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Charge-Transfer Spectra of Permethylated Polygermanes–TCNE To Afford 1:1 Adducts

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Summary: Charge-transfer spectra of permethylated polygermane–tetracyanoethylene (TCNE) complexes were observed. The frequency of charge-transfer spectra was linearly related to ionization potentials (or electrochemical oxidation potentials) of the polygermanes. Polygermanes inserted into TCNE to afford 1:1 adducts under mild conditions.

Organometallic compounds, particularly those with metal–metal σ bonds, are excellent electron donors. As electron-rich species, they are subject to cleavage by various organic electrophiles as well as transition complexes.[1] Since group 14 element catenates have rather low ionization potentials, electron-transfer mechanisms are very important in which the rate is limited by the ability of the group 14 element catenates to transfer an electron to an electrophile acting as an electron acceptor. While the charge-transfer (CT) interactions between silicon–silicon σ bonds and common electron acceptors such as tetracyanoethylene (TCNE) have been amply investigated,[2,3] those of germanium–germanium σ bonds have not been reported except for hexamethyldigermane.[3] We herein describe the first report on CT spectra of permethylated polygermanes ($Me(Me_2Ge)_nMe$ (n = 2–5) and $(Me_2Ge)_6$–TCNE, followed by insertion of permethylated polygermanes into TCNE under mild conditions.

Results and Discussion

New absorption bands are observed in the visible region immediately upon mixing a dichloromethane solution of TCNE (0.01–0.02 M) with permethylated polygermanes, $Me(Me_2Ge)_nMe$ (n = 2–5) and $(Me_2Ge)_6$ (0.1–0.5 M). The bands are broad, as is characteristic of intermolecular CT spectra and sometimes unsymmetrical. The absorbance increases with the concentrations of both permethylated polygermanes and TCNE. The use of relatively high concentrations of the germanes and TCNE was necessitated by the rather low absorbances. The spectra of CT complexes are red-shifted as the number of germanium atoms in the chain increases. The frequencies of the CT bands, ionization potentials, as determined by photoelectron spectroscopic (PE) methods,[4] and electrochemical oxidation potentials of permethylated polygermanes[5] are listed in Table I.

Table I. Frequencies for Charge-Transfer Absorption in Complexes of TCNE with Permethylpolygermanes, $Me(Me_2Ge)_nMe$ (n = 2–5) and $(Me_2Ge)_6$, in Dichloromethane at Room Temperature

compd	ν_{max} cm^{-1}	ν_{max} eV	IP/eV[4]	$E_{p/2}$/V[5]
$Me_3GeGeMe_3$	23 400	2.90	8.58, 8.60[6,7]	1.28
	23 000	2.85[3]		
$Me(Me_2Ge)_3Me$	20 600	2.56	8.15	0.93
$Me(Me_2Ge)_4Me$	18 200	2.26	7.80	0.72
$Me(Me_2Ge)_5Me$	17 700	2.19	7.67	0.61
$(Me_2Ge)_6$	18 800	2.33	7.88	0.66

A good linear relationship between the frequencies of CT bands and ionization potentials (or electrochemical oxidation potentials) of respective polygermanes was obtained as shown in Figure 1.

$$\nu_{CT}\ (\text{eV}) = 0.798\,\text{IP(PE)} - 3.95\ (r = 0.998)$$

However, the relationship may be complicated because some CT complex bands appear to be overlapping.

The CT complexes may be considered σ–π complexes arising from a charge-transfer interaction between the σ HOMO of permethylated polygermanes and the π LUMO of TCNE.

Permethylated polygermanes also appear to form colored CT complexes with other acceptors; for example, new absorption bands appear in the spectra of solutions of Me_8Ge_3 with chloranil (λ_{max} 438 nm) and Me_8Ge_3 with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (λ_{max} ca. 540 nm).

Interestingly, polygermane–TCNE complexes, which are stable at room temperature, lead to simple 1:1 adducts, $Me(Me_2Ge)_{m'}(TCNE)$–$(Me_2Ge)_{n'}Me$; $n = m' + n'$, at 50 °C.

$$Me(Me_2Ge)_nMe + TCNE \overset{\text{room temp}}{\rightleftarrows} [\text{CT complex}] \xrightarrow{50\ ^\circ\text{C}} \text{1:1 adducts}$$

The course of reaction can be followed readily by changes in the ^1H NMR spectrum. For example, the reaction of octamethyltrigermane, Me_8Ge_3, and TCNE in dichloromethane-d_2 was observed by the disappearance of Me_8Ge_3 (δ 0.15 and δ 0.19) and the concomitant appearance of trimethylgermyl group (δ 0.43) and pentamethyldigermyl group (δ 0.30 and δ 0.46) resonances of the insertion products, 1-(trimethylgermyl)-2-(pentamethyldigermyl)-

