

INTERACTION OF TETRACYANOETHYLENE WITH SOME ORGANO-TIN AND -MERCURY COMPOUNDS *

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Summary

The reactions of tetracyanoethylene (TCNE) with organo-tin and -mercury compounds containing carbon-metal, metal-sulphur and metal-metal bonds have been studied. With completely substituted benzyl organometallics in CH_2Cl_2 the reaction proceeds via quantitative insertion of TCNE into the metal-benzyl bond to yield metallated derivatives of 1,1,2,2-tetracyanopropylbenzene $\text{PhCH}_2-\text{C}(\text{CN})_2\text{C}(\text{CN})_2\text{M}$ ($\text{M} = \text{SnMe}_3, \text{HgCH}_2\text{Ph}$), whose structure was established by elemental analysis, IR and PMR spectra, and by a study of their chemical properties. The rate of the insertion reactions was found to depend both on the nature of the metal atom ($\text{Sn} > \text{Hg}$) and on the type of the substituent in the benzene ring of dibenzylmercury ($p\text{-CF}_3 \ll \text{H} < p\text{-CH}_3$). The data obtained are discussed in terms of the general problem of a dual (σ - or π -) regioselectivity of the reactions of π -acids with ambifunctional organometallic donors. The reactions of TCNE with tin mercaptides either yield stable complexes, $(\text{PhS})_3\text{Sn}$, or (as is the case with PhSSnMe_3) proceed via quantitative insertion into the S-Sn bond to give $\text{PhSC}(\text{CN})_2\text{C}(\text{CN})_2\text{SnMe}_3$ whose structure was established by elemental analysis, IR and PMR spectra, and by examination of its chemical properties. The products of TCNE insertion into the carbon-metal bond exhibit a dual reactivity in acid and thermal cleavage reactions, which can be attributed to the presence in their structure of two competing σ, π - and σ, σ -conjugated chains of the C-metal bonds with neighbouring α - and β -nitrile groups. The reaction of TCNE with hexamethyldistannane in CH_2Cl_2 produces a colourless 1/2 adduct identified by elemental analysis, IR and PMR spectroscopy, and the results of acid cleavage, as dimetallated tetracyanoethane complexes with a second TCNE molecule ($\text{Me}_3\text{SnC}(\text{CN})_2\text{C}(\text{CN})_2\text{SnMe}_3 \cdot \text{TCNE}$). This latter compound exhibits extremely high susceptibility to homolysis resulting in the formation of the iminotricyanoallyl radical

* Dedicated to Professor H. Normant on the occasion of his 72nd birthday on June 25th 1979

$\text{Me}_3\text{SnNCC}(\text{CN})\text{C}(\text{CN})_2$ This suggests a new two-stage mechanism for the formation of a radical species in the reaction of Me_6Sn_2 with TCNE. The mechanism involves the insertion of a π -acid into the tin-tin bond as the first stage with the subsequent homolysis or atmospheric oxidation of the unstable adduct.

Introduction

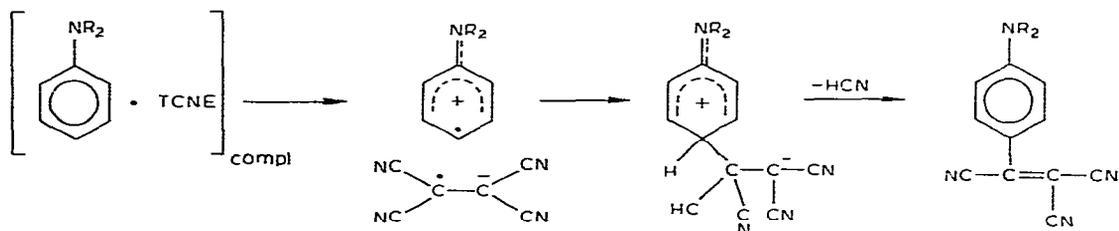
The present paper summarizes the results of our studies of the reactions of tetracyanoethylene (TCNE) with organo-mercury and -tin compounds, initiated in 1973–1974 [1–3]. It was then already known that some organometallic compounds of non-transition metals could react with electron-acceptor olefins via 1,2 or 1,4 insertion into σ -bonds [4–9]. As for TCNE, the study in this series was limited only to the observation of coloured charge transfer complexes [9–13]. Very little data on the further chemical transformations of the complexes was available.

Our studies touched on a number of interrelated problems such as the regioselectivity of the reactions of TCNE with ambifunctional organometallic donors, the reactivity of polycyano-substituted organometals, and the mechanisms of formation of radical species in the reactions of organometals with π -acids. While the studies were being made a number of independent reports in this field appeared [14–18]. The results of these studies together with our own data suggest that the reactions of TCNE with organometals are of substantial interest both as syntheses and for their reaction mechanism. The capacity of TCNE to act as a universal electrophilic agent in the reactions of non-transition organometals seems to be nearly as good as in another series of transition metal complexes which have been studied in more detail elsewhere [19,20].

Discussion

The reaction of TCNE with completely substituted benzyl organometals

It is known that TCNE is capable of reacting with a great variety of aromatic hydrocarbons to give coloured charge transfer complexes. If the benzene ring, however, is activated with electron-donor substituents (such as the NR_2 group [21]) the reaction is not confined to a complexation but is followed by the insertion of TCNE into the aromatic nucleus (eq. 1).



