cycloadducts with various alkenes.[5-8] TCNE also readily inserts into carbon–hydrogen bonds in ketones and arenes, as well as transition metal–carbon bonds.[7,9-11] These systems all involve nucleophiles less powerful than the substitution-labile organometals such as alkyllithium and magnesium reagents. However, in spite of the extensive and varied studies carried out on TCNE, the reaction with Grignard reagents has not been reported. Indeed, the poor yields and incomplete stoichiometry obtained with organometals in a few cited cases have been attributed to the high reactivity of TCNE and its primary products.[10] The participation of multiple reaction paths and the well-known tendency of cyanoolefins to form tarry materials have also discouraged study heretofore.

The diversity of reactions shown by TCNE suggests that it may react by a variety of mechanisms. Thus, the facile

formation of the anion radical [TCNE·⁻] and the ubiquitous charge-transfer complexes[12] lend support to one-electron processes as alternatives to the more common two-electron or nucleophilic routes. These complications are compounded during the exposure of TCNE to potent nucleophiles such as Grignard reagents which are also electron donors. We report, however, that under proper experimental conditions the direct alkylation of TCNE with Grignard reagents can be carried out in high yields for the convenient synthesis of two interesting classes of polycyanocarbons: 1,1,2,2-tetracyanoalkanes and 1,1,2,4,5,5-hexacyanopentadienide salts.
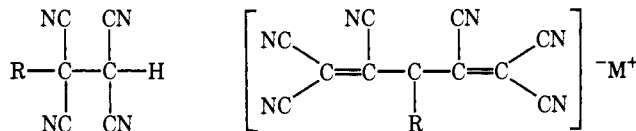
Mechanistic routes for the formation of these new series of cyanocarbons will also be described, together with the formation of a novel class of polycyano aromatic compounds, 4-alkyl-2,3,5,6-tetracyanoanilines, by the spontaneous rearrangement of the hexacyanopentadienide ions.

Results

1,1,2,2-Tetracyanoalkanes from 1:1 Adducts. The slow addition of 1 equiv of phenylmagnesium bromide to a sus-

Table I. 1,1,2,2-Tetracyanoalkanes (R-C(CN)$_2$C(CN)$_2$H)
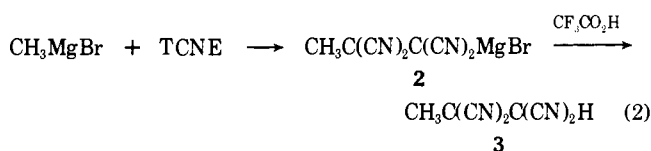Prepared by the Reaction between Grignard Reactions and TCNE

Compd	R	Yield, %	Mp, °C	^{1}H NMR δ, ppm[a]
3	CH$_3$	96	96–97	5.21 (s, 1), 2.13 (s, 3)[b]
4	C$_2$H$_5$	85	63–64	4.48 (s, 1), 2.38 (q, 2, J = 7.5 Hz), 1.45 (t, 3, J = 7.5 Hz)
5	i-C$_3$H$_7$	81	78–79	4.46 (s, 1), 2.65 (sep, 1, J = 7 Hz), 1.41 (d, 6, J = 7 Hz)
6	t-C$_4$H$_9$	46	108–109	4.40 (s, 1), 1.47 (s, 9)
7	Ph	97	160–163[c]	7.74 (s, 5), 4.53 (s, 1)

[a] In CDCl$_3$. [b] In CD$_3$CN. [c] With decomposition.

pension of TCNE in tetrahydrofuran (THF) at −78°C results in the formation of a highly colored mixture which becomes homogeneous and colorless (pale yellow) again when 1 equiv has been added. On warming the solution to room temperature, the solution turns yellow–brown but the product, 2-phenyl-1,1,2,2-tetracyanoethylmagnesium bromide (1), is stable for months.

$$\text{PhMgBr} + \text{TCNE} \longrightarrow \text{PhC(CN)}_2\text{C(CN)}_2\text{MgBr} \qquad (1)$$
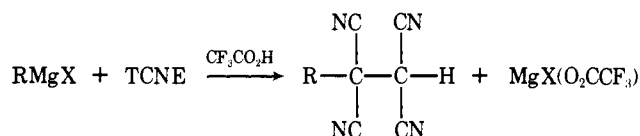$$1$$
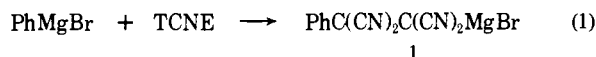
The addition of methylmagnesium bromide to TCNE in a similar manner affords a deep red mixture which lightens to a pale yellow solution at the equivalence point. However, warming this solution to room temperature leads to tar formation, and hydrogen cyanide is evolved over a 2-day period. On the other hand, acidification of the cold, *freshly* prepared solution of 2 with trifluoroacetic acid afforded 1,1,2,2-tetracyanopropane (3) in high yields.

$$\text{CH}_3\text{MgBr} + \text{TCNE} \longrightarrow \text{CH}_3\text{C(CN)}_2\text{C(CN)}_2\text{MgBr} \xrightarrow{\text{CF}_3\text{CO}_2\text{H}}$$
$$2$$
$$\text{CH}_3\text{C(CN)}_2\text{C(CN)}_2\text{H} \qquad (2)$$
$$3$$

A moderately strong acid is required to neutralize 2 since the conjugate acid has a pK_a of about 3.5 [compare the pK_a of 3.6 for 1,1,2,2-tetracyanoethane[7]]. Quenching the reaction mixture with acetic acid only leads to partial protonation of 2.

Other 1,1,2,2-tetracyanoalkanes can be readily prepared in the same manner from ethyl, isopropyl, *tert*-butyl, and phenyl Grignard reagents (Table I). The lower yields of the
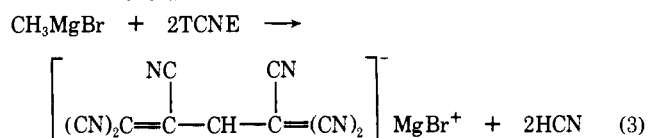
$$\text{RMgX} + \text{TCNE} \xrightarrow{\text{CF}_3\text{CO}_2\text{H}} \begin{array}{c} \text{NC} \quad \text{CN} \\ | \quad\quad | \\ \text{R}-\text{C}-\text{C}-\text{H} \\ | \quad\quad | \\ \text{NC} \quad \text{CN} \end{array} + \text{MgX(O}_2\text{CCF}_3)$$

tert-butyl adduct could be partly traced to the formation of isobutane and isobutylene in 12% yield (vide infra).

The 1,1,2,2-tetracyanoalkanes 3–7 were identified by elemental and mass spectral analysis and are all colorless solids, strongly acidic, and readily sublimed. The sharp strong ir bands around 2910 and 740 cm^{-1} were assigned to the -CH(CN)$_2$ moiety,[13] and a weak (or absent) nitrile absorption (stretch) at about 2250 cm^{-1} was noted. The proton NMR resonances are listed in Table I. The parent compound 1,1,2,2-tetracyanoethane (R = H) has been previously made by the reduction of TCNE.[7]

3-Alkyl-1,1,2,4,5,5-hexacyanopentadienide Ions from 1:2 Adducts. A. Methyl and Primary Alkyl Grignard Reagents. The addition of 1 equiv of methylmagnesium bromide to a suspension of 2 equiv of TCNE in THF at −78°C afforded a red mixture. The reaction turned darker upon warming it to room temperature and liberated 2 equiv of hydrogen cyanide over several hours.

$$\text{CH}_3\text{MgBr} + 2\text{TCNE} \longrightarrow$$

$$\left[\begin{array}{c} \text{NC} \quad\quad\quad \text{CN} \\ | \quad\quad\quad\quad | \\ \text{(CN)}_2\text{C}{=}\text{C}-\text{CH}-\text{C}{=}\text{(CN)}_2 \end{array} \right]^{-} \text{MgBr}^{+} + 2\text{HCN} \qquad (3)$$

1,1,2,4,5,5-Hexacyanopentadienide could be isolated in 96% yield as the tetramethylammonium salt 9, appearing as a beautiful dark red crystalline material with a gold luster. Similar results were obtained if a solution of the 1:1 adduct 2 prepared beforehand in eq 2 was added to a solution of TCNE in THF at room temperature.

$$2 + \text{TCNE} \longrightarrow 8 + 2\text{HCN} \qquad (4)$$
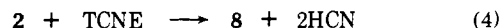
Compound 9 is identical with that previously obtained in 7% yield after a difficult multistep sequence.[14]

The same procedure was followed with other primary alkyl Grignard reagents including the ethyl, *n*-propyl, isobutyl, and benzyl derivatives to afford dark blue solutions from which analogous salts could also be isolated in high yields (Table II).