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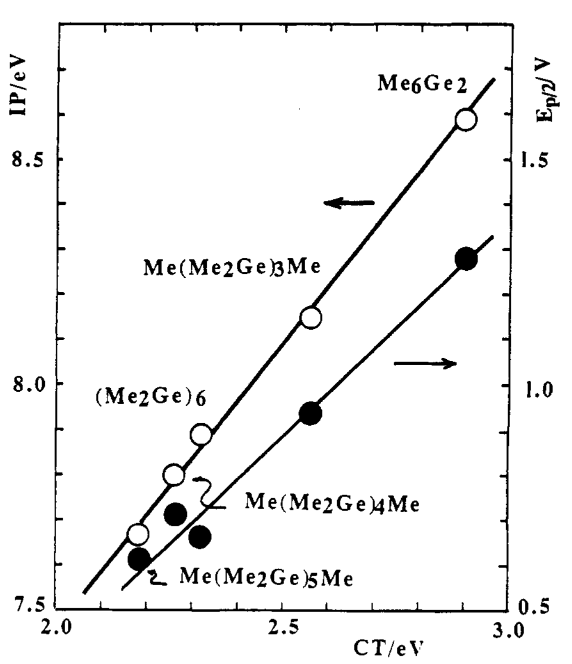
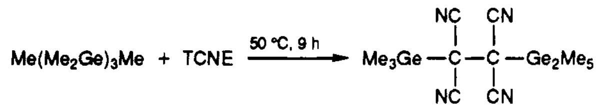


Figure 1. Plot of charge-transfer transition energies for polygermane–TCNE complexes against the first ionization potentials (or electrochemical oxidation potentials) of polygermanes.

tetracyanoethane, in yield 35%. TCNE inserts cleanly into only the Ge–Ge bond in this reaction.



$$Me(Me_2Ge)_3Me + TCNE \xrightarrow{50\ ^\circ C,\ 9\ h} Me_3Ge-C(CN)_2-C(CN)_2-Ge_2Me_5$$

Similarly, decamethyltetragermane also inserted into TCNE to give 1,2-bis(pentamethyldigermyl)tetracyanoethane and 1-(trimethylgermyl)-2-(octamethyltrigermyl)tetracyanoethane in 25% yields, respectively. In the reaction of dodecamethylcyclohexagermane and TCNE, 1,1,2,2-tetracyano-3,3,4,4,5,5,6,6,7,7,8,8-dodecamethyl-3,4,5,6,7,8-hexagermacyclooctane was formed in 3% yield. However, Me_6Ge_2-TCNE complex is stable at 50 °C for 9 h.

The frequency of the CT band measured in solutions can be approximated by

$$h\nu_{CT} \propto E^\circ_{ox} - E^\circ_{red}$$

where E°_{ox} and E°_{red} refer to the oxidation potential of the donor and the reduction potential of the acceptor, respectively.[8] The plot for permethylpolygermane–TCNE in this study shows the same general trend as those of permethylpolysilanes and tetraalkyltin compounds previously reported.[2,3,9] Thus, permethylpolygermanes interact with TCNE to form the same transient CT complexes as in the case of other group 14 element compounds. The frequencies of permethylpolygermane–TCNE complexes are near to those of $Me(Me_2Si)_nMe$–TCNE complexes and are lower than those of the Me_4Sn–TCNE complex. However, $Me(Me_2Si)_nMe$–TCNE complexes are thermally stable and the Me_4Sn–TCNE complex is very unstable to easily form a simple 1:1 adduct, $Me_3Sn(TCNE)Me$, at even low temperature. The difference of reactivities in group 14 element compound–TCNE complexes may be explained by the stability of cation radicals of group 14 element compounds acting as donors. In fact, the unpaired electron has been reported to be localized in σ-bonding orbitals between the two metal atoms for radical cations of hexamethyldisilane and hexamethyldigermane[10] and to be largely localized in the vertical tin–carbon bond for the radical cation of trigonal-pyramidal tetramethylstannane.[11,12] The bond cleavage of radical cations may have preference in the order Si–Si < Ge–Ge ≪ Sn–C.

Experimental Section

^1H NMR spectra were recorded on a JEOL GX 270 using cyclohexane as the internal standard. UV spectra were obtained with a Shimazu 2200 instrument. GC–MS spectra were obtained with a JEOL JMX-DX 303 mass spectrometer. Gas chromatography was performed on a Shimazu GC-8A with 1-m SE30 columns.

Materials. Tetracyanoethylene (TCNE) and dichloromethane were commercially available. Trimethylchlorogermane, Me_3GeCl,[13] dimethylchlorogermane, Me_2GeCl_2,[13] and dodecamethylcyclohexagermane $(Me_2Ge)_6$,[14] were prepared as described in the cited reference.