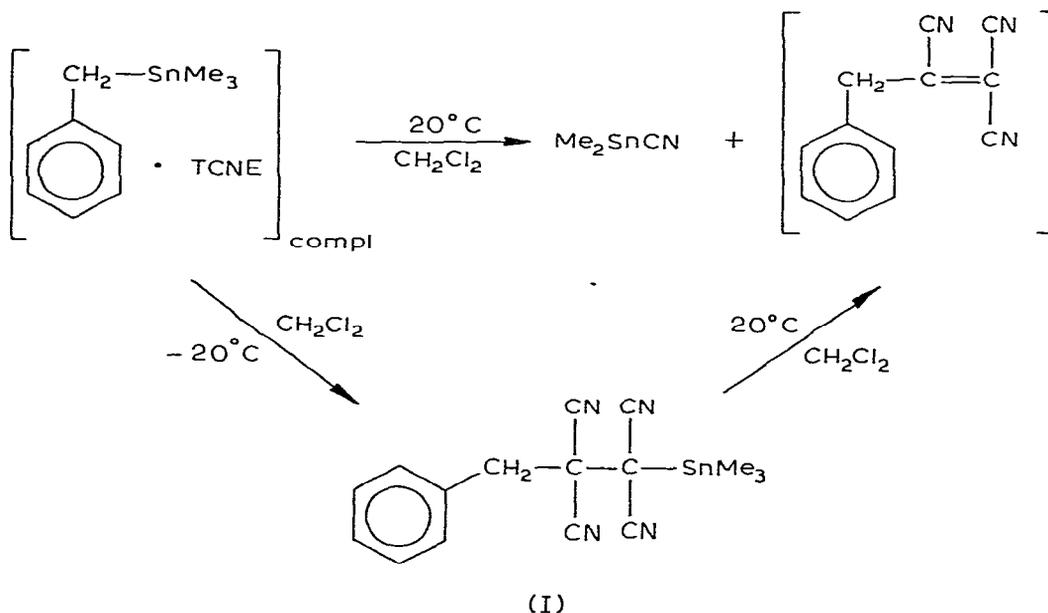
In the present work we were interested to discover what would be the result of this reaction if we were to use a metal-carbon σ -bond instead of n -donor

groups as the activating substituent in the ring (according to the UV spectral data [11–13] the groups $\text{CH}_2\text{—M}$ ($\text{M} = \text{Sn}, \text{Hg}$) and NR_2 are comparable in their electron-donating ability)

For this purpose we studied the reaction of TCNE with completely substituted benzyl derivatives of tin and mercury. It was already known that benzyl organometals were capable of reacting with TCNE in CH_2Cl_2 to give coloured solutions of charge transfer complexes [11–13], but the products of subsequent chemical transformations of these complexes had not to our knowledge ever been investigated.

At ambient temperature the violet colour of the charge transfer complex of $\text{PhCH}_2\text{SnMe}_3$ with TCNE in CH_2Cl_2 proved to change rapidly to a stable red colour due to the formation of reaction products. Me_2SnCN was isolated from the mixture in quantitative yield, together with a red oil (probably 1,1,2-tricyanoallylbenzene or its derivatives). We assumed, however, that these substances were not primary reaction products but were formed as a result of decomposition of an unstable intermediate which appeared during the chemical transformation of the charge transfer complex. Indeed, on cooling to -20°C a well pronounced interval of colour change was observed which enabled the expected colourless intermediate to be isolated in high yield by treating the reaction mixture with hexane at the point of greatest decolouration. The intermediate corresponded to trimethyl(3-phenyl-1,1,2,2-tetracyanopropyl)stannane which is a 1/1 adduct of the starting components and was identified by elemental analysis, PMR and IR spectroscopy (Table 1), and acid cleavage results (see pp XX-XX (Scheme 1))

SCHEME 1



The reaction of TCNE with dibenzylmercury proceeds in a similar manner,

TABLE I

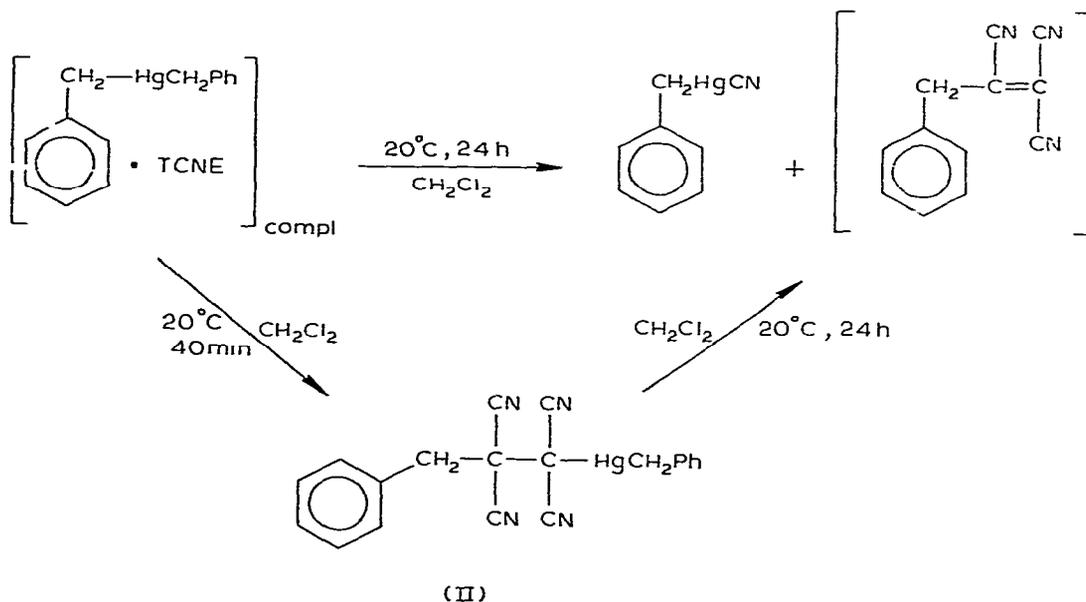
IR AND PMR DATA FOR REACTION PRODUCTS OF TETRACYANOLETHYLENE WITH MERCURY AND TIN ORGANOMETALLIC DERIVATIVES

Compound	$\nu(\text{CN})$ (cm^{-1})	δ (ppm)
$\text{PhCH}_2\text{C}(\text{CN})_2\text{C}(\text{CN})_2\text{SnMe}_3$ I ^a	2225 2145 ^b	0.10 (CH_3 $J(\text{H}-\text{Sn})$ 66 Hz) 3.30 (CH_2) 7.34 (C_6H_5)
$\text{PhCH}_2\text{C}(\text{CN})_2\text{C}(\text{CN})_2\text{HgCH}_2\text{Ph}$ II ^c	2238	2.70 (CH_2 $J(\text{H}-\text{Hg})$ 248 Hz) 3.48 (CH_2) 6.97 (C_6H_5) 7.30 (C_6H_5)
$\text{PhCH}_2\text{C}(\text{CN})_2\text{C}(\text{CN})_2\text{H}$ IV ^c	2918 ^d	3.61 (CH_2) 5.16 (CH) 7.40 (C_6H_5)
$\text{PhSC}(\text{CN})_2\text{C}(\text{CN})_2\text{SnMe}_3$ VIII ^e	2225 2160 ^b	0.62 (CH_3 $J(\text{H}-\text{Sn})$ 60 Hz) 7.55 (C_6H_5)
$(\text{Me}_3\text{Sn})_2\text{C}(\text{CN})_2\text{C}(\text{CN})_2$ IX ^f	2215 2156	0.70 (CH_3 $J(\text{H}-\text{Sn})$ 64 Hz)

