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Syntheses and reactivities of ferrocenyl organyl tellurides

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Abstract

Twenty new ferrocenyl organyl (alkyl, alkenyl and alkynyl) tellurides were synthesized by using diferrocenyl ditelluride and characterized spectroscopically. Cinnamyl and benzyl ferrocenyl tellurides were revealed to be air stable enough to be isolated, in sharp contrast to the corresponding air sensitive phenyl tellurides. Treatment of some alkyl ferrocenyl tellurides with 1 mol equiv of m-chloroperbenzoic acid (MCPBA) in diethyl ether at 25°C for 2 h in the presence of triethylamine or tetracyanoethylene (TCNE) afforded the corresponding alkenes in fair to good yields via telluroxide elimination. The MCPBA or air oxidation of some allylic ferrocenyl tellurides in ethanol produced the corresponding allylic alcohols via [2,3] sigmatropic rearrangement. ^{1}H NMR and electronic absorption spectroscopic studies revealed that donor-acceptor complexes between alkyl ferrocenyl tellurides and TCNE were produced, an improvement of telluroxide elimination in the presence of TCNE being attributed to this complex formation.

Key words: Ferrocene; Tellurium; Oxidation; Allyl; Benzyl

1. Introduction

The ease of telluroxide elimination whether via hydrolysis of dibromides of various alkyl aryl tellurides [1] or by direct oxidation of the tellurides [2] depends on the nature of aryl and alkyl groups as well as on the additives. Thus, when elimination was by direct oxidation, a pyridyltellurium moiety was found to be a much more facile leaving group than a phenyltellurium moiety and the addition of triethylamine gave a remarkable increase of the yield of elimination products [2b]. Recent reports [3,4] on the synthesis and the physical properties of diferrocenyl ditelluride $(FcTe)_2$ prompted us to examine the effect of a ferrocenyltellurium moiety on the stability and the reactivity of the corresponding tellurides. Here we present the syntheses of many new ferrocenyl organyl (alkyl, alkenyl and alkynyl) tellurides by using $(FcTe)_2$, their chemical reactivities to several oxidizing agents and their donor-acceptor complex formation with tetracyanoethylene (TCNE). Organic compounds containing a ferrocenyl group have recently attracted much interest in material [5] and biological [6] sciences.

2. Results and discussion

2.1. *Synthesis of ferrocenyl organyl tellurides*

All alkyl ferrocenyl tellurides (**1–18**) were prepared by treatment of the corresponding alkyl bromides or tosylates with diferrocenyl ditelluride [3] and $NaBH_4$ in ethanol (Scheme 1, 64–100% yield). The compounds **9** and **15**, benzylic and allylic ferrocenyl tellurides, were stable enough to be isolated in the atmosphere in the solid state. This is in sharp contrast to the stability of benzylic phenyl tellurides [7] and allylic phenyl tellurides [8] which were very air sensitive and could not be isolated. Other allylic ferrocenyl tellurides such as **16–18**, however, were revealed to be unstable in air, but their formation in high yield was confirmed *in situ* by ^{1}H-NMR under nitrogen. A vinylic ferrocenyl telluride (**19**) was prepared by the addition of ferrocenyltellurenyl anion to phenylacetylene [9], while an alkynyl

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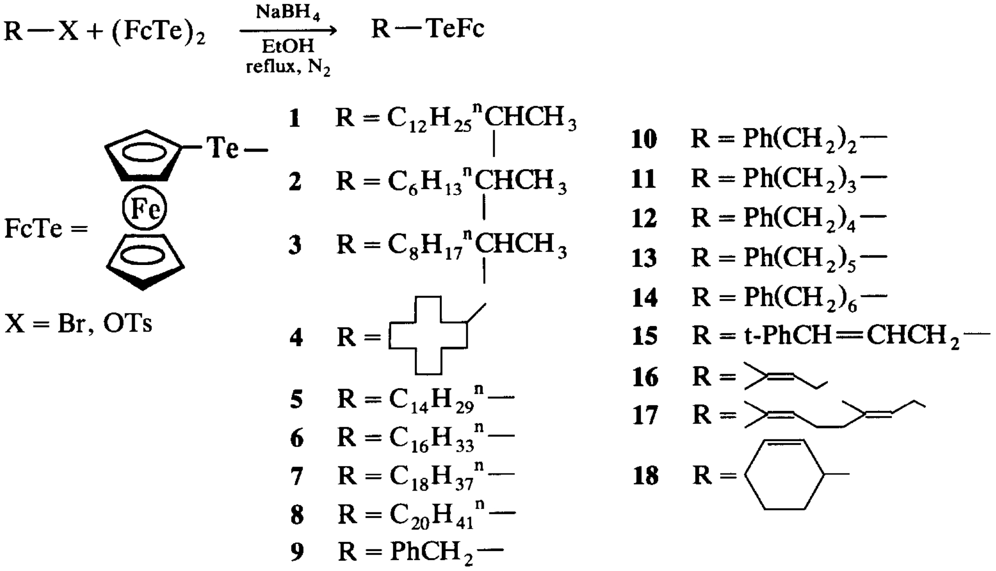


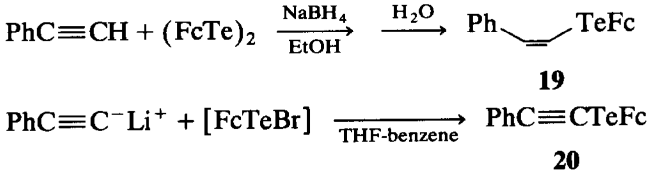
Scheme 1. Preparation of alkyl ferrocenyl tellurides.

compound (**20**) was obtained by a lithium-ferrocenyltellurium exchange method (Scheme 2).