The identity of these salts was established by an x-ray crystal structure of tetramethylammonium 3-isopropyl-1,1,2,4,5,5-hexacyanopentadienide (14), the bond distances and planar angles of which are shown in Figure 1 and a ste-

Table II. Hexacyanopentadienide Ions Prepared from the Reaction between Grignard Reagents and TCNE

Compd	R'	Yield, %[a]	Recrystallization[a] solvent	Mp,[a] °C	λ_{max}, nm (ϵ, M^{-1} cm^{-1})	$\nu_{C{\equiv}N}$, cm^{-1}	^{1}H NMR[a,d] δ, ppm
9	H	96	MeOH	289–902	540 (82 000)	2183	6.43 (s, 1)
10	CH$_3$	70	DMK–Et$_2$O[b]	191–192[c]	589 (34 500)	2185	2.37 (s, 3)
11	C$_2$H$_5$	82	DMK–Et$_2$O[b]	149–150[c]	592 (27 000)	2185	2.82 (q, 2, J = 7 Hz) 1.18 (t, 3, J = 7 Hz)
13	n-C$_3$H$_7$	85	H$_2$O	111–112	593 (25 000)	2185	2.75 (q, 2, J = 8 Hz) 1.65 (m, 2, J = 7 Hz) 0.99 (t, 3, J = 7 Hz)
14	i-C$_3$H$_7$	73	DMK–Et$_2$O[b]	151[c]	600 (18 500)	2220, 2180, 2156	~3.20 (sep, 1, J = 7 Hz) 1.40 (d, 6, J = 7 Hz)
15	Ph	74	DMK–Et$_2$O[b]	172	594 (25 000)	2183	7.75–7.25 (m, 5)

[a] NMe$_4^+$ salts. [b] Acetone–ether. [c] With decomposition. [d] In acetone-d_6; δ 3.45–3.47 (s, 12) for NMe$_4^+$; m = multiplet, q = quartet.
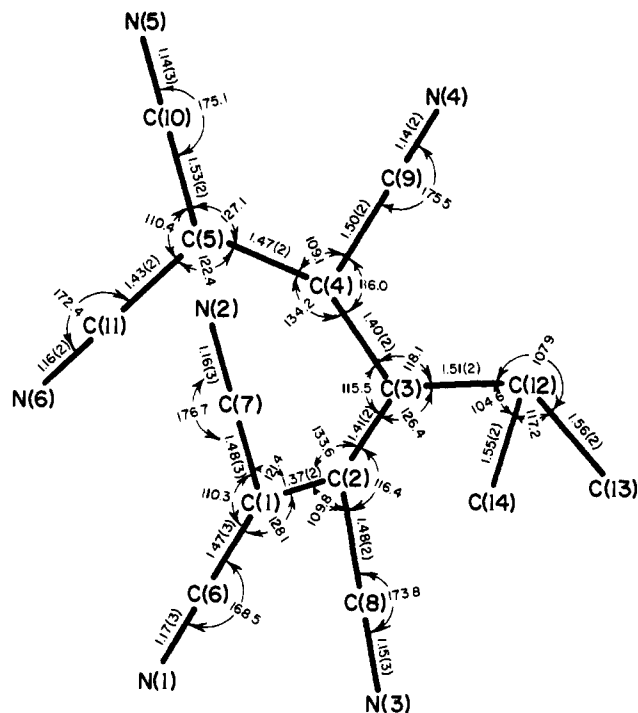
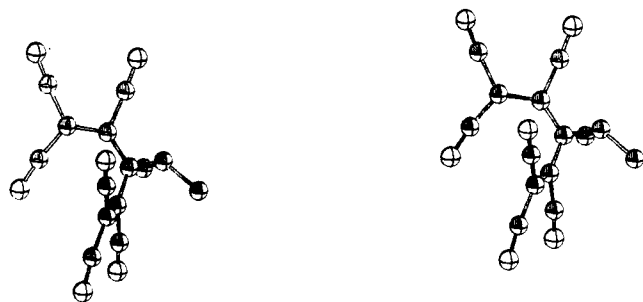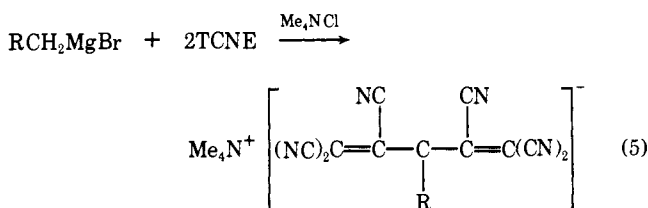Figure 1. The crystal structure of 3-isopropyl-1,1,2,4,5,5-hexacyano-pentadienide ion.

Figure 2. A stereoscopic view of the structure of 3-isopropyl-1,1,2,4,5,5-hexacyanopentadienide in with ⊕ = carbon and ⊕ = nitrogen.

$$\text{RCH}_2\text{MgBr} \ + \ 2\text{TCNE} \ \xrightarrow{\text{Me}_4\text{NCl}}$$

$$\text{Me}_4\text{N}^+ \left[(\text{NC})_2\text{C}\!=\!\overset{\overset{\displaystyle\text{NC}}{|}}{\text{C}}\!-\!\overset{\overset{\displaystyle\ }{|}}{\underset{\underset{\displaystyle R}{|}}{\text{C}}}\!-\!\overset{\overset{\displaystyle\text{CN}}{|}}{\text{C}}\!=\!\text{C}(\text{CN})_2 \right]^{\!-} \qquad (5)$$

reoscopic view in Figure 2.[15] The dihedral angles of **14** are listed in Table III.

The hexacyanopentadienide salts isolated in this manner have similar spectroscopic properties shown in Table II. The proton chemical shifts of the alkyl substituents are further downfield (relative to other carbanions), characteristic of delocalized anions. The maxima in the electronic spectra of cyanopentadienide ions all occur in a narrow band between 590 and 600 nm, with large extinction coefficients (ϵ >10^4 M^{-1} cm^{-1}), except the parent ion **9** which absorbs at significantly shorter wavelengths and more intensely than the others.

Electrochemical Reduction of Hexacyanopentadienide Ions. 1,1,2,4,5,5-Hexacyanopentadiene is an extremely strong acid with a pK_a value of −3.5.[16] The methyl- and phenyl-substituted anions **10** and **15**, respectively, were electrochemically reducible in dimethylformamide solu-

Table III. Torsion Angles for the 3-Isopropyl-1,1,2,4,5,5-hexacyanopentadienide ion as Found in the X-Ray Crystal Structure Determination

| Atoms[a]	Angle, (deg)
[C(7)–C(1)–C(2)–C(8)]	174.4
[C(6)–C(1)–C(2)–C(8)]	−11.1
[C(7)–C(1)–C(2)–C(3)]	−0.7
[C(6)–C(1)–C(2)–C(3)]	−175.2
[C(1)–C(2)–C(3)–C(4)]	−42.3
[C(8)–C(2)–C(3)–C(4)]	−144.3
[C(1)–C(2)–C(3)–C(12)]	136.6
[C(8)–C(2)–C(3)–C(12)]	−36.8
[C(2)–C(3)–C(4)–C(5)]	−23.1
[C(12)–C(3)–C(4)–C(5)]	−157.9
[C(2)–C(3)–C(4)–C(9)]	167.3
[C(12)–C(3)–C(4)–C(9)]	11.7
[C(3)–C(4)–C(5)–C(10)]	−179.9
[C(9)–C(4)–C(5)–C(10)]	−9.6
[C(3)–C(4)–C(5)–C(11)]	−3.1
[C(9)–C(4)–C(5)–C(11)]	167.0

[a] See Figure 1 for numbering.

tions. Polarograms of **10** showed two well-defined one-electron waves at +0.13 and −0.56 V vs. a cadmium amalgam/cadmium chloride reference. Two half-wave potentials of **15** were observed at +0.16 and −0.49 V, suggestive of the formation of di- and trianions.[17] The ability of hexacyanopentadienide ions to accept two additional electrons at rather low potentials is rather unusual as anions are concerned. Furthermore, the recovery of **10** in 27% yield by air oxidation of the electrolyzed solution suggests their potential use as electron-transfer reagents in "controlled potential" reductions.