^a PMR spectrum in CH_2Cl_2 ^b in principle ketenimine forms of compounds I and VIII ($\text{PhCH}_2\text{C}(\text{CN})_2\text{C}(\text{CN})=\text{C}=\text{N}-\text{SnMe}_3$ and $\text{PhSC}(\text{CN})_2\text{C}(\text{CN})=\text{C}=\text{N}-\text{SnMe}_3$ respectively) should also be considered because of the presence of bands at 2145 cm^{-1} and 2160 cm^{-1} (cf refs 6 16 19 36) however thermal cleavage results for compound I (Scheme 1 and p 108) and acid cleavage results for the compound (VIII) (Scheme 5 and p 110) show a better agreement with the structures of C-metalated isomers ^c PMR spectrum in MeCN ^d CH-vibration region ^e PMR spectrum in CH_2Cl_2 (-40°C) ^f PMR spectrum in dioxane

though much more slowly. The PMR spectrum of the dark blue solution of the charge transfer complex of $(\text{PhCH}_2)_2\text{Hg}$ with TCNE in CH_2Cl_2 at 30°C displays after a few minutes a decrease in the integral intensity of the resonance absorption signals of $(\text{PhCH}_2)_2\text{Hg}$, followed by the appearance of two pairs of new signals from non-equivalent benzyl groups. One of the latter remains bonded to the mercury atom, as evidenced by the change in $J(^1\text{H}-^{199}\text{Hg})$, while the other shows an appreciable shift downfield. The reaction is complete in 40 min and shows no side reactions.

SCHEME 2



The product of this reaction was isolated in high yield as a pale yellow substance which was shown by elemental analysis, PMR and IR spectroscopy (Table 1) and acid cleavage results (see pp 107–108) to be an equimolecular adduct of TCNE and the organometal benzyl(3-phenyl-1,1,2,2-tetractanopropyl)mercury (II)

Both the compounds isolated (I and II) proved to be stable in the solid state and in an inert atmosphere only. On being dissolved in organic solvents they decompose as shown in Schemes 1 and 2, to yield Me_3SnCN and PhCH_2HgCN , i.e. the same compounds that were found after prolonged storing of the corresponding reaction mixtures at room temperature. Thus, each of the reactions under consideration represent a two-stage process: to start with TCNE is inserted into the metal–carbon bond and then fast decomposition of the primary adduct occurs. The last reaction, if carried out without isolation of the intermediate II, can be used as a convenient quantitative method for synthesizing PhCH_2HgCN (ref. 22)

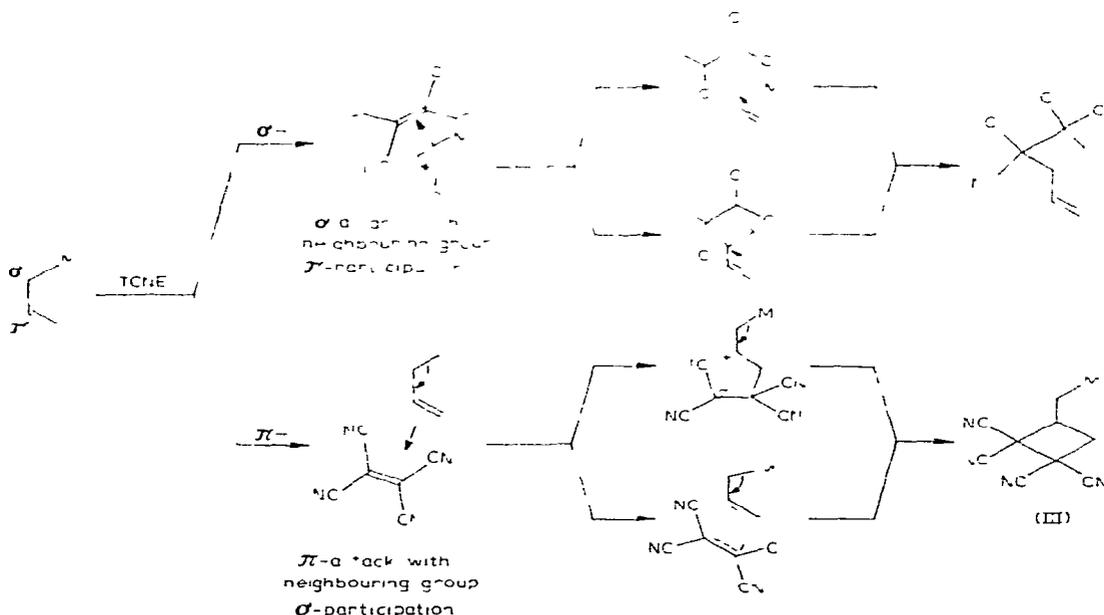
The data obtained testify that in the reactions with completely substituted organo-mercury and -tin benzyl compounds the attack of TCNE occurs not on the benzene ring but exclusively at the metal–carbon bond, in just the same manner as the reaction of TCNE with alkylmetals [15–17]. Thus, the benzyl organometals differ from PhNMe_2 [21] principally because their exocyclic group is not a ring-activating substituent, but rather is a reaction site itself.