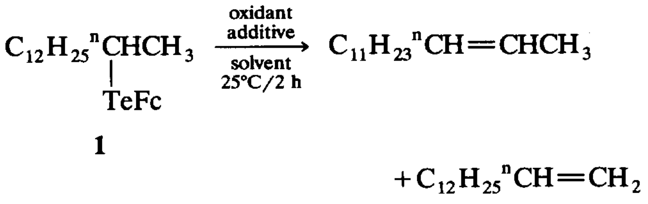
2.2. Telluroxide elimination of alkyl ferrocenyl tellurides under various reaction conditions

Regarding telluroxide elimination we have found that a 2-pyridyltellurium moiety is a better leaving group than a phenyltellurium moiety [2b] probably because of its electron withdrawing property, as has been observed in selenoxide elimination [10]. We were therefore interested in the aptitude of a ferrocenyltellurium moiety as a leaving group, since there are so far no data. First, we examined the suitable conditions for the elimination by using ferrocenyl 2-tetradecyl telluride (**1**) as a substrate. When the telluride was allowed to react with 1 mol equiv of *m*-chloroperbenzoic acid (MCPBA) in acetonitrile, diethyl ether and benzene at 25°C for 2 h, 1- and 2-tetradecenes were obtained in 17–83% yield together with small amounts of 2-tetradecanol and 2-tetradecanone (Scheme 3).

Since the starting telluride was not observed after 30 min by TLC monitoring, it is evidently oxidized to the corresponding telluroxide or its MCBA adducts [2b] which might be stable enough to resist a facile elimination of telluroxide. When the oxidation was



Scheme 2. Preparation of alkenyl and alkynyl ferrocenyl tellurides.



Scheme 3. Oxidation of ferrocenyl 2-tetradecyl telluride (**1**) under various conditions.

TABLE 1. Oxidation of ferrocenyl 2-tetradecyl telluride (**1**) under various conditions

Oxidant (mol equiv) [a]	Additive (mol equiv) [a]	Solvent	Tetradecenes (GLC yield%) [b]
MCPBA (1)	–	Et_2O	25
MCPBA (1)	–	CH_3CN	17
MCPBA (1)	–	benene	33
MCPBA (2)	Et_3N (1)	Et_2O	63 [c]
MCPBA (1)	TCNE (1)	Et_2O	67 [d]
MCPBA (1)	TCNQ (1)	Et_2O	45
MCPBA (1)	TCNE (1)	CH_3CN	20
MCPBA (1)	TCNE (1)	benzene	32
MCPBA (1)	TCNE (1)	THF	6
H_2O_2 (1)	TCNE (1)	THF	19 [e]
^tBuOOH (1)	TCNE (1)	Et_2O	9 [f]

[a] Mol equiv to **1**.

[b] Other products: 2-tetradecanol and/or 2-tetradecanone, 0–3% yield.

[c] 1-Tetradecene/2-tetradecenes = 54/46 (by GLC).

[d] 1-Tetradecene/2-tetradecenes = 59/41 (by GLC).

[e] Other product: 2-tetradecanol, 7%.

[f] Other product: 2-tetradecanol, 4%.

carried out in the presence of triethylamine, the yield of tetradecenes was much increased as has been observed in the cases of oxidation of alkyl phenyl tellurides [2b]. Further, as the formation of CT-complex between ferrocene derivatives and TCNE or TCNQ (7,7,8,8-tetracyano-*p*-quinodimethane) is well known [11,12] it is expected that the complex formation may help a ferrocenyl moiety in **1** become a more electron-withdrawing group leading to a faster telluroxide elimination. The oxidation was therefore carried out in the presence of TCNE or TCNQ and TCNE was revealed to have a remarkable effect in increasing the yield of alkenes (up to 67% yield), TCNQ being slightly effective (up to 45% yield). Various combinations of oxidants, solvents, and additives were examined, and eventually the use of MCPBA, Et$_2$O and TCNE or Et$_3$N was revealed to be the best. Typical results are shown in Table 1.

Next, various primary and secondary alkyl ferrocenyl tellurides (**2**–**8**, **10**, **11**, **14**) were treated mainly under the above conditions. For comparison the oxidation was also carried out in the absence of TCNE or Et$_3$N. In almost all cases, TCNE as well as Et$_3$N showed a good effect in improving the yield of alkenes. Typical results are summarized in Table 2. In the cases of acyclic secondary and primary alkyl ferrocenyl tellurides (**1**–**4** and **5**–**8**, **10**, **11** and **14** respectively), the reactivity for elimination depended much on the chain length of the alkyl group; the longer the alkyl chain the higher the reactivity, as has been observed in alkyl

TABLE 2. Oxidation of various alkyl ferrocenyl tellurides with MCPBA [a]