Tetracyanoanilines from the Rearrangement of Hexacyanopentadienide Ions. Solutions of 3-substituted hexacyanopentadienide ions were unstable on prolonged standing. For example, 3-n-propyl-1,1,2,4,5,5-hexacyanopentadienide after 2 weeks gave 4-n-propyl-2,3,5,6-tetracyanoaniline (**16**) in low yield. Compound **16** and its ethyl analog **17** are yellow solids. They sublime readily and fluoresce blue in solution. The structure of **17** was established by x-ray methods and is illustrated in Figures 3 and 4.[15] Cyclization of alkylhexacyanopentadienide ions to **16** and **17** probably involves the steps shown in eq. 6. The oxidative aromatization

$$ \text{(eq 6 reaction scheme)} \qquad + \ (\text{CN})_2 \qquad (6) $$
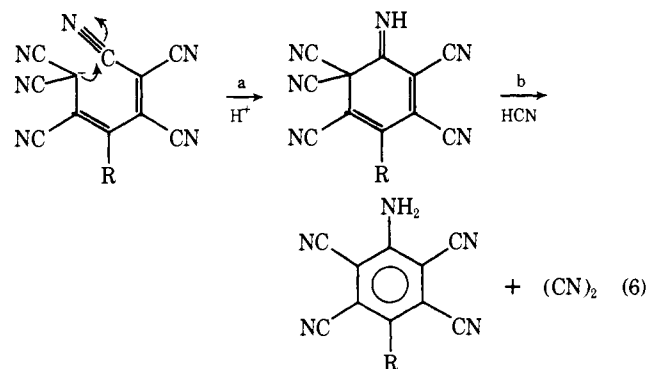
induced by cyanide in step 6b has precedence in cyanocarbon chemistry as shown by the reaction in eq 7.[18]

$$\text{PhC(CN)}_3 \ + \ \text{CN}^- \ \xrightarrow[\ 60\%\ ]{-60°\text{C}} \ \text{PhC(CN)}_2{}^- \ + \ (\text{CN})_2 \qquad (7)$$
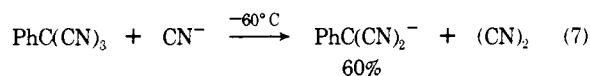
4-Alkyl-2,3,5,6-tetracyanoanilines represent a new class of aromatic compounds. The absorption spectrum [λ_{max} 423 nm (ϵ 8500)] resembles that of the p-chloro analog [λ_{max} 432 nm (ϵ 7720), blue fluorescence in solution] more than that of tetracyano-p-phenylenediamine [λ_{max} 498 nm (ϵ 6930)].[19]
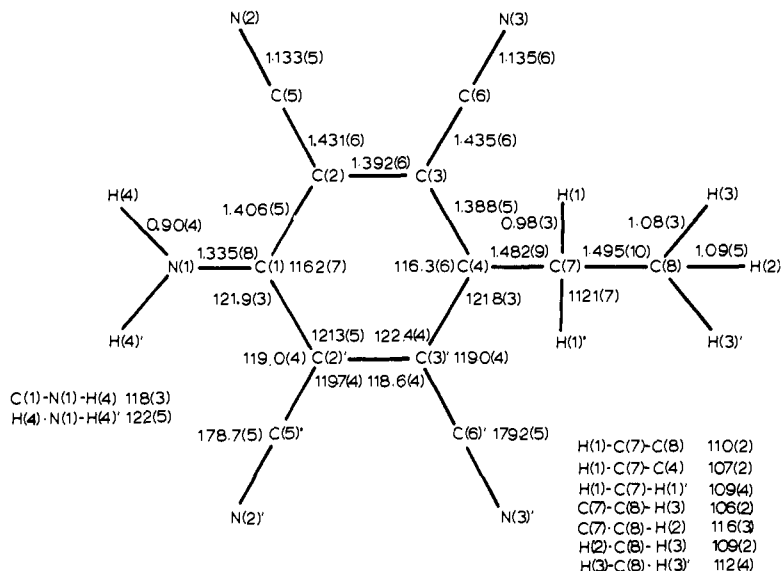
Figure 3. The crystal structure of 4-ethyl-2,3,5,6-tetracyanoaniline.

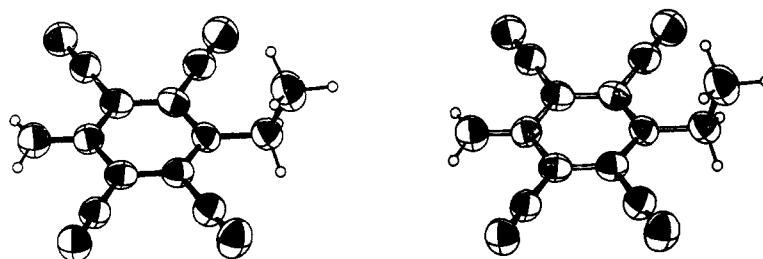|		
H(1)-C(7)-C(8)	110(2)
H(1)-C(7)-C(4)	107(2)
H(1)-C(7)-H(1)'	109(4)
C(7)-C(8)-H(3)	106(2)
C(7)-C(8)-H(2)	116(3)
H(2)-C(8)-H(3)	109(2)
H(3)-C(8)-H(3)'	112(4)

Figure 4. A stereoscopic view of the structure of 4-ethyl-2,3,5,6-tetracyanoaniline.

The Structures of 3-Alkyl-1,1,2,4,5,5-hexacyanopentadienide Ions. The electronic spectrum is the most striking characteristic of the hexacyanopentadienide ion **9**, showing absorptions bands at long wavelengths with large extinction coefficients. Alkyl substitution at the 3-position in cyanopentadienide ions shifts the maximum from 538 to a narrow band between 590 and 600 nm. As a result, alkyl-substituted hexacyanopentadienides are blue instead of red. The position and extinction coefficient (82 000 M^{-1} cm^{-1}) for the lowest energy band of **9** in solution suggest a planar structure of the ion, which is consistent with an x-ray crystal structure.[20] On the other hand, the 3-isopropyl derivative **14** adopts a twisted U shape in the crystal. As shown in Table III, the large torsional angles of −42 and −23° for the planes determined by C(1)-C(2)-C(3)-C(4) and C(2)-C(3)-C(4)-C(5), respectively, illustrate the degree of nonplanarity of the pentadienide backbone in **14**. Thus, the presence of a 3-alkyl substituent causes a conformation change of the carbon skeleton from **W** to **U** in the solid state.


W   **U**
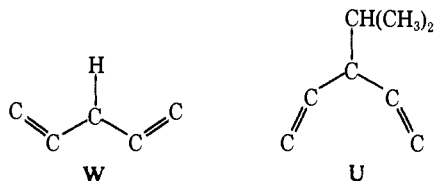
Examination of molecular models shows that a change in conformation from **W** to **U** (in addition to others[21]) is qualitatively in accord with a greater steric congestion imposed by substitution at C-3.

The importance of the U shape conformation in solution for alkyl hexacyanopentadienide ions is not completely clear. It is notable, however, that the increase in λ_{max} and
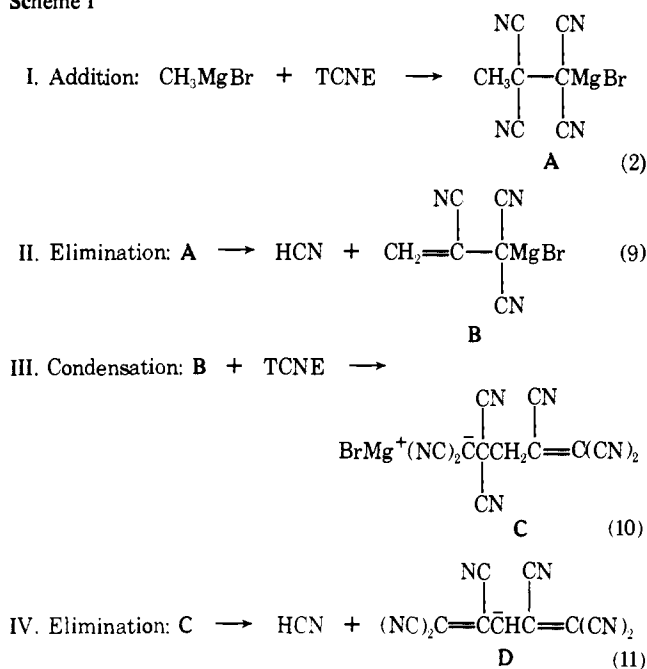
decrease in ϵ_{max} roughly parallel the size of the alkyl substituent. The changes may reflect the degree of nonplanarity induced by steric crowding of the 3-alkyl substituent against the pair of 2-(Z)- and 4-(Z)-cyano groups. Furthermore, the infrared frequencies of the hexacyanopentadienide ions fall in the range of 2180-2185 cm^{-1} for conjugated nitriles.[22] The presence of additional bands at 2250 and 2156 cm^{-1} for the isopropyl compound suggests that the nonconjugated form of **14** contributes to the structure.