Nevertheless, the evidence we obtained does not rule out the possibility of attack on the benzene ring when using other arylmethyl systems and other π -acids or when the conditions of the process are varied. For instance in reaction with allyltrimethylsilane, as shown by Hartman and Traylor [14], TCNE attacks not the C–Si bond but the double bond adjacent to the metal to give the silyl-carbinyl derivative of cyclobutane (III). The observed difference can, however, be reconciled if the results of the other work [14] and our own data are considered as the dual (σ - or π) regioselectivity which occurs in the reactions of π -acids with ambifunctional organometallic donors (Scheme 3). For instance, of TCNE is regarded as a “soft” Lewis acid [23], in the case of tin or mercury benzyl derivatives it would prefer to attack a “softer” σ -donor fragment, the metal–carbon bond (attack on the ring would be less preferable owing to the loss of aromaticity), whereas in the case of the allyl derivative of silicon the role of the “softer” electron donor fragment of the ambifunctional system might be played by the C=C double bond. Indirect support for this conclusion is provided by the fact that in the reaction of TCNE with allyl derivatives of germanium and tin no cyclobutane products are formed [14] (cf. ref. 6), and that in the reaction of TCNE with toluene which has the “hardest” σ -donor side chain (the $\text{CH}_2\text{—H}$ bond), together with attack of this chain, traces of the products of tricyanovinylolation of the benzene ring itself are also observed [24]*. However considering the possibility of 1,4-addition involving TCNE $((\text{CN})_2\text{C}=\overset{\curvearrowright}{\text{C}}-\overset{\curvearrowright}{\text{C}}\equiv\text{N})$ [4–6],



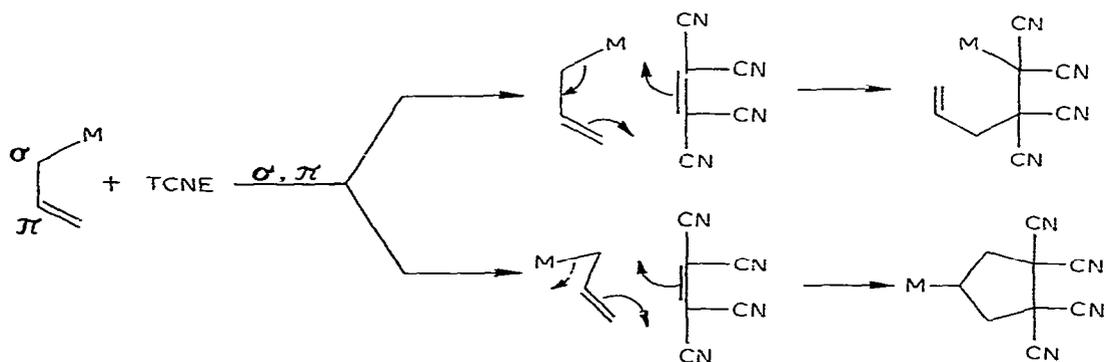
* In interpreting the data of this work [24] it should be taken into account that the process is only observed on photoirradiation (which may invert thermal regioselectivity) and is also catalyzed by protic acids. It therefore may proceed not via TCNE insertion into the C–H bond but by a radical-chain mechanism involving the tetracyanoethyl radical $\text{HC}(\text{CN})_2\text{C}(\text{CN})_2$.

SCHEME 3



and of a combined attack on the σ - and π -bonds of an organometal (Scheme 4) [25], it becomes clear that a better insight into the nature of regioselectivity

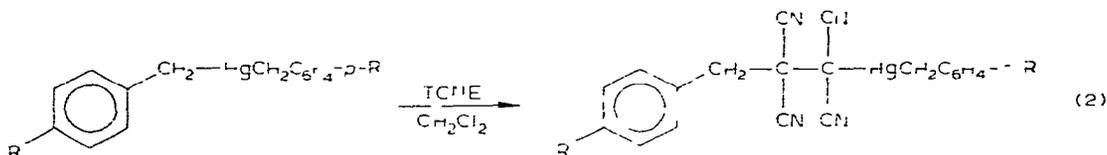
SCHEME 4



of such processes requires a special study of a variety of ambiofunctional systems in the reactions with various π -acids

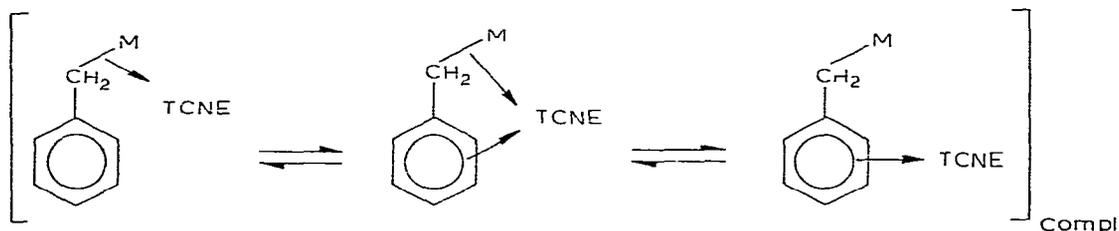
The reactions of the type shown in Scheme 3 are also of interest because of their mechanism. According to the orbital symmetry conservation principle [26], four-electron reactions of olefin insertion into both σ - and π -bonds should proceed by a non-concerted route via ionic or ion-radical intermediates. For the reaction of allyltrimethylsilane with TCNE some evidence has indeed been obtained [14] in favour of the non-concerted mechanism involving formation of the zwitterion intermediate stabilized by σ -participation of the adjacent metal-carbon bond. However, in our studies the reactions of benzyl deriva-

tives of tin and mercury with TCNE, were shown to proceed quantitatively and were not accompanied by the formation of intermediate radical species oxidation products. Therefore, the possibility of a concerted mechanism for them cannot be ruled out all the more since orbital restriction [26] in this case may be appreciably lowered due to the presence of heavy metals. Still, certain evidence of π -involvement of the aromatic system in the reaction we studied is undoubtedly shown by the dependence of their rates not only on the nature of the metal atom ((PhCH₂SnMe₃ reacts with TCNE about a hundred times as fast as (PhCH₂)₂Hg) but also on the type of the substituent in the benzene ring (electron donors promote the reaction while electron acceptors inhibit it) (eq. 2)



(R = CF₃ no reaction, $t_{1/2}$ 12 min CH₃ $t_{1/2}$ 3 min)

Such π -participation may be realized at the stage of preliminary complexing of TCNE with the benzene ring of the organometal

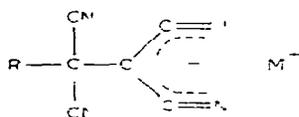


and/or via electronic delocalization of the charge appearing in the transition state or in a short-lived intermediate of the reactions