Telluride	MCPBA [b] (mol equiv.)	Additive [b] (mol equiv.)	Products (GLC yield%) [c]
1	1	TCNE (1)	tetradecenes (67) [d,e]
1	2	Et$_3$N (1)	tetradecenes (63) [d,e]
1	1	–	tetradecenes (25) [54]
2	1	TCNE (1)	octenes (9), 2-octanol (4), 2-octanone (6)
2	2	Et$_3$N (1)	octenes (5), 2-octanol (2), 2-octanone (2)
2	1	–	octenes (trace) [9], 2-octanol (2), 2-octanone (8)
3	1	TCNE (1)	decenes (15)
3	2	Et$_3$N (1)	decenes (8)
3	1	–	decenes (trace) [16]
4	1	TCNE (1)	cyclododecenes (73) [f]
4	2	Et$_3$ (1)	cyclododecenes (80) [f]
4	1	–	cyclododecenes (63) [f] [67]
5	1	TCNE (1)	1-tetradecene (40)
5	2	Et$_3$N (1)	1-tetradecene (27)
5	1	–	1-tetradecene (0) [0]
6	1	TCNE (1)	1-hexadecene (39)
6	2	Et$_3$N (1)	1-hexadecene (33)
6	1	–	1-hexadecene (8)
7	1	TCNE (1)	1-octadecene (31)
7	2	Et$_3$N (1)	1-octadecene (23)
7	1	–	1-octadecene (9)
8	1	TCNE (1)	1-icosene (72)
8	2	Et$_3$N (1)	1-icosene (79)
8	1	–	1-icosene (31)
10	1	TCNE (1)	styrene (3)
10	2	Et$_3$N (1)	styrene (2)
10	1	–	styrene (4) [48]
11	1	TCNE (1)	allylbenzene (7)
11	2	Et$_3$N (1)	allylbenzene (3)
11	1	–	allylbenzene (6) [trace]
14	1	TCNE (1)	4-phenyl-1-hexene (7)
14	2	Et$_3$N (1)	4-phenyl-1-hexene (16)
14	1	–	4-phenyl-1-hexene (21)

[a] Solvent Et$_2$O, at 25°C for 2 h.

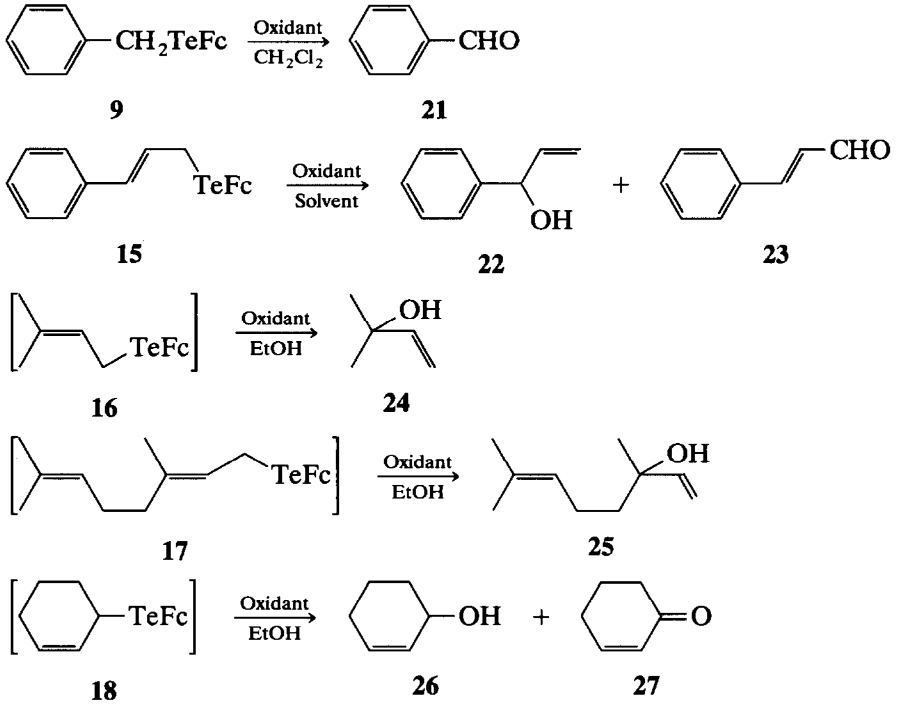
[b] Mol equiv. to telluride.

[c] The GLC yield (%) from the corresponding phenyl telluride is shown in brackets [2b].

[d] Other products: 2-tetradecanol and/or 2-tetradecanone, 1–3%.

[e] For the isomer ratio, see the footnote of Table 1.

[f] A mixture of *cis* and *trans* isomers. Other product: cyclododecanone, 2–5%.



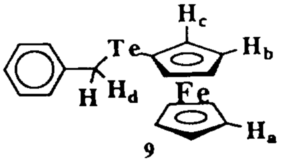
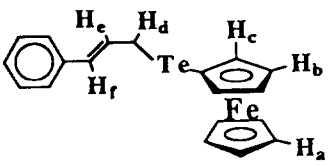
Scheme 4. Oxidation of various benzylic and allylic ferrocenyl tellurides.