B. Other Grignard Reagents. Phenylmagnesium bromide reacts with 2 equiv of TCNE to form tricyanovinylbenzene (**18**) in 77% yield, together with 25% TCNE·⁻ and 30% recovered TCNE.

$$\text{18}$$
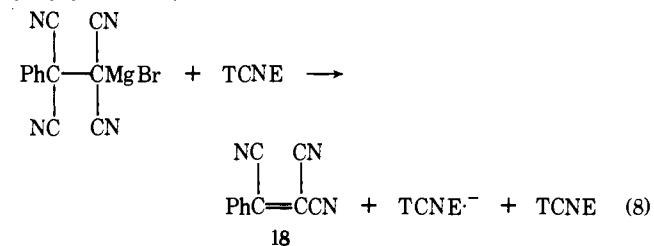
Reactions of TCNE with isopropyl and tert-butyl Grignard reagents afford complex mixtures. Low yields and tar formation are common. Thus, an off-white solid, tentatively identified as 3-amino-6,6-dimethyl-1,2,3,4,4,5,5-heptacyanocyclohexene (**19**) has been isolated in low yield from the reaction of isopropylmagnesium bromide and 3 equiv of TCNE. The reaction of tert-butylmagnesium bromide and 2 equiv of TCNE gives significant amounts of TCNE anion radical. Approximately one-half of the TCNE charge can be observed as pentacyanopropenide (**20**) and tricyanoethenolate (**21**) ions, which are known to arise from the reaction of TCNE·⁻ with oxygen.[18]

Scheme I

I. Addition: CH_3MgBr + TCNE $\longrightarrow$

$$\underset{\underset{NC}{|}\quad\underset{CN}{|}}{\overset{\overset{NC}{|}\quad\overset{CN}{|}}{CH_3C-CMgBr}}$$

$$\mathbf{A} \qquad (2)$$

II. Elimination: A $\longrightarrow$ HCN +

$$\underset{\underset{CN}{|}}{\overset{\overset{NC}{|}\quad\overset{CN}{|}}{CH_2=C-CMgBr}}$$

$$\mathbf{B} \qquad (9)$$

III. Condensation: B + TCNE $\longrightarrow$

$$BrMg^+(NC)_2\underset{\underset{CN}{|}}{\overset{\overset{CN}{|}}{\bar{C}}}\overset{\overset{CN}{|}}{C}CH_2C=C(CN)_2$$

$$\mathbf{C} \qquad (10)$$

IV. Elimination: C $\longrightarrow$ HCN +

$$(NC)_2\overset{\overset{NC}{|}}{C}=\bar{C}\overset{\overset{CN}{|}}{C}HC=C(CN)_2$$
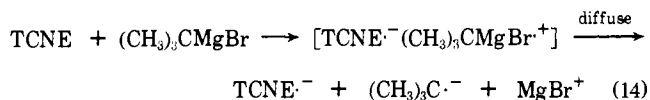
$$\mathbf{D} \qquad (11)$$

Discussion

The successful alkylation of TCNE with selected Grignard reagents under controlled conditions has provided considerable opportunity to gain insight into the mechanism of the complex processes extant in this system. In order to facilitate the presentation of our conclusions, we first introduce the principal reactions in Scheme I by illustrating the formation of hexacyanopropenide ion (8) from methylmagnesium bromide. Each step in the reaction sequence will be discussed separately in the following presentation.

Step I. Addition of Grignard Reagents to TCNE. The ready formation of the 1:1 adduct **A** of methylmagnesium bromide to TCNE at $-78°C$ can be observed by the characteristic color and NMR spectrum of the 1,1,2,2-tetracyanopropanide ion. The rate of addition of methylmagnesium bromide to TCNE is so fast that it can compete with hydrolysis (see Table VII and Experimental Section).

$$CH_3MgBr + TCNE/H_2O \longrightarrow \begin{cases} CH_4 + Mg(OH)Br & (12) \\ CH_3\text{-}TCNE\text{-}MgBr & (13) \end{cases}$$
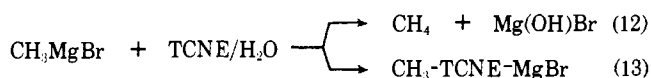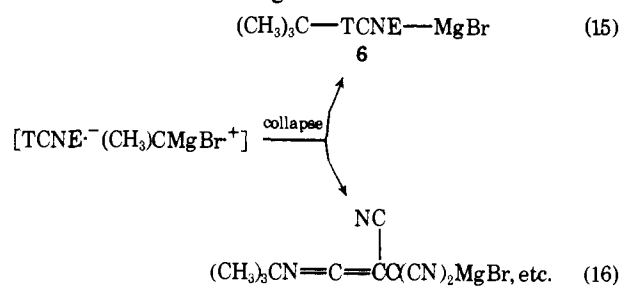
In contrast, *tert*-butylmagnesium bromide does not afford adducts to TCNE like **A** as readily, apparently due to steric reasons. More importantly, the production of TCNE anion radical in relatively high yields during the reaction suggests that an electron-transfer process has occurred such as:

$$TCNE + (CH_3)_3CMgBr \longrightarrow [TCNE\text{-}^-(CH_3)_3CMgBr^+] \xrightarrow{diffuse}$$

$$TCNE^- + (CH_3)_3C\text{-}^- + MgBr^+ \qquad (14)$$

Diffusion apart of the initial ion pair in eq 14 would lead to TCNE anion radical which we have observed by its characteristic electron spin resonance and visible absorption spectra. Moreover, the concomitant formation of *tert*-butyl radicals in eq 14 is supported by the presence of isobutylene and isobutane, which are well-known products of disproportionation (Table VIII and Experimental Section). The yield of isobutylene represents the lower limit on the number of *tert*-butyl radicals produced in the system since there are other competing processes such as hydrogen abstraction from the solvent and homolytic addition to TCNE.[7] Furthermore, coupling of the *tert*-butyl radical with TCNE anion radical by collapse of the ion pair formed in eq 14 to

afford 3,3-dimethyl-1,1,2,2-tetracyanobutanide ion may not be regiospecific at the ethylenic carbon due to an alternative site of attack on a nitrogen center.

$$(CH_3)_3C-TCNE-MgBr \qquad (15)$$
$$\mathbf{6}$$

$$[TCNE\text{-}^-(CH_3)_3CMgBr^+] \xrightarrow{collapse}$$

$$\underset{\overset{NC}{|}}{(CH_3)_3CN=C=C(CN)_2MgBr, etc.} \qquad (16)$$

More direct evidence for an electron transfer from a Grignard reagent to TCNE is shown by the simultaneous observation of the trityl radical and the TCNE anion radical in eq 17.[23]

$$Ph_3CMgCl + TCNE \xrightarrow{THF} Ph_3C\cdot + TCNE^- + MgCl^+ \qquad (17)$$
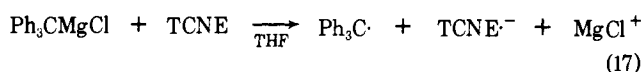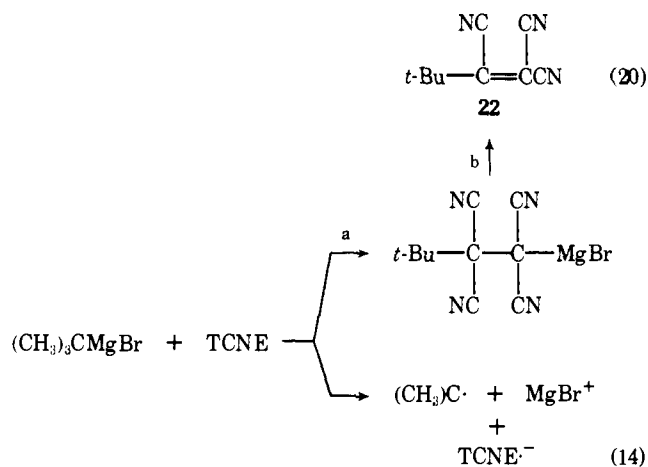
Nucleophilic addition and electron transfer as presented above may, in general, represent the competing modes of reaction when various Grignard reagents are exposed to TCNE.