The structure of the metallated tetracyanoalkanes I and II (the products of TCNE insertion into the metal-carbon bond of the benzyl organometal), was ascertained by acid cleavage. Compounds such as I and II are derivatives of the comparatively strong CH-acid* and hence, according to present day ideas should possess a lowered reactivity under the conditions of bimolecular electrophilic substitution [28]. In spite of apparent steric hindrances and lowered electron density of the carbon atom bonded to the metal, compounds I and II proved to react with HCl in CH₂Cl₂ almost instantaneously, even at room temperature, to give the corresponding organometallic chlorides and 1,1,2,2-tetracyanopropylbenzene (IV). The high reactivity of both compounds I and II and other poly-

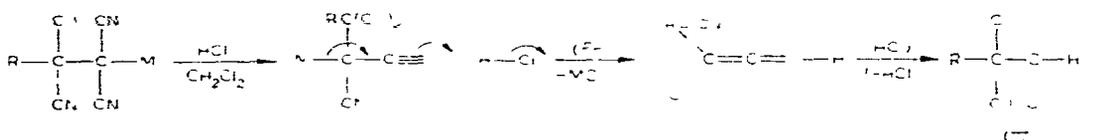
* The value of pK_a for the cyanohydrocarbon IV as determined by potentiometric titration of its sodium salt in water, is 7.03 ± 0.13 (the acidity of some related systems is discussed elsewhere [27])

cyano-substituted organometals [14–17], seems to result from the acid cleavage reaction proceeding either via a contact ion pair such as V or the electrophilic fragmentation mechanism (F_{Σ} [29]) involving transfer of the reaction centre

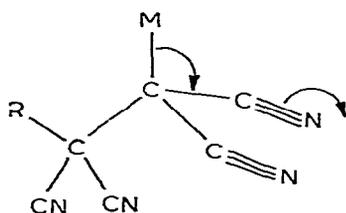
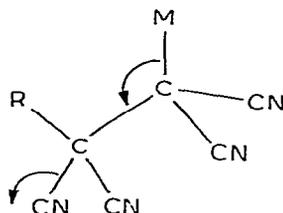


(V)

from the carbon atom to the nitrogen atom of the α -nitrile group (eq 3)



On the other hand, it has been mentioned above that compounds I and II, as well as other polycyano-substituted organometals [19], undergo quantitative fragmentation even in low-polar solvents, resulting in the cleavage of two σ -bonds and the formation of organometallic cyanides (Schemes 1 and 2) Thus, in acid and thermal cleavage reactions they exhibit a peculiar dual reactivity which, in our opinion, may be attributed to the presence of two competing chains of σ, π - and σ, σ -conjugation of the carbon–metal bond with the adjacent α - and β -nitrile groups

 σ, π -conjugation σ, σ -conjugation

Interaction of TCNE with trimethyltin phenylmercaptide

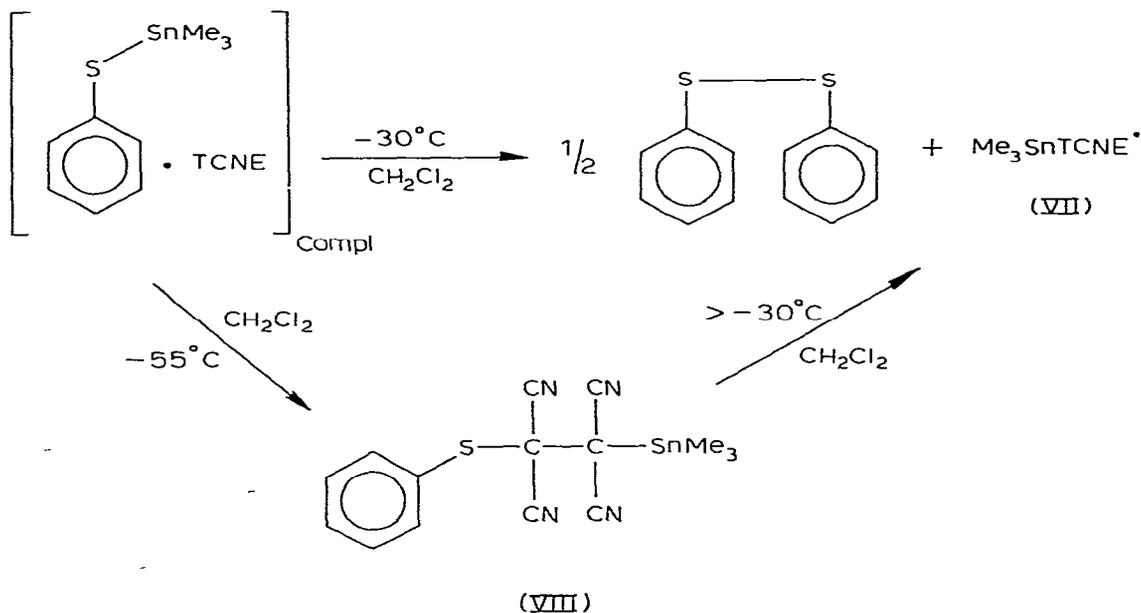
Arylmercaptides of heavy metals (Ph–S–M) comprising several electron-donor fragments (the π -system of the benzene ring, the metal–sulphur σ -bond, and the n -electrons of the sulphur atom) can in a sense be considered as heteroanalogues of benzyl organometals. In view of the findings reported in the previous section, it was of interest to estimate the regioselectivity of TCNE in its reactions with ambiofunctional compounds of this type.

The symmetrical tin phenylmercaptide (PhS)₄Sn (VI) with TCNE in benzene forms a stable solution of a charge transfer complex, orange in colour, from which the starting components can be isolated in quantitative yield even after boiling for 72 h. The low reactivity seems to result from the weak electron-donor

properties inherent in this compound, and, hence, from a low degree of charge transfer in the resulting complex

However, with the non-symmetrical trimethyltin phenylmercaptide the charge transfer complexes which first appeared in the solution enter very easily into further chemical reactions (Scheme 5)

SCHEME 5



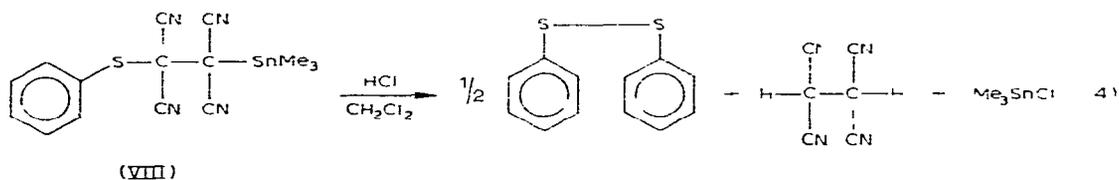
While carrying out this reaction at temperatures above -30°C we found (in quantitative yield) diphenyl-disulphide and *N*-trimethylstannylated iminotri-cyanoallyl radical (VII), which was black-brown in colour and identical in its properties to the compound described earlier in the reaction of Me_3SnCl with Li^+TCNE^- [30]. As with the benzyl organometals (cf Schemes 1, 2 and 5), we assumed that these substances are not the primary reaction products but result from decomposition of an unstable product of TCNE insertion into the tin-sulphur bond. Indeed on cooling to -55°C and treating the reaction mixture with cooled hexane we isolated an extremely unstable diamagnetic product (VIII), which was a cream-coloured substance with m.p. 50°C (Scheme 5).