TABLE 3. Oxidation of various benzylic and allylic ferrocenyl tellurides under various conditions [a]

Telluride	Oxidant [b]	Solvent	Reaction time (h)	Products (GLC yield, %)						
				21	**22**	**23**	**24**	**25**	**26**	**27**
9	air [c]	CH_2Cl_2	5	5						
9	air [c]	CH_2Cl_2	48	56						
9	MCPBA	CH_2Cl_2	24	0						
15	air [c]	MeOH	24		0	4				
15	MCPBA [c]	CH_2Cl_2	2		4	10				
15	${}^tBuOOH$ [c,d]	CH_2Cl_2	2		0	9				
15	$NaIO_4$ [c]	THF	2		0	15				
16	air [c]	EtOH	2				37			
16	MCPBA	EtOH	21 [e]				28			
16	$NaIO_4$	EtOH	2				15			
16	${}^tBuOOH$ [c,d]	EtOH	2				12			
17	air [c]	EtOH	2					31		
17	air [c]	EtOH	24					54		
17	MCPBA	EtOH	24					15		
18	MCPBA	EtOH	2						60	6
18	MCPBA	EtOH	9 [e]						100	0
18	$NaIO_4$	EtOH	2						35	5
18	${}^tBuOOH$ [d]	EtOH	2						45	10
18	H_2O_2 [f]	EtOH	2						54	6
18	air [c]	EtOH	2						22	19
18	air [c]	EtOH	72						45	46

[a] The reaction was carried out under N_2 at room temperature unless otherwise mentioned.
[b] An equimolar amount to the telluride.
[c] Under atmospheric condition.
[d] 70% Aqueous solution.
[e] At reflux temperature.
[f] 30% Aqueous solution.

TABLE 4. Chemical shift (δ ppm) of oxidized species of **9** and **15**

	Proton	**9**	After oxidation [a]	Difference
 **9**	H_a	4.117	4.275	0.158
	H_b	4.197	4.480	0.280
	H_c	4.223	4.495	0.272
	H_d	3.961	4.488	0.527
	Proton	**15**	After oxidation [b]	Difference
 **15**	H_a	4.145	4.320	0.175
	H_b	4.205	4.568	0.363
	H_c	4.322	4.732	0.410
	H_d	3.514	4.119	0.605
	H_e	6.340	6.200	−0.140
	H_f	6.000	6.390	0.390

[a] Oxidized with MCPBA under N_2 and after 48 h.
[b] Oxidized with MCPBA under N_2 and after 24 h.

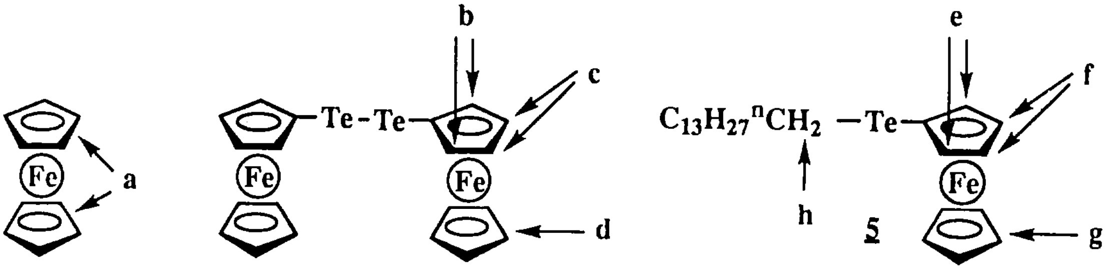
phenyl tellurides [2b]. For cyclododecyl ferrocenyl telluride, **4** elimination was rather facile even in the absence of additives as in the case of the corresponding phenyl telluride [2b]. Generally, leaving ability of a ferrocenyltellurium moiety in oxidation was lower than that of a phenyltellurium moiety, as shown in brackets in Table 2. Thus, the leaving ability of aryltellurium moiety may be ranked thus: 2-PyTe > PhTe > FcTe.

2.3. *Oxidation of benzylic and allylic ferrocenyl tellurides*

As described above, benzylic and allylic phenyl tellurides are quite labile to air and could not be isolated under ambient conditions. In contrast, benzyl and cinnamyl ferrocenyl tellurides (**9** and **15**) were air stable and isolated as an orange solid, respectively. Their stability might parallel the low reactivity of alkyl ferrocenyl tellurides to telluroxide elimination. Some other allylic ferrocenyl tellurides (**16–18**) were stable under nitrogen and their almost quantitative formation was confirmed *in situ* by ^{1}H-NMR. All these tellurides were revealed to be fairly stable even to various oxidants, but oxidation under forced conditions afforded the corresponding allylic alcohols, enals and enones in fair to good yields (Scheme 4). Typical results are summarized in Table 3, the compound **18** and the compounds **9** and **15** being the most reactive and the

TABLE 5. Comparison of ^{1}H NMR spectra (δ ppm) of some ferrocenyl compounds with their charge transfer complexes

	a	b	c	d	e	f	g	h
Ferrocene	2.62							
Ferrocene-TCNE	3.06							
Ferrocene-TCNQ	2.90							
Diferrocenyl ditelluride		4.36	4.27	4.14				
Diferrocenyl ditelluride-TCNE		4.67	4.50	4.43				
Diferrocenyl ditelluride-TCNQ		4.34	4.27	4.14				
5					4.39	4.24	4.17	2.64
5-TCNE					4.66	4.50	4.43	3.10
5-TCNQ					4.39	4.24	4.17	2.64



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least reactive, respectively. The formation of such oxidation products has already been observed in the oxidation of some corresponding phenyl tellurides, presumably via [2,3] sigmatropic rearrangement and [1,2] alkyl shift from tellurium to oxygen in the intermediate telluroxides [7,8].

One reason for the stability of these tellurides to oxidants seems to be the stability of the oxidized species which is sufficient to resist further reaction. We observed by ^{1}H-NMR and TLC monitoring that, in the MCPBA oxidation of **9** and **15**, the tellurides were completely oxidized. Thus, all benzylic and allylic protons and ferrocene ring protons suffered downfield shift (0.158–0.605 ppm) after oxidation, benzylic and allylic protons being most affected (Table 4). A similar phenomenon has already been observed in the oxidized species of cyclohexyl phenyl telluride with MCPBA, $PhTe(OH)(OCOC_6H_4\text{-}m\text{-}Cl)C_6H_{11}$: the methine proton of cyclohexyl group suffered δ 0.30 ppm downfield shift compared with that of the starting telluride [2].