$$R-MgX + TCNE \longrightarrow \begin{cases} R-TCNE^-MgX^+ & (18) \\ RMgX\cdot^+TCNE\cdot^-, etc. & (19) \end{cases}$$
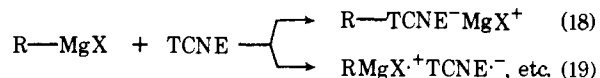
The competition between these two processes in eq 18 and 19 should depend on at least two factors: the ease of electron removal from the Grignard reagent and the steric interaction. The former is measured by the values of the oxidation potentials, but they are not available for Grignard reagents due to the irreversibility of the anodic processes. However, the electrochemical reactivity of Grignard reagents obtained from Tafel plots follow the order: *t*-Bu (1.16) > *i*-Pr (1.28) > Et (1.57) > Me (1.98), where the numbers in parentheses represent the anodic overvoltage at constant current density and are related to the ease of oxidation.[24]

The dichotomy between nucleophilic and electron-transfer processes is most noticeable with the *tert*-butyl moiety for several reasons. The relatively facile oxidation of *tert*-butyl Grignard reagent allows electron-transfer processes to be competitive. Secondly, steric factors retard addition of the alkyl moiety to the ethylenic carbon of TCNE. If a 1:1 adduct were formed between *tert*-butyl Grignard reagent and excess TCNE in high yields, we would have expected 3,3-dimethyl-1,1,2-tricyanobutene (22), by analogy with the formation of 18 from the phenyl analog in eq. 8.

$$\underset{\mathbf{22}}{t\text{-}Bu-\underset{\underset{}{}}{\overset{\overset{NC}{|}}{C}}=\overset{\overset{CN}{|}}{C}CN} \qquad (20)$$

$$\mathbf{b}\uparrow$$

$$(CH_3)_3CMgBr + TCNE \xrightarrow{a} \begin{cases} t\text{-}Bu-\underset{\underset{NC}{|}}{\overset{\overset{NC}{|}}{C}}-\underset{\underset{CN}{|}}{\overset{\overset{CN}{|}}{C}}-MgBr \\ \\ (CH_3)_3C\cdot + MgBr^+ \\ + \\ TCNE^- \qquad (14) \end{cases}$$
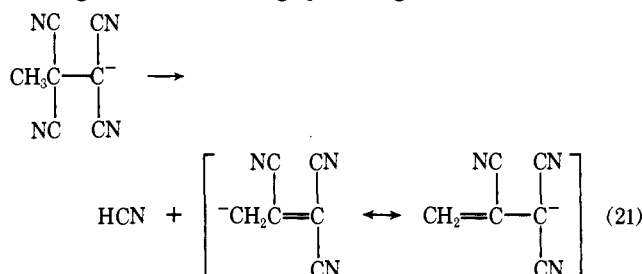
The failure to isolate **22** suggests that reaction 20, particu-

larly eq 20b, is minor, and it is supported by the low yield of **6** isolated under conditions optimum for the formation of 1:1 adducts.

A similar trend in electron-transfer reactivity of Grignard reagents has been found with other acceptors as structurally diverse as benzophenones, *tert*-butyl peroxide, nitrosoarenes, and quinol esters.[26-31] More rigorous criteria for distinguishing nucleophilic from electron-transfer processes in the reactions of other group 4B organometallic derivatives with TCNE is discussed in the following report.[32]

Step II. Elimination of HCN from Cyanocarbanions to form Polycyanoallyl Carbanions. The 1:1 adducts **A** of Grignard reagents to TCNE are thermally unstable, slowly liberating HCN on standing. [The singular absence of meth-

$$HCN + \left[\begin{array}{c} NC \quad CN \\ | \quad | \\ ^-CH_2C{=}C \\ | \\ CN \end{array} \longleftrightarrow \begin{array}{c} NC \quad CN \\ | \quad | \\ CH_2{=}C{-}C^- \\ | \\ CN \end{array} \right] \quad (21)$$

ane during the reaction of methylmagnesium bromide with TCNE (Table VII) suggests that addition to TCNE is faster than any subsequent proton-transfer reaction such as the neutralization of HCN.] The increased rate of formation of HCN in the presence of TCNE indicates that TCNE may assist in the formation of the tricyanoallyl carbanion **B**. The driving force for the formation of **B** can be judged from the high acidities of the conjugate acids, i.e., tricyanoalkenes, in which the remarkable ability of the tricyanovinyl group to stabilize carbanions is indicated by the difference in pK_a's of malononitrile (11.2) and pentacyanopropene (<-8.5).[2,16] Thus, tricyanoalkenes are generally unknown except for those like the aryl and *tert*-butyl homologues which have no α-hydrogens.[33]

In the absence of an α-hydrogen, elimination from the cyano carbanion may occur by loss of cyanide. Thus the 1:1 phenyl adduct to TCNE (**1**) is reasonably stable in the absence of excess TCNE (eq 1). The presence of an equivalent amount of TCNE induces loss of cyanide to afford tricyanobenzene as described in eq 8. The accompanying formation of TCNE anion radical in eq 8 is consistent with the suggestion by Webster et al. that it can be formed from the disproportionation of cyanide and TCNE.[18]

$$2TCNE + 2CN^- \longrightarrow 2TCNE^{\cdot-} + [(CN)_2] \quad (22)$$
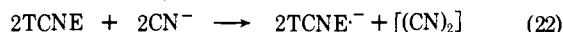
Steps III and IV. Condensation and Elimination. The weakly nucleophilic anion **B** may be trapped by a second molecule of TCNE to afford the 1:2 adduct **C** in step III which is analogous to step I. The final elimination of another HCN in step IV to generate the hexacyanopentadienide ion **D** is formally akin to step II. The overall liberation of 2 equiv of HCN for each hexacyanopentadienide ion formed is consistent with this formulation.

It is noteworthy that the addition of TCNE to the ambident ion **B** occurs exclusively at the alkyl terminus. This regiospecificity implies that additions at the $-C(CN)_2$ terminus are relatively slow. The formation of the 1:2 adducts, identified as the 1,1,2,4,5,5-hexacyanopentadienide ions, is only possible from Grignard reagents with primary alkyl centers since two α-hydrogens are lost. Thus, the reaction of isopropylmagnesium bromide and 3 equiv of TCNE afforded in poor yield only a single adduct, tentatively characterized as **19**, 3-amino-6,6-dimethyl-1,2,3,4,4,5,5-heptacyanocyclohexene (see Experimental Section). The low yields of **19** may be partly attributed to the steric hindrance at the

$$(23)$$
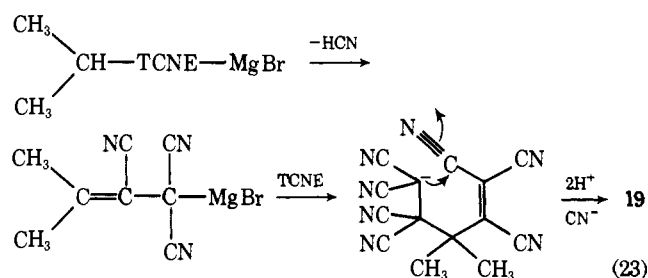
α,α-dimethyl center which impedes addition to another TCNE. The formation of **19** by the subsequent rearrangement of the 1:2 adduct is analogous to the generation of the tetracyanoanilines from hexacyanopentadienides in eq 6.

Scheme I thus represents a rational basis for discussing the complex processes which occur during the reaction of TCNE with various Grignard reagents. The mechanistic conclusions should also serve as a general model for describing the interactions of other nucleophiles with polycyanoalkenes as electron acceptors.[34] The optimum synthetic procedures described in this study require tetrahydrofuran as a solvent, a slow addition at low temperatures, and Grignard reagents as alkylating agents. The use of diethyl ether as a solvent gave poor yields of hexacyanopentadienides partly due to the precipitation of the 1:1 adducts. The increased basicity of THF may also aid in the removal of HCN from the adduct. The low temperature addition of methyllithium to TCNE was accompanied by numerous side reactions and yielded less than 10% of the desired hexacyanopentadienides. In each case, the metastability of the 1:1 adduct due to the loss of HCN is crucial to the formation of 1,1,2,4,5,5-hexacyanopentadienide salts in high yields.
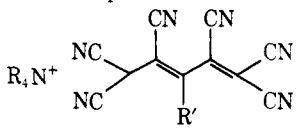
Experimental Section

Materials. TCNE was generously supplied by Dr. O. W. Webster of E. I. duPont (Wilmington, Del.). Tetrahydrofuran (THF) was purified by vacuum transfer from a solution containing potassium benzophenone ketyl and was stored under nitrogen. Tetramethylammonium chloride (Eastman Organic Chemicals) and trifluoroacetic acid (Sigma Chemical Co.) were used as received. Methyllithium (Alfa Inorganics) was recrystallized from ether at −78°C. Analyses by total base titration (phenolphthalein) and methane evolution from aqueous THF solutions by quantitative gas chromatography indicated a purity of >98%. Grignard reagents were prepared by standard methods in THF using commercial grade magnesium turnings. Isobutylene and isobutane were removed from *tert*-butylmagnesium bromide by removal of about half of the THF solvent under vacuum. THF stirred over potassium benzophenone ketyl was transferred into the Schlenk tube containing the Grignard reagent under vacuum.