The substance isolated proved to be a 1/1 adduct of the starting components, as determined by elemental analysis. To establish its chemical structure, IR and PMR spectroscopy was employed (Table 1). The nature of the aromatic proton spin-spin decoupling together with the relation between the integral intensities of the resonance absorption signals in the PMR spectrum of compound VIII suggest that the benzene ring and the tin-methyl bond remain unaffected during the reaction. Compared with the original Ph-S-SnMe_3 , the PMR spectrum of compound VIII exhibits an increase by 0.2 ppm in the proton chemical shift of the methyl groups bonded to the tin atom, and a corresponding increase by 14 Hz of the spin-spin decoupling constant $J(^1\text{H}-^{117}\text{Sn})$. These data, which

point to an increase in the degree of the tin atom deshielding, suggest that during the reaction with TCNE cleavage of the Sn—S bond and formation of a new bond between the tin atom and the electronegative tetracyanoalkyl substituent occur ν . Thus all the data obtained suggest that compound VIII is 2-thiophenyl-1,1,2,2-tetracyanoethyltrimethylstannane

Compound VIII is extremely unstable and can only be stored in solid state under inert atmosphere. In solutions of organic solvents it decomposes homolytically at temperatures as low as -30°C to yield amounts of quantitative PhSSPh and the stable radical VII. It can therefore be supposed that at temperatures above -30°C the interaction of TCNE with PhSSnMe₃ represents a two-stage process. To start with TCNE is inserted quantitatively into the tin—sulphur bond and then a rapid decomposition of the unstable intermediate adduct VIII occurs.

Evidence in favour of the structure suggested for compound VIII is also provided by its cleavage with HCl which results in the formation of Me₃SnCl, diphenyldisulphide, and tetracyanoethane in quantitative yield (eq. 4)



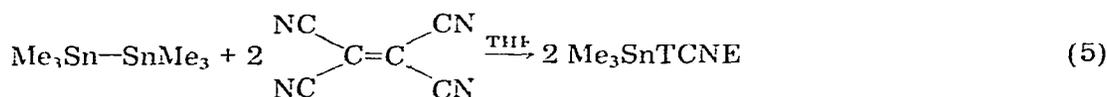
The direction of this reaction differs from that for the acid cleavage of compounds I and II (cf. ref. 6) under the same conditions, and this may be due to the presence of σ, σ -conjugation of the C—Sn bond with the C—S bond of compound VIII. The analogous of compound VIII, β -stannylated organosulphides of the type $\text{RS}-\text{CH}_2-\text{CH}_2-\text{SnR}_3'$, are known to be capable of reacting with electrophilic reagents by attack on the sulphur atom to give olefins [32]. It is likely that in the case we have studied acid cleavage of compound VIII proceeds in a similar fashion and yields thiophenol and TCNE, which in turn are capable of reacting with one another [33] to give the final reaction products, tetracyanoethane and diphenyldisulphide.

Interaction of TCNE with hexamethyldistannane

Studies on the nature of the donor-acceptor reaction of organometals with TCNE, the latter being considered as an one-electron oxidant of the C—metal bond, [15–17] have recently aroused much interest. In reactions with organometals containing a metal—metal bond, TCNE is assigned the same role [34]. Such a viewpoint is based primarily on the presence of paramagnetic species among the reaction products. Thus, it had been reported recently [18] that the reaction of equimolecular quantities of hexamethyldistannane and TCNE in tetrahydrofuran leads to formation of a black paramagnetic substance (VII) with m.p. 180°C which, according to the literature [18,30,35] is the trimethyl-

* Similar changes (by 0.2 ppm and 16 Hz respectively) have been observed when proceeding from Me₄Sn to Me₃SnCF₃ and Me₃SnCF₂CF₂R [31]

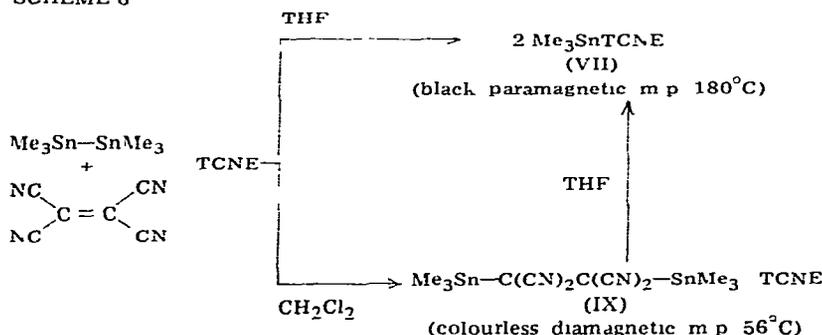
stannyl derivative of the TCNE anion-radical (eq 5)



(VII)

For the reaction of TCNE with PhSSnMe_3 , which was discussed in the preceding section of this paper we have, however, found that the metallated radical VII can be formed, not through one-electron oxidation of the initial organometallic compound, but by homolytical decomposition of the unstable intermediate VIII, a product of TCNE insertion into the tin-sulphur bond (Scheme 5) This gives grounds for us to suppose that a similar sequence of chemical transformations involving the intermediate formation of an unstable product from TCNE insertion into the tin-tin bond, can take place in the case of the reaction of hexamethyldistannane with TCNE as well (Scheme 6)

SCHEME 6



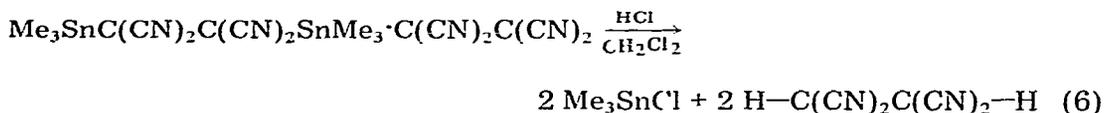
In the present work the expected organotin compound IX was isolated in 30% yield by carrying out this reaction in low-polar CH_2Cl_2 where the compound proved to be practically insoluble. The isolated compound IX was a colourless crystalline substance with m p 56°C, identical in its elemental composition to the metallated radical VII described elsewhere [18] but differing from the latter in its m p and also by the absence of colour and paramagnetic properties.