Preparation of Permethylated Polygermanes, $Me(Me_2Ge)_nMe$ (n = 2–5). Approximately 200 mL of tetrahydrofuran (THF) was distilled under nitrogen from sodium wire into a 500-mL three-necked flask fitted with a reflux condenser, dropping funnel, and mechanical stirrer. Lithium dispersion (5.8 g, 0.83 g-atom) was introduced and to this a mixture of trimethylchlorogermane (58.2 g, 0.38 mol) and dimethyldichlorogermane (39.4 g, 0.23 mol) was added with stirring for 1 h. Gentle heat and the formation of a light colored precipitate gave evidence of reaction. After stirring for 10 h, the mixture began to exhibit a yellow to light green color which slowly became darker. Several milliliters of methanol was added to the solution containing unreacted lithium metal. The mixture was extracted with ether, and the combined organic layer was dried over anhydrous sodium sulfate. The solution was evaporated to dryness and distilled to yield $(Me_3Ge)_2$,[15] bp 40–48 °C/34 mmHg, 8.1 g (0.034 mol, 17.9%), $Me(Me_2Ge)_3Me$,[16] bp 95 °C/36 mmHg, 12.5 g (0.037 mol, 19.5%), $Me(Me_2Ge)_4Me$,[16] bp 80–82 °C/2 mmHg, 7.8 g (0.018 mol, 9.5%), $Me(Me_2Ge)_5Me$, bp 85 °C/0.5 mmHg, 4.6 g (0.084 mol, 4.4%), and unidentified high boiling point products. $Me(Me_2Ge)_5Me$: NMR (δ in CD_2Cl_2) 0.212 (s, 3 H), 0.286 (s, 2 H), 0.317 (s, 1 H); IR (neat, cm^{-1}) 1230; n^{20} 1.5475; M^+ 548. Anal. Calcd for $C_{12}H_{36}Ge_5$: C, 26.52; H, 6.68. Found: C, 6.22; H, 6.72.

Charge-Transfer Spectra between Permethylated Polygermanes and TCNE. As a representative example, the charge-transfer spectrum between octamethyltrigermane and TCNE is described. To a solution of dichloromethane containing TCNE (0.015 M) was added by syringe $Me(Me_2Ge)_3Me$ (0.05 g, 2.2 mmol). The solution immediately turned to red, and the absorption peak at 485 nm was recorded with a Shimazu UV 2200 instrument.

NMR Studies of Insertion Reactions of Permethylated Polygermanes and TCNE. The sample was prepared in a 5-mm NMR tube from $Me(Me_2Ge)_3Me$ (0.01 mL, 0.048 mmol), TCNE (6.2 mg, 0.048 mmol), and deuterated dichloromethane (0.6 mL). The NMR tube was degassed and sealed. The NMR

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tube was kept at 50 °C, and the reaction was periodically monitored by NMR spectroscopy. After 9 h, TCNE insertion products into the trigermane were characterized very carefully by comparing the ^{1}H NMR data of similar compounds. $Me(Me_2Ge)_3Me$: δ 0.15 (18 H, Me_3Ge), 0.19 (6 H, Me_2Ge). $Me_3Ge(TCNE)GeMe_2GeMe_3$: δ 0.43 (9 H, Me_3Ge), 0.30 (9 H, Me_3GeMe_2Ge), 0.46 (6 H, $Me_3Ge\mathit{Me}_2Ge$). $Me(Me_2Ge)_4Me$: δ 0.22 (18 H, Me_3Ge), 0.29 (12 H, Me_2Ge). $(Me_3GeMe_2Ge)_2(TCNE)$: δ 0.32 (18 H, Me_3Ge), 0.54 (12 H, Me_2Ge). $Me_3Ge(TCNE)(GeMe_2)_3Me$: δ 0.44 (9 H, Me_3Ge), 0.40 (9 H, $\mathit{Me}_3GeMe_2GeMe_2Ge$), 0.41 (6 H, $Me_3Ge\mathit{Me}_2GeMe_2Ge$), 0.58 (6 H, $Me_3GeMe_2Ge\mathit{Me}_2Ge$). $(Me_2Ge)_6$: δ 0.32, 1,1,2,2-Tetracyano-3,3,4,4,5,5,6,6,7,7,8,8-dodecamethyl-3,4,5,6,7,8-hexageramcyclooctane: δ 0.48 (12 H, $\mathit{Me}_2GeMe_2GeMe_2Ge(TCNE)$), 0.51 (12 H, $Me_2Ge\mathit{Me}_2GeMe_2Ge(TCNE)$), 0.60 (12 H, $Me_2GeMe_2GeMe_2Ge(TCNE)$).

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