1,1,2,2-Tetracyanopropane (3). Methylmagnesium bromide (6.3 mmol) was added by syringe over a 2-min period to a magnetically stirred suspension of 0.81 g (6.3 mmol) of TCNE in 75 ml of THF at −78°C. Initially the reaction mixture was red; at the end of the addition, it was pale yellow. Trifluoroacetic acid, 0.50 ml (6.6 mmol), was quickly added by syringe to the cold solution. The flask was transferred to a rotary evaporator and the solvent removed under vacuum. The residue was dissolved in 30 ml of CH_2Cl_2 and washed with two 15-ml portions of 1 M HCl. The organic layer was dried over $MgSO_4$. Solvent removal under vacuum yielded 0.89 g (96%) of **3** as a white solid, mp 96–97°C. An analytical sample was prepared by sublimation [89–95°C (0.01 mm)] followed by recrystallization from $CHCl_3$: mp 97–98°C; ir 2900 (s), 1456 (s), 1444 (s), 1391 (w), 1285 (m), 1274 (s), 1163 (s), 1145 (s), 1070 (w), 1002 (m), 968 (s), 862 (m), and 738 (m); mass spectrum m/e (%) 117 (18), 90 (19), 79 (79), 77 (17), 66 (58), 64 (10), 63 (17), 52 (100), and 41 (29). The proton NMR data for 1,1,2,2-tetracyanoalkanes are included in Table I.

Anal. Calcd for $C_7H_4N_4$: C, 58.33; H, 2.80; N, 38.87. Found: C, 58.06; H, 2.65; N, 38.96.

1,1,2,2-Tetracyanobutane (4). Ethylmagnesium bromide (4.3 mmol) reacted with TCNE (0.55 g, 4.3 mmol) as described for **3.**

Table IV. Infrared Spectral Data for Tetraalkylammonium Hexacyanopentadienide Compounds

Compd	NR_4	R'	$\nu,$ [a], [b] cm^{-1} (intensity)
9	NMe_4^+	H	2183 (s), 1500 (br, s), 1476 (s), 1385 (m), 1277 (br, s), 1224 (m), 945 (m), 833 (w)
12	NEt_4^+	H	2987 (w), 2183 (s), 1535 (br, s), 1520 (s), 1482 (m), 1453 (2), 1389 (m), 1329 (br, s), 1291 (m), 993 (w), 837 (m), 780 (w)
10	NMe_4^+	CH_3	2185 (s), 1481 (m), 1409 (br, s), 1382 (br, s), 948 (m), 677 (w)
11	NMe_4^+	C_2H_5	2960 (vw), 2185 (s), 1473 (m), 1424 (br, s), 1376 (br, s), 1320 (w), 1060 (w), 948 (m), 700 (w)
13	NMe_4^+	$n\text{-}C_3H_7$	2950 (w), 2182 (s), 1482 (m), 1420 (br, s), 1371 (br, s), 1206 (w), 946 (m), 689 (w)
14	NMe_4^+	$i\text{-}C_3H_7$	2978 (w), 2200 (m), 2180 (s), 2156 (w), 1486 (m), 1422 (br, s), 1373 (br, s), 1268 (m), 946 (m), 698 (w)
15	NMe_4^+	Ph	3020 (w), 2183 (s), 1482 (m), 1419 (br, s), 1362 (m), 946 (m), 690 (m)

[a] KBr pellet. [b] Abbreviations: s = strong; m = medium; w = weak; br = broad.

Work-up gave **4** [0.58 g (85%)] as a white solid, mp 59–62°C. An analytical sample was prepared by sublimation [50–58°C (0.01 mm)] followed by recrystallization from CHCl₃–hexane: mp 63–64°C; ir 2905 (s), 1465 (s), 1459 (s), 1440 (w), 1392 (w), 1308 (w), 1120 (m), 979 (m), 943 (s), 883 (m), 792 (w), 739 (s); mass spectrum m/e (%) 131 (18), 130 (13), 104 (20), 93 (15), 77 (9.5), 66 (30), 53 (28), and 29 (100).

Anal. Calcd for $C_8H_6N_4$: C, 60.75; H, 3.82; N, 35.42. Found: C, 60.31; H, 3.76; N, 35.65.
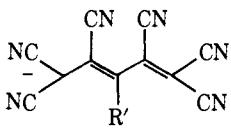
3-Methyl-1,1,2,2-tetracyanobutane (5). Isopropylmagnesium bromide (5.2 mmol) was treated with TCNE (0.65 g, 5.1 mmol) as described for **3**. Work-up yielded a tan solid (0.81 g), which was recrystallized from 2:1 CHCl₃–hexane to yield 0.70 g (81%) of **5**, a white solid, mp 76–77°C. An analytical sample was prepared by sublimation [65–75°C (0.01 mm)] followed by recrystallization from a 2:1 (v/v) CHCl₃–hexane mixture: mp 78–79°C; ir 2979 (w), 2920 (s), 1468 (m), 1460 (w), 1396 (m), 1378 (m), 1329 (w), 1283 (w), 1254 (m), 1170 (w), 1142 (m), 1035 (w), 1000 (w), 961 (w), 903 (m), and 737 (m); mass spectrum m/e (%) 130 (8), 118 (5), 107 (5), 103 (5), 91 (6), 80 (9), 76 (8), 66 (11), 53 (11), 43 (100), and 41 (44).

Anal. Calcd for $C_9H_8N_4$: C, 62.78; H, 4.68; N, 32.54. Found: C, 62.49; H, 4.72; N, 32.62.

3,3-Dimethyl-1,1,2,2-tetracyanobutane (6). *tert*-Butylmagnesium bromide (6.3 mmol) was added over a 2-min period to a magnetically stirred suspension of 0.81 g (6.3 mmol) of TCNE in 6 ml of THF at −78°C. Two minutes later, 0.6 ml (7.9 mmol) of trifluoroacetic acid was added by syringe and the cooling bath was removed. Removal of solvent under vacuum yielded a brown oil, which was dissolved in 20 ml of CH₂Cl₂. The organic layer was washed with 15 ml of 1 M HCl and 15 ml of 1 M sodium bisulfate solution and was dried over MgSO₄. The solvent was removed under vacuum to yield a pink solid (0.80 g), mp 85–103°C dec. Sublimation [70–85°C (0.01 mm)] of this solid resulted in extensive decomposition. The sublimate (0.54 g, 46%) was recrystallized from CHCl₃–hexane to yield **6** as white platelets: mp 108–109°C; ir 2973 (s), 2922 (s), 2240 (vw), 2170 (vw), 2122 (vw), 1470 (s), 1412 (m), 1388 (s), 1193 (m), 1105 (w), 1022 (w), 994 (w), 955 (2), 883 (w), 739 (m); mass spectrum m/e (%) 171 (4), 159 (5), 144 (89), 132 (29), 117 (100), 90 (42), 76 (23), 57 (78), and 42 (57).

Anal. Calcd for $C_{10}H_{10}N_4$: C, 64.50; H, 5.41; N, 30.09. Found: C, 64.33; H, 5.44; N, 30.36.

1-Phenyl-1,1,2,2-tetracyanoethane (7). Phenylmagnesium bro-

Table V. Ultraviolet–Visible Spectral Data[a] for the Hexacyanopentadienide Ions

Compd	R'	λ_{max}, nm (ϵ, M^{-1} cm^{-1})
9	H[b]	296 (5750), 309 (6900), 347 (2060), 368 (2000), 505 (38 000), 538 (82 000)
10	CH_3	207 (14 500), 225 sh (8800), 296 (11 100), 370 (1800), 589 (34 500)
11	C_2H_5	209 (13 900), 227 sh (10 000), 297 (15 600), 367 (1700), 592 (27 000)
13	$n\text{-}C_3H_7$	212 (12 000), 230 sh (8000), 299 (14 500), 366 (1450), 593 (25 000)
14	$i\text{-}C_3H_7$	208 (13 500), 227 sh (10 000), 299 (17 000), 363 (2000), 600 (18 500)
15	Ph	235 sh (12 300), 316 (18 000), 366 sh (2800), 594 (25 000)
	CN	528 (33 000)[c]

[a] In CH₃CN, for NMe_4^+ salts. [b] The same spectrum was observed for **12**. Literature[13] values for **9**: λ_{max} (EtOH) 296 (6200), 308 (6900), 350 (2200), 368 (2100), 504 (37 000), 538 (82 000). [c] For sodium heptacyanopentadienide, from ref 30.

mide (7.0 mmol) was added to 0.89 g (6.9 mmol) of TCNE as described for **3**. Work-up yielded **7** [1.38 g (97%)], as a white solid, mp 155–160°C dec. Recrystallization from CH₂Cl₂ raised the mp to 160–163°C dec (lit.[13] mp 130–132°C dec): ir 2912 (s), 1499 (s), 1460 (s), 1345 (w), 1290 (w), 1187 (w), 1055 (w), 1005 (w), 950 (w), 922 (vw), 878 (w), 764 (s), 740 (m), 699 (s), (lit.[11] 2912, 740); mass spectrum m/e (%) 206 (2), 179 (100), 142 (43), 103 (57), 77 (17), and 51 (22).