The PMR spectrum of adduct IX (Table 1) shows only one signal of methyl groups bonded to the tin atom. This indicates that these groups are equivalent and that the tin-methyl bond remains unaffected during the course of the reaction. The shift of this signal by 0.5 ppm downfield, the increase in the spin-spin decoupling constant $J(^1\text{H}-^{117}\text{Sn})$ from 47 to 64 Hz as well as the disappearance of the spin-spin decoupling $J(^1\text{H}-^{117}\text{Sn}-^{117}\text{Sn})$ present in the initial hexamethyldistannane, all suggest that the formation of compound IX involves cleavage of the Sn-Sn bond and the insertion of a TCNE molecule. The second equivalent of TCNE present in compound IX as indicated by elemental analysis, seems to be in a complexed form. That the second equivalent should be involved in the formation of compound IX is also confirmed by the fact that a two-fold excess of TCNE in the reaction with hexamethyldistannane

brings about an increase in its yield from 30 to 70%

The IR spectrum of compound IX (Table 1) displays an absorption band at 556 cm^{-1} due to the carbon-tin bond. There are also two bands at 2156 and 2215 cm^{-1} in the nitrile group absorption region, the first of which can be attributed to the keteneimine fragment ($-\text{N}=\text{C}=\text{C}$). However, the almost complete absence of colour and the presence of only one kind of methyl group at the tin atom, as evidenced by PMR spectral data (Table 1), allow us to consider that compound IX is a C- rather than an N-metallated derivative.

Further evidence to support the suggested structure of compound IX was obtained from the results of acid cleavage, which immediately produces trimethylchlorostannane and tetracyanoethane (eq 6)



(IX)

Compound IX, which is fairly stable in the solid state if kept in vacuo at lowered temperatures, proved to readily undergo homolysis and atmospheric oxidation. Thus, on standing in air for a few minutes or in a solution of CH_2Cl_2 under argon for a day, compound IX isomerized quantitatively to give a black paramagnetic substance identical in its physical properties to compound VII obtained earlier [18]. Consequently, the formation of compound IX as a precursor of compound VII cannot either be ruled out when the reaction is carried out in tetrahydrofuran. To verify this assumption we treated compound IX with tetrahydrofuran and found it to be transformed immediately into a black residue of the paramagnetic substance VII (Scheme 6)

All the data obtained suggest that the reaction of hexamethyldistannane with TCNE proceeds as a stage-by-stage process involving the intermediate formation of an unstable diamagnetic adduct of the 1/2 composition IX. Depending on the solvent used, this adduct may be isolated or be subject to further transformations to the metallated radical VII.

Experimental

PMR spectra were taken with Varian T-60 and XL-100 spectrometers. IR spectra (vaseline oil) were obtained using a UR-20 spectrometer. The reactions of TCNE with organometallic compounds, and the isolation and purification of products were all carried out under argon atmosphere. TCNE (Chemapol) was purified according to literature methods [37] by sublimation in vacuo through a layer of activated charcoal.

Reaction of $\text{PhCH}_2\text{SnMe}_3$ with TCNE

$\text{PhCH}_2\text{SnMe}_3$ (0.255 g) was added to a magnetically stirred suspension of 0.128 g of TCNE in 20 ml of CH_2Cl_2 . The initial violet colour of the mixture faded in 25 min and then changed to a stable red. The reaction product was isolated by treating the reaction mixture with cooled hexane at the moment of greatest decolouration and reprecipitated from tetrahydrofuran with hexane

to yield 0.3 g (80%) of I (Found C, 50.00, H, 4.05, N, 14.49, Sn, 31.60
 $C_{16}H_{16}N_4Sn$ calcd C, 50.19, H, 4.19, N, 14.62, Sn, 31.00%)

Acid cleavage of I 4 ml of CH_2Cl_2 saturated with HCl (2.5 mol/l) was added, with stirring to a solution of 0.1915 g of I in 3 ml of CH_2Cl_2 . By using quantitative GLC with an internal standard, Me_3SnCl was identified in the reaction mixture (100% yield). An oil remaining after distilling off the volatile components was recrystallized from a benzene/hexane mixture to yield 0.1 g (30%) of IV, m.p. 127° *

Thermal cleavage of I A solution of 0.1915 g of I in 10 ml of CH_2Cl_2 was kept at 20° for a minute, after which time it had turned red in colour. The mixture was allowed to stand for 24 h and was then passed through a layer of Al_2O_3 (*h* 3 cm). The filtrate was evaporated and the remaining Me_3SnCN reprecipitated with hexane from chloroform to yield 0.09 g (96%), m.p. 182° (lit. [38] m.p. 183°)

Reaction of $(PhCH_2)_2Hg$ with TCNE

To a magnetically stirred solution of 0.128 g of TCNE in 20 ml of CH_2Cl_2 was added 0.383 g of $(PhCH_2)_2Hg$. The solution was observed to be blue for 15 min, the colour then faded and finally turned red. At the moment of decolouration (after approx. 40 min) the reaction mixture was treated with hexane (160 ml). The precipitated residue was separated and reprecipitated with hexane from tetrahydrofuran to yield 0.37 g (73%) of II, m.p. 95° (Found C, 46.87, H, 2.76, Hg, 39.04, N, 10.50. $C_{20}H_{14}HgN_4$ calcd C, 47.06, H, 2.74, Hg, 39.21, N, 10.96%)

Acid cleavage of II To a stirred solution of 0.123 g of II in 3 ml CH_2Cl_2 was added 2 ml of a solution of HCl in CH_2Cl_2 (2.5 mol/l). The volatile fraction was evaporated. According to PMR spectra, the residue represented an equimolecular mixture of $PhCH_2HgCl$ and IV. After extraction on a column containing Al_2O_3 , $PhCH_2HgCl$ was isolated in 95% yield, m.p. 104° .