2.4. Formation of donor-acceptor complexes between TCNE and alkyl ferrocenyl tellurides

The addition of TCNE promoted in some cases elimination of telluroxide from alkyl ferrocenyl tellurides. One possible explanation for this is formation of donor-acceptor complexes between TCNE or TCNQ and alkyl ferrocenyl tellurides, as it is well known that TCNE produces a charge-transfer (CT) complex with ferrocene [11,12]. In order to check such complex formation, analyses with ^{1}H-NMR (in $CDCl_3$) and electronic absorption (in hexane and $CHCl_3$) spectra were carried out. Typical ^{1}H-NMR results are shown in Table 5. In each spectrum of the mixtures of ferrocene-TCNE and ferrocene-TCNQ, only one single peak was observed at δ 3.06 and 2.90 ppm, respectively, 0.44 and 0.28 ppm downfield from ferrocene itself. This shows that ferrocene completely interacts with such electron acceptors at room temperature. A mixture of diferrocenyl ditelluride and TCNE also showed new peaks of ring protons at δ 4.43–4.67 ppm, 0.23–0.31 ppm downfield from those of the ditelluride. Here, the intensity of new peaks is about half that of the starting ditelluride, suggesting that the degree of the interaction of TCNE with the ditelluride is one third; namely, donor-acceptor complex between the two exists in equilibrium with the uncomplexed ditelluride (*ca.* 1 : 2). Similarly, in the case of ferrocenyl 1-tetradecyl telluride (**5**) new peaks of ferrocene ring protons and a peak of methylene protons adjacent to Te appeared at δ 4.43–4.66 and 3.10 ppm, respectively, 0.26–0.27 ppm and 0.46 ppm downfield from **5** itself, the intensity of which shows that the degree of complex formation is *ca.* 11%. Similar downfield shifts were also observed with several other alkyl ferrocenyl tellurides. Although the reason is not known, no change was observed in the mixtures of TCNQ-diferrocenyl ditelluride and TCNQ-**5**.

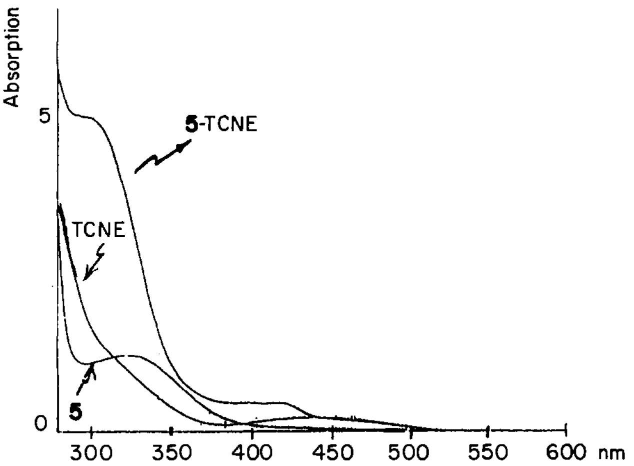

Fig. 1. Electronic absorption spectra of **5**, TCNE and **5**-TCNE mixture in n-hexane.

The downfield shift of methylene protons by complexation is in parallel with that (0.35 ppm) observed in methylene protons of phenyl 2-tetradecyl telluride (at δ 3.50 ppm) and 2′-pyridyl 2-tetradecyl telluride (at δ 3.85 ppm). This means that the electron-withdrawing property of a ferrocenyl group is increased by complexation with TCNE, leading to the improvement of alkene yields in telluroxide elimination by increasing the rate of the oxidation step at the telluride.

When TCNE was added to a yellow ether solution of the telluride **5**, the solution turned green, suggesting also some interaction between the two. In fact, analy-

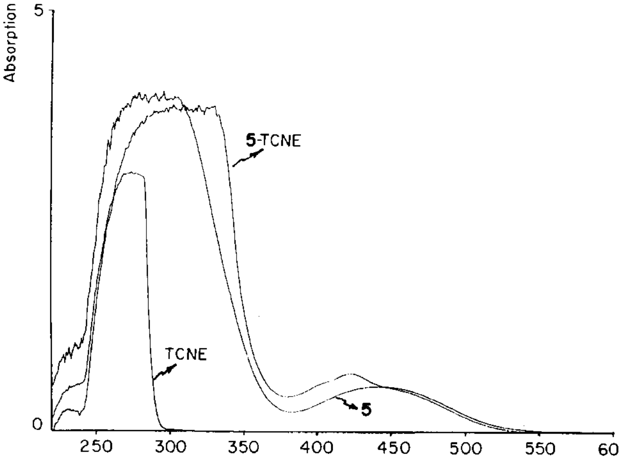

Fig. 2. Electronic absorption spectra of **5**, TCNE and **5**-TCNE mixture in $CHCl_3$.

ses with electronic absorption spectra showed the presence of weak new absorption bands ($\epsilon < 100$) at 310 and *ca.* 420 cm^{-1} in hexane (Fig. 1) and at 423 cm^{-1} in $CHCl_3$ (Fig. 2), probably due to a small degree of complex formation. Although donor-acceptor complex formation between organotellurium compounds and TCNQ is known [13] besides that between ferrocene and TCNE, it is not yet clear whether electron donation is from the ferrocene ring, from tellurium or from both in the case of **5**.