Tetramethylammonium 1,1,2,4,5,5-Hexacyanopentadienide (9). Methylmagnesium bromide (5.0 mmol) was added over a 5-min period to a magnetically stirred suspension of 1.28 g (10.0 mmol) of TCNE in 50 ml of THF at −78°C. The cooling bath was removed after 20 min, and 30 ml of deoxygenated CH₃CN was added 1 hr later. The solution was stirred for an additional 6 hr. Solvent removal under vacuum yielded a red solid which was dissolved in 100 ml of H₂O. Addition of 1.0 g of tetramethylammonium chloride in 10 ml of H₂O caused **9** to precipitate. Filtration of the chilled mixture yielded 1.40 g (96%) of **9** as a gold solid. Spectrophotometric analysis of the precipitate indicated a purity of 95%. An analytical sample was prepared by chromatography followed by recrystallization from methanol: mp 289–290°C dec (lit.[13] 297–299°C dec). NMR, ir, and uv-visible spectral data and elemental analyses appear in Tables II, IV, V, and VI, respectively.

Tetraethylammonium 1,1,2,4,5,5-Hexacyanopentadienide (12). Methylmagnesium bromide (1.0 mmol) and TCNE (1.0 mmol) were reacted as described for **9**. The aqueous solution of the red solid was treated with 0.3 g of tetraethylammonium chloride in 3 ml of H₂O. The precipitate, **12**, was chromatographed on alumina and recrystallized from methanol to yield pleochroic brown needles: mp 267–268°C dec. Ir and uv-visible spectral data appear in Tables IV and V, respectively.

Tetramethylammonium 3-substituted hexacyanopentadienides were prepared by reaction of the appropriate Grignard reagent and TCNE. The preparation of tetramethylammonium 3-n-propyl-1,1,2,4,5,5-hexacyanopentadienide is a typical example.

Tetramethylammonium 3-n-Propyl-1,1,2,4,5,5-hexacyanopentadienide (13). n-Butylmagnesium bromide (10.3 mmol) was added over a 5-min period to a magnetically stirred suspension of 2.6 g (20.3 mmol) of TCNE in 60 ml of THF at −78°C. The cooling bath was removed after 20 min and the reaction stirred for an additional 8 hr. Solvent removal under vacuum yielded a blue oil which was dissolved in 100 ml of water and filtered. The filtrate was cooled in an ice–water bath, while 2.0 g of tetramethylammonium chloride in 10 ml of H₂O was added dropwise. The precipitate, **13**, a gold solid, weighed 2.82 g (85%). Spectrophotometric analysis of the precipitate at 592 nm indicated a purity of 92%. An analytical sample was prepared by chromatography followed by rapid recrystallization from H₂O: mp 111–112°; NMR, ir, and uv-visi-

Table VI. Analytical Data for Tetramethylammonium Hexacyanopentadienide Compounds

Analysis, %

Compd	R'	C Calcd	C Found	H Calcd	H Found	N Calcd	N Found
9	H	61.85	61.59	4.50	4.74	33.66	33.56
10	CH_3	62.94	62.78	4.95	4.88	32.11	31.94
11	C_2H_5	63.93	63.95	5.36	5.74	30.70	30.25
13	$n\text{-}C_3H_7$	64.85	64.90	5.74	5.69	29.41	29.44
14	$i\text{-}C_3H_7$	64.85	64.63	5.74	5.81	29.41	29.27
15	Ph	68.65	68.37	4.67	4.85	26.68	26.43

Table VII. Production of Methane from the Reaction between Methylmagnesium Bromide and TCNE[a]

CH_3MgBr, mmol	TCNE, mmol	H_2O, mmol	CH_4,[b] mmol
1.45	0	5.5	1.45
1.45	1.45	0	0.04
1.40	1.40	1.40	0.90[c]

[a]At −78°C in 10 ml of THF. [b]By quantitative GLC. [c]0.13 mmol of 1,1,2,4,5,5-hexacyanopentadienide also formed (detected by uv–visible spectrophotometric analysis).

ble spectral data and elemental analyses appear in Tables II, IV, V, and VI, respectively.

Spectrophotometric analyses of crude 3-substituted 1,1,2,4,5,5-hexacyanopentadienide salts indicated a purity of 85–92% except for the 3-phenyl derivative (purity, ∼80%).

Tricyanovinylbenzene (18). Phenylmagnesium bromide (10.2 mmol) was added over a 13-min period to a magnetically stirred suspension of 2.58 g (20.2 mmol) of TCNE in 60 ml of THF at −78°C. The cooling bath was removed after 12 min, and the mixture was stirred for an additional 2 hr. Solvent removal under vacuum yielded a brown tar, which was extracted with three 100-ml portions of $CHCl_3$. The extracts were filtered through Celite and concentrated under vacuum to yield a brown solid, which was sublimed (90–95°C (0.01 mm)) to give 1.4 g (78%) of pure **18**, a yellow crystalline solid: mp 96–98°C (lit.[13] 96–98°C); λ_{max} ($CHCl_3$) 342 nm (ϵ 16 800) [lit.[33] λ_{max} ($CHCl_3$) 343 nm (ϵ 16 600)].

4-n-Propyl-2,3,5,6-tetracyanoaniline (16). The addition of n-butylmagnesium bromide (10 mmol) to TCNE (2.56 g, 20 mmol) was performed as described for the preparation of **13**. However, the reaction mixture was allowed to stand 2 weeks before work-up. Solvent removal under vacuum yielded a brown oil which was chromatographed on acid-washed alumina with $CHCl_3$. The first band to elute was yellow. Concentration of this fraction afforded a yellow solid which was recrystallized from aqueous acetone to give 130 mg (5.5%) of pure **16**: mp 227°C; ir 3440 (m), 3340 (s), 3227 (w), 2983 (vw), 2211 (m), 1645 (s), 1570 (w), 1469 (w), 1451 (w), 1295 (s), 1244 (m); NMR (acetone-d_6) δ 7.10 (s, 2), 3.02 (t, 2, J = 7 Hz), 1.83 (m, 2, J = 7 Hz), 1.07 (t, 3, J = 7.5 Hz); mass spectrum m/e (%) 235 (22), 226 (9), 207 (40), 206 (100), 179 (12), 152 (8); λ_{max} (EtOH) 423 nm (ϵ 8500), 259 (ϵ 33 000), and 220 (ϵ 33 000).

Anal. Calcd for $C_{13}H_9N_5$: C, 66.37; H, 3.86; N, 29.77. Found: C, 65.95; H, 3.89; N, 29.83.

16 is also formed in low yield in aqueous solutions of **13** on prolonged standing.

4-Ethyl-2,3,5,6-tetracyanoaniline (17). The reaction of n-propyl magnesium bromide (5 mmol) to TCNE (1.28 g, 10.0 mmol) was carried out in a manner analogous to that described above for **16**. The yellow solid isolated by chromatography was purified by sublimation [150–160°C (0.01 mm)] to yield pure **17**, 60 mg (5.4%): mp 259°C; ir 3396 (m), 3340 (s), 3240 (w), 2213 (m), 1658 (s), 1569 (w), 1470 (w), 1452 (m), 1291 (s), 1245 (m); NMR (acetone- d_6) δ 7.18 (s, ∼2), 3.05 (q, 2, J = 7 Hz), 1.32 (t, 3, J = 7 Hz); mass spectrum m/e (%) 221 (21), 207 (13), 206 (100), 179 (10), 151 (5); λ_{max} (EtOH) 422 nm (ϵ 8800), 257 (ϵ 30 000) and 217 (ϵ 34 000).