Thermal cleavage of II 0.51 g of II was dissolved, with stirring, in 30 ml of CH_2Cl_2 and allowed to stand for a day. The solvent was evaporated in vacuo and the remaining semicrystalline brown mass was dissolved in $CHCl_3$ and passed through a column containing Al_2O_3 (*h* 3 cm). After the eluate was evaporated, 0.31 g of $PhCH_2HgCN$ was isolated (97% yield), m.p. 128° (lit. [22] m.p. 128°)

Reaction of $(p-CH_3C_6H_4CH_2)_2Hg$ with TCNE

0.411 g of $(p-CH_3C_6H_4CH_2)_2Hg$ was added, with stirring, to a solution of 0.128 g TCNE in 20 ml of CH_2Cl_2 . A turquoise colour appearing at the moment the reagents were mixed disappeared within 5 min. At the moment of greatest decolouration 150 ml of cooled hexane was added to the reaction mixture. The precipitated residue was separated and reprecipitated from tetrahydrofuran with hexane. According to its PMR spectra, the reaction was quantitative. 0.37 g of the product (60% yield) was isolated preparatively, m.p. 75° (dec.) (Found

* Ref. 1 contains a misprint: the melting point of 1,1,2,2-tetracyanopropylbenzene (IV) actually obtained according to ref. 1 is 128°

C, 49.10, H, 3.82, Hg, 37.64, N, 10.66 $C_{22}H_{14}HgN_4$, calcd C, 49.02, H, 3.34, Hg, 37.24, N, 10.40%

Reaction of PhSSnMe₃ with TCNE

A solution of 0.237 g of PhSSnMe₃ in 5 ml of CH₂Cl₂ was added, with stirring, to a suspension of 0.128 g of TCNE in 15 ml of CH₂Cl₂ cooled to -65°. The temperature of the mixture was increased to -55° and then to the resulting transparent solution hexane, cooled to -60°, was added. A cream-coloured residue obtained was filtered and dried in vacuo to yield 0.4 g (62%) of VIII, m.p. 50° (dec.) (Found: C, 44.58, H, 3.75, S, 7.78, Sn, 30.05 $C_{15}H_{13}N_4SSn$ calcd C, 44.92, H, 3.49, S, 7.98, Sn, 29.62%)

Acid cleavage of VIII A solution of VIII obtained from 0.545 g of PhSSnMe₃ and 0.256 g of TCNE in 5 ml of CH₂Cl₂ was treated with 8 ml of a solution of HCl in CH₂Cl₂ (5.5 mol/l) at -55°. A white precipitate was formed immediately. By using quantitative GLC, Me₃SnCl (95%) was identified in the reaction mixture. After the reaction was completed the mixture was evaporated to dryness and the residue treated with boiling hexane. The extract was washed with water, dried over MgSO₄ and evaporated. The resulting residue was recrystallized from hexane to yield 0.19 g (99%) of PhSSPh, m.p. 58°C. The hexane-insoluble fraction of the dry residue was purified by sublimation at 105° followed by reprecipitation with hexane from ethylacetate to yield 0.23 g (89%) of tetracyanoethane, m.p. 168° (dec.) (lit. [39] m.p. 168°) IR spectrum $\nu(CN)$ 2270, $\nu(CH)$ 2926 cm⁻¹

Thermal cleavage of VIII A solution of 0.4 g of VIII in 8 ml of CH₂Cl₂, prepared at -55°, was slowly warmed to -30°. During the warming a reddish-brown colour developed, gradually darkening as the temperature was further increased and finally producing a black residue. After being warmed to room temperature, the mixture was evaporated and the resulting black-brown residue was dried in vacuo and repeatedly extracted with boiling hexane. The filtrate was evaporated, the residue dissolved in CH₂Cl₂ and filtered through a small column packed with Al₂O₃. After the solvent had been evaporated, the residue was recrystallized from hexane to yield 0.094 g (98%) of PhSSPh, m.p. 58°. The hexane-insoluble matter was purified by reprecipitating with ether from tetrahydrofuran to yield 0.276 g (92%) of the paramagnetic substance VII, m.p. 180°C (Lit. [18] m.p. 180°). IR spectrum $\nu(CN)$ 2225 cm⁻¹

Reaction of TCNE with hexamethyldistannane

A solution of 0.327 g of Me₆Sn₂ in 5 ml of CH₂Cl₂ was added, with stirring, to a solution of 0.256 g of TCNE in 15 ml of CH₂Cl₂ at room temperature. A yellow colour immediately appeared and after a minute a practically colourless residue began to precipitate. After 35 min the residue was filtered, washed with hexane, dried in vacuo over paraffin and CaCl₂ to yield 0.415 g (71%) of IX, m.p. 56°. (Found: C, 37.34, H, 3.20, Sn, 39.96 $C_9H_9N_4Sn$ calcd C, 37.04, H, 3.10; Sn, 40.67%).

When compound IX (0.11 g) was treated with tetrahydrofuran (5 ml), the suspended material immediately darkened while the solution turned red. After standing for a day, the solvent was evaporated and compound VII, an amorphous black substance, was isolated, m.p. 180° (lit. [18] m.p. 180°). After

being purified by reprecipitating with ether from tetrahydrofuran and dried in vacuo the substance did not melt. A 90% yield was obtained (0.1 g) (Found C, 37.39, H, 3.25 C₇H₉N₄Sn calcd C, 37.04, H, 3.10%) IR spectrum $\nu(\text{CN})$ 2225 cm⁻¹

Acid cleavage of IX A suspension of 0.291 g of IX in 6 ml of CH₂Cl₂ was treated with 4 ml of CH₂Cl₂ saturated with HCl (2.5 mol/l). The mixture turned pink, and a white residue was precipitated. By using quantitative GLC, Me₃SnCl (96%) was identified in the reaction mixture. The volatile components of the mixture were evaporated in vacuo, the residue was sublimed at 105° (1 mmHg) and reprecipitated with hexane from ethyl acetate to yield 0.031 g (90%) of tetracyanoethane, m.p. 168° (lit [39] m.p. 168°)

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