3. Experimental details

^1H (270 MHz) and ^{13}C (67.5 MHz)NMR spectra were recorded on JEOL GSX-270 spectrometers as solutions in $CDCl_3$. Chemical shifts are reported in δ units downfield from the internal reference Me_4Si. Melting points were determined on a Yanaco MP-S3 micro apparatus and are uncorrected. Electronic absorption spectra of **5**, TCNE and their mixture were recorded on a Hitachi U-3200 apparatus in hexane and $CHCl_3$ (0.008 mol/l). GLC analyses were performed on a Hitachi 163 instrument (1 m × 3 mm stainless steel column packed with 20% PEG on Shimalite) and a Shimadzu GC-14A instrument (25 m HiCap-CBP-10-S25 capillary column) with flame-ionization detectors and N_2 as carrier gas. All column chromatographies on SiO_2 were performed with Wakogel C-300 (hexane and hexane/ethyl acetate as eluent). Elemental analyses were performed at the Microanalytical Center of Kyoto University.

All oxidation products such as alkenes, alcohols and ketones are commercially available compounds which were used as authentic samples for GLC analysis.

3.1. Preparations

Preparation of diferrocenyl ditelluride $(FcTe)_2$: Commercial t-butyllithium (33 ml of 1.5 N pentane solution; 50 mmol) was slowly added to a THF solution (50 ml, distilled over $LiAlH_4$) of ferrocene (11.2 g, 60.3 mmol) at 0°C with stirring under N_2. After 30 min, a grey tellurium powder (7.54 g, 59 mmol) was added portion by portion to the solution and the resulted suspension left for 1.5 h at room temperature. The solution was then opened to the atmosphere and stirred for one day. Addition of brine, extraction with dichloromethane, drying over $MgSO_4$ and evaporation of the solvent from the extract afforded a red solid which was submitted to chromatographic purification (n-hexane and 10% AcOEt/hexane). Diferrocenyl ditelluride was obtained as a red solid: 16.1 g (25.8 mmol), m.p. 114–115°C (lit. [6] decomp. 136°C). ^1H NMR δ 4.13 (10H, s), 4.26 (4H, t, $J = 1.70$ Hz), 4.36 (4H, t, $J = 1.80$ Hz). Anal. Found: C, 38.69: H, 2.96. $C_{20}H_{18}Fe_2Te_2$ calc. C, 38.42; H, 2.90%.

Preparation of new alkyl ferrocenyl tellurides. Ferrocenyl 2-tetradecyl telluride (**1**). In a two-necked 50 ml round bottom flask containing a magnetic stirring bar were placed $(FcTe)_2$ (1.17 g, 1.87 mmol) and $NaBH_4$ (0.47 g, 12.4 mmol) under nitrogen. Ethanol (20 ml) was added to the flask by syringe at 0°C, and the resulting mixture was stirred at room temperature for 30 min during which the solution became homogeneous and turned from orange to pale yellow. An ethanol (10 ml) solution of 2-bromotetradecane (1.16 g, 3.98 mmol) was then added and the resulted solution stirred at reflux for 4 h. After it had cooled down, the mixture was treated with brine and then extracted with CH_2Cl_2 (3 × 50 ml), and the extract was dried over $MgSO_4$. Removal of the solvent under reduced pressure left a red oily residue, which was subjected to column chromatography on SiO_2 (hexane) providing ferrocenyl 2-tetradecyl telluride as a red oil. (1.21 g, 3.01 mmol, 81% yield). ^1H NMR δ 0.89 (3H, t, $J =$ 6.21 Hz), 1.20–1.65 (25H, m), 3.12 (1H, sex., $J =$ 6.75 Hz), 4.16 (5H, s), 4.22 (2H, t, $J = 1.62$ Hz), 4.34 (2H, t, $J = 1.62$ Hz). ^{13}C NMR δ 15.20 (q), 23.74 (d), 24.09 (q), 25.71 (d), 30.27 (t), 30.40 (t), 30.55 (t), 30.60 (t), 30.69 (t), 31.24 (t), 32.82 (t), 32.97 (t), 37.83 (t), 40.71 (t), 44.32 (s), 70.21 (d), 72.28 (d), 81.08 (d). Anal. Found: C, 56.71; H, 7.55. $C_{24}H_{38}FeTe$ calc. C, 56.51; H, 7.51%. The preparation of other tellurides was similar

Ferrocenyl 2-octyl telluride (**2**): a red oil, isolated yield 77%. ^1H NMR δ 0.87 (3H, t, $J = 6.48$ Hz), 1.15–1.60 (13H, m), 3.11 (1H, sex., $J = 7.02$ Hz), 4.15 (5H, s), 4.22 (2H, t, $J = 1.89$ Hz), 4.33 (2H, t, $J = 1.89$ Hz). ^{13}C NMR δ 13.94 (q), 22.63 (t), 23.12 (d), 24.64 (q), 28.92 (t), 29.47 (t), 31.79 (t), 39.70 (t), 43.35 (s), 69.20 (d), 71.27 (d), 80.07 (d). Anal. Found: C, 50.51; H, 6.03. $C_{18}H_{26}FeTe$ calc. C, 50.77; H, 6.15%.

2-Decyl ferrocenyl telluride (**3**): an orange oil, isolated yield 76%. ^1H NMR δ 0.88 (3H, t, $J = 6.48$ Hz), 1.25–1.63 (17H, m), 3.11 (1H, sex., $J = 6.75$ Hz), 4.15 (5H, s), 4.21 (2H, t, $J = 1.62$ Hz), 4.35 (2H, t, $J =$ 1.62 Hz). ^{13}C NMR δ 14.11 (q), 22.66 (t), 23.14 (d), 24.63 (q), 29.23 (t), 29.26 (t), 29.37 (t), 29.50 (t), 31.87 (t), 39.66 (t), 43.29 (s), 69.18 (d), 71.25 (d), 80.05 (d). Anal. Found: C, 53.02; H, 6.58. $C_{20}H_{30}FeTe$ calc. C, 52.92; H, 6.66%.

Cyclododecyl ferrocenyl telluride (**4**): a yellow solid; mp. 39–40°C, isolated yield 73%. ^1H NMR δ 1.20–1.76 (22H, m), 3.16 (1H, t, $J = 6.00$ Hz), 4.15 (5H, s), 4.22 (2H, t, $J = 1.62$ Hz), 4.33 (2H, t, $J = 1.62$ Hz). ^{13}C NMR δ 23.86 (t), 23.97 (t), 24.08 (t), 24.41 (t), 26.62 (d), 33.23 (t), 47.50 (s), 69.49 (d), 71.49 (d), 80.15 (d). Anal. Found: C, 55.07; H, 6.79. $C_{22}H_{32}FeTe$ calc. C, 55.06; H, 6.72%.

Ferrocenyl 1-tetradecyl telluride (**5**): an orange solid;

mp 27–28°C, isolated yield 98%. ^{1}H NMR δ 0.88 (3H, t, *J* = 6.75 Hz), 1.20–1.75 (24H, m), 2.61 (1H, t, *J* = 7.83 Hz), 4.15 (5H, s), 4.21 (2H, t, *J* = 1.89 Hz), 4.35 (2H, t, *J* = 1.89 Hz). ^{13}C NMR δ 9.08 (t), 14.1 (t), 22.7 (t), 28.9 (t), 29.4 (t), 29.5 (t), 29.6 (t), 29.7 (t), 31.8 (t), 31.9 (t), 43.4 (s), 69.2 (t), 71.0 (t), 76.2 (t), 76.6 (d), 77.0 (d), 77.2 (t), 79.2 (d). Anal. Found: C, 56.35; H, 7.59. $C_{24}H_{38}FeTe$ calc. C, 56.51; H, 7.51%.

Ferrocenyl 1-hexadecyl telluride (**6**): a yellow solid; mp 37–38°C, isolated yield 74%. ^{1}H NMR δ 0.88 (3H, t, *J* = 6.75), 1.20–1.30 (26H, m), 1.60 (2H, m), 2.61 (1H, t, *J* = 7.29 Hz), 4.15 (5H, s), 4.20 (2H, t, *J* = 1.62 Hz), 4.35 (2H, t, *J* = 1.62 Hz). ^{13}C NMR δ 9.10 (t), 14.14 (t), 28.93 (t), 29.37 (t), 29.41 (t), 29.45 (t), 29.47 (t), 29.54 (t), 29.56 (t), 29.57 (t), 29.60 (t), 29.61 (t), 29.65 (t), 29.70 (t), 31.79 (t), 31.94 (t), 43.40 (s), 69.24 (d), 71.00 (d), 79.27 (d). Anal. Found: C, 58.06; H, 7.95. $C_{26}H_{42}FeTe$ calc. C, 58.04; H, 7.87%.

Ferrocenyl 1-octadecyl telluride (**7**): an orange solid; mp 44–45°C, isolated yield 64%. ^{1}H NMR δ 0.88 (3H, t, *J* = 6.75), 1.20–1.30 (30H, m), 1.69 (2H, m), 2.61 (1H, t *J* = 7.29 Hz), 4.15 (5H, s), 4.20 (2H, t, *J* = 1.62 Hz), 4.35 (2H, t, *J* = 1.62 Hz). ^{13}C NMR δ 9.08 (t), 14.11 (q), 22.67 (t), 28.91 (t), 29.34 (t), 29.35 (t), 29.40 (t), 29.45 (t), 29.47 (t), 29.49 (t), 29.52 (t), 29.55 (t), 29.57 (t), 29.58 (t), 29.60 (t), 29.68 (t), 31.77 (t), 31.91 (t), 43.39 (s), 69.21 (d), 70.97 (d), 79.24 (d). Anal. Found: C, 59.43; H, 8.34. $C_{28}H_{46}FeTe$ calc. C, 59.41; H, 8.19%.

Ferrocenyl 1-icosyl telluride (**8**): a yellow solid; mp 39–40°C, isolated yield 93%. ^{1}H NMR δ 0.88 (3H, t, *J* = 6.75), 1.20–1.30 (34H, m), 1.69 (2H, m), 2.61 (1H, t, *J* = 7.29 Hz), 4.15 (5H, s), 4.21 (2H, t, *J* = 1.62 Hz), 4.35 (2H, t, *J* = 1.62 Hz). ^{13}C NMR δ 9.10 (t), 14.11 (q), 22.67 (t), 28.92 (t), 29.35 (t), 29.51 (t), 29.69 (t), 31.78 (t) 31.91 (t), 43.41 (s), 69.23 (d), 70.97 (d). Anal. Found: C, 60.42; H, 8.63. $C_{30}H_{50}FeTe$ calc. C, 60.64; H, 8.48%.

Benzyl ferrocenyl telluride (**9**): an orange solid; mp 41–42°C, isolated yield 93%. ^{1}H NMR δ 3.96 (2H, s), 4.12 (5H, s), 4.20 (2H, t, *J* = 1.70 Hz), 4.22 (2H, t, *J* = 1.65 Hz), 7.0–7.2 (5H, m). ^{13}C NMR δ 12.26 (t), 44.93 (s, C-ferrocene), 69.10 (d), 71.35 (d), 79.60 (d), 125.77 (d), 128.18 (d), 128.23 (d), 141.45 (s, C-phenyl). Anal. Found: C, 50.57; H, 3.99. $C_{17}H_{16}FeTe$ calc. C, 50.44; H, 3.95%.

Ferrocenyl 2-phenylethyl telluride (**10**): an orange solid; mp 48–51°C, isolated yield 73%. ^{1}H NMR δ 2.85 (2H, t, *J* = 8.43 Hz), 3.02 (2H, t, *J* = 8.43 Hz), 4.15 (5H, s), 4.22 (2H, t, *J* = 1.84 Hz), 4.34 (2H, t, *J* = 1.84 Hz), 7.1–7.3 (5H, m). ^{13}C NMR δ 9.21 (t), 38.34 (t), 43.33 (s, C-ferrocene), 69.24 (d), 71.16 (d), 79.36 (d), 126.17 (d), 128.11 (d), 128.42 (d), 142.87 (s, C-phenyl). Anal. Found: C, 51.38; H, 4.10. $C_{18}H_{18}FeTe$ calc. C, 51.75; H, 4.34%.

Ferrocenyl 3-phenylpropyl telluride (**11**): a red solid; mp 42–43°C, isolated yield 92%. ^{1}H NMR δ 2.01 (2H, m), 2.58–2.67 (4H, m), 4.15 (5H, s), 4.21 (2H, t, *J* = 1.89 Hz), 4.35 (2H, t, *J* = 1.89 Hz), 7.1–7.3 (5H, m). ^{13}C NMR δ 8.16 (t), 33.43 (t), 37.72 (t), 43.24 (s, C-ferrocene), 69.24 (d), 71.11 (d), 79.36 (d), 125.80 (d), 128.30 (d), 128.53 (d), 141.46 (s, C-phenyl). Anal. Found: C, 52.53; H, 4.77. $C_{19}H_{20}FeTe$ calc. C, 52.85; H, 4.67%.

Ferrocenyl 4-phenylbutyl telluride (**12**): a red solid; mp 37–39°C, isolated 100%. ^{1}H NMR δ 1.71 (4H, m), 2.60 (4H, m), 4.15 (5H, s), 4.20 (2H, t, *J* = 1.62 Hz), 4.33 (2H, t, *J* = 1.62 Hz), 7.1–7.3 (5H, m). ^{13}C NMR δ 8.57 (t), 31.45 (t), 33.45 (t), 35.18 (t), 43.26 (s, C-ferrocene), 69.23 (d), 71.06 (d), 79.31 (d), 125.65 (d), 128.23 (d), 128.38 (d), 142.31 (s, C-phenyl). Anal. Found: C, 53.79; H, 5.10. $C_{20}H_{22}FeTe$ calc. C, 53.88; H, 4.97%.

Ferrocenyl 5-phenylpentyl telluride (**13**): a red oil, isolated yield 95%. ^{1}H NMR δ 1.3–1.8 (6H, m), 2.5–2.6 (4H, m), 4.15 (5H, s), 4.21 (2H, t, *J* = 1.62 Hz), 4.34 (2H, t, *J* = 1.62 Hz), 7.1–7.3 (5H, m). ^{13}C NMR δ 8.72 (t), 30.70 (t), 31.32 (t), 31.75 (t), 35.74 (t), 43.28 (s, C-ferrocene), 69.17 (d), 70.99 (d), 79.24 (d), 125.55 (d), 128.18 (d), 128.30 (d), 142.51 (s, C-phenyl). Anal. Found: C, 55.12; H, 5.19. $C_{21}H_{24}FeTe$ calc. C, 54.85; H, 5.26%.

Ferrocenyl 6-phenylhexyl telluride (**14**): a red solid; mp 32–33°C, isolated yield 87%. ^{1}H NMR δ 1.3–1.7 (8H, m), 2.5–2.7 (4H, m), 4.15 (5H, s), 4.20 (2H, t, *J* = 1.62 Hz), 4.34 (2H, t, *J* = 1.62 Hz), 7.1–7.3 (5H, m). ^{13}C NMR δ 8.96 (t), 28.52 (t), 31.29 (t), 31.54 (t), 31.80 (t), 35.85 (t), 43.35 (s, C-ferrocene), 69.21 (d), 71.00 (d), 79.26 (d), 125.55 (d), 128.19 (d), 128.36 (d), 142.72 (s, C-phenyl). Anal. Found: C, 55.82; H, 5.74. $C_{22}H_{26}FeTe$ calc. C, 55.76; H, 5.53%.

Cinnamyl ferrocenyl telluride (**15**): an orange solid; mp 80–85°C, isolated yield 93% (it contains *ca.* 16% (by ^{1}H-NMR) of the starting ditelluride. Several attempts to isolate pure **15** were unsuccessful). ^{