Anal. Calcd for $C_{12}H_7N_5$: C, 65.15; H, 3.19; N, 31.66. Found: C, 65.18; H, 3.09; N, 31.82.

3-Amino-6,6-dimethyl-1,2,3,4,4,5,5-heptacyanocyclohexene (19). Isopropylmagnesium bromide (6.8 mmol) was added over a 8-min period to a magnetically stirred suspension of 2.58 g (20.2 mmol) of TCNE in 60 ml of THF at −78°C. The cooling bath was removed after 15 min, and the reaction mixture was stirred for an additional 16 hr. Removal of the solvent under vacuum yielded a brown solid which was extracted with three 100-ml portions of $CHCl_3$. The extracts were combined and concentrated to 50 ml under vacuum. A brown gummy solid formed during this process. The concentrated extract was clarified with decolorizing carbon, filtered, and cooled to −33°C, yielding yellow crystals of crude **19**, 60 mg (1.8%), mp 185–210°C dec. The solid was recrystallized with decomposition from $CHCl_3$–hexane to give off-white crystals: mp 213–216°C dec with darkening of the sample beginning at 195°C: ir 3356 (s), 3307 (w), 3189 (s), 2240 (w), 2213 (m), 1662 (s), 1609 (s), 1470 (w), 1460 (w), 1411 (m), 1389 (m), 940 (w); NMR (acetone-d_6) 8.5 (s, 2), 2.08 (s, 6); mass spectrum m/e (%) 300 (2), 248 (40), 233 (30), 222 (82), 221 (29), 207 (21), 206 (45), 195 (16), 194 (63), 179 (26), 128 (46), 76 (83), 28 (100); λ_{max} (CH_3CN) 268 nm (ϵ 8500).

Anal. Calcd for $C_{15}H_8N_8$: C, 60.00; H, 2.69. Found: C, 59.30; H, 3.52.

Reaction of tert-Butylmagnesium Bromide and TCNE. tert-Butylmagnesium bromide (10.0 mmol) was added over a 10-min period to 2.57 g (20.1 mmol) of TCNE in 60 ml of THF at −78°C. The mixture was allowed to warm to room temperature after an additional 10 min and was sampled periodically for spectrophotometric analysis. The uv-visible spectra of the samples taken after 1 hr and after 18 hr were identical, and they indicated that ∼2.4 mmol of TCNE.−[18] and 3 mmol of TCNE [λ_{max} (CH_3CN) 271 nm (ϵ 16 000), 265 (ϵ 17 000), and 256 (ϵ 17 500)] were present. Solvent removal under vacuum after 18 hr yielded a brown tar which was extracted with five 100-ml portions of $CHCl_3$. The extracts were concentrated under vacuum to a brown solid. Sublimation [120°C (0.01 mm)] yielded a cream-colored solid, 0.4 g, mp 40–150°C, which was shown to be mainly TCNE by uv-visible spectral analysis. The chloroform-insoluble residue was dissolved in 125 ml of H_2O. Spectrophotometric analysis of the solution indicated that 3.3 mmol of pentacyanopropenide ion [λ_{max} (CH_3CN) 414 nm (ϵ 22 100) and 396 (ϵ 21 000)][5] and 3.1 mmol of tricyanoethenolate ion [λ_{max} (CH_3CN) 299 nm (ϵ 11 300)][5] were present in solution.

Determination of the Yield of Hydrogen Cyanide in the Preparation of Tetramethylammonium 1,1,2,4,5,5-Hexacyanopentadienide (9). Tetramethylammonium 1,1,2,4,5,5-hexacyanopentadiene (9) was prepared as described above. However, after the reaction mixture was stirred for 8 hr, the flask was transferred to a vacuum line. The volatile components were transferred under vacuum into a flask cooled in liquid nitrogen containing 15 ml of 1 M aqueous NaOH. When the transfer was complete, the contents of the receiving flask were allowed to warm to room temperature. The contents were vigorously stirred. Then, the organic solvents were removed under vacuum. The aqueous phase was diluted with 50 ml of deionized H_2O, cooled in an ice-water bath, and acidified to a phenolphthalein end point with nitric acid. Silver nitrate (15 ml of 1 M solution) was added. The white precipitate was filtered,

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Table VIII. Production of Isobutane and Isobutylene from the Reaction between *tert*-Butylmagnesium Bromide and TCNE[a]

t-BuMgBr mmol	TCNE, mmol	H$_2$O, mmol	Isobutane, mmol	Iso-butylene, mmol	[% *t*-Bu°][d]
0.286[b]	0	5.5	0.282	0.002	0
0.320[c]	0.650	0	0.017	0.017	10
0.640[c]	0.638	0	0.045	0.032	10
0.640[b]	0.662	0	0.064	0.038	12

[a] In 9 ml of THF. [b] Reaction carried out at room temperature. [c] Reaction at −78°C. [d] = 2[isobutylene]/[*t*-BuMgBr] × 100 = percent of *tert*-butyl radicals formed in the reaction (lower limit).

washed with water, and dried in a vacuum oven at 100°C. The solid was identified as AgCN, 1.19 g (8.9 mmol), by comparison of its ir spectrum with that of an authentic sample: $\nu_{C\equiv N}$ 2122 cm^{-1} (KBr). The yield of HCN was 89% based on AgCN and the stoichiometry in eq 3.

Reactions of Grignard Reagents with TCNE–GLC Analyses. Methylmagnesium bromide was added by syringe over a 2-min period to a stirred suspension of TCNE in 10 ml of (aqueous) THF at −78°C in a 100-ml round-bottomed flask fitted with a serum stopper. The flask was then warmed to 29°C in a water bath, and samples of gas above the solution were removed for quantitative GLC analysis by the internal standard method (Table VII).

The reaction between *tert*-butylmagnesium bromide and TCNE was carried out in the same manner as for methylmagnesium bromide. GLC analyses of isobutane and isobutylene were performed on a thermal conductivity gas chromatograph fitted with a 15 ft × 0.25 in. o.d. Dowtherm column on firebrick. *n*-Butane was the internal standard. Table VIII summarizes these results.

Electrochemical Reductions. A 2.2 × 10^{-3} M solution of **10** in DMF containing 0.1 F *n*-Bu$_4$NClO$_4$ was transferred to a polarographic cell[35] equipped with a dropping mercury electrode, a platinum wire working electrode, and a Cd amalgam/CdCl$_2$ reference.[17] Polarographic reduction of **10** yielded two well-defined waves: $E_{1/2}(1) = +0.125$ V ($i_d = 3.3$ μA) and $E_{1/2}(2) = -0.56$ V ($i_d = 3.0$ μA). Similarly, a 2.8 × 10^{-3} M solution of **15** in DMF containing 0.1 F *n*-Bu$_4$NClO$_4$ was examined in the manner described for **10**. Two well-defined waves were observed: $E_{1/2}(1) = +0.16$ V ($i_d = 4.8$ μA) and $E_{1/2}(2) = -0.49$ V ($i_d = 4.0$ μA). The DMF solution of **15** was subjected to controlled potential electrolysis at −1.0 V. At the end of the electrolysis, the solution was brown. Spectrophotometric analysis of the solution indicated maxima at ∼850, 507, 440, 365, and 300 nm. Exposure of the solution to air caused the absorbance bands at ∼850 and 507 nm to disappear and the absorbance band for **10** (λ_{max} 589 nm) to reappear. Spectrophotometric analysis of the band at 589 nm indicated that 27% of the original charge of **10** had been re-formed.

General. Nuclear magnetic resonance spectra were recorded on a Varian EM-360 spectrometer. Chemical shifts are reported as δ values in parts per million downfield from Me$_4$Si. Infrared spectra (KBr pellets) were recorded on a Perkin-Elmer Model 621 grating spectrophotometer using the 1601.4 cm^{-1} band of polystyrene as a reference. Mass spectra were recorded on a Varian MAT CH-7 spectrometer. Ultraviolet-visible spectra were recorded on a Beckman DB-G spectrophotometer. Wavelengths and extinction coefficients are reported in nm and M^{-1} cm^{-1}, respectively. Microanalyses were performed by Midwest Microlabs (Indianapolis, Ind.) and Galbraith Laboratories (Knoxville, Tenn.). Melting points are uncorrected. Chromatographic separations were performed on alumina using CHCl$_3$–CH$_3$CN mixtures as eluents. All manipulations involving Grignard reagents were carried out under a nitrogen atmosphere using syringe techniques. Hydrogen cyanide is produced in many of these reactions. Due precautions (such as the use of a well-ventilated hood, etc.) should be employed in the handling of these solutions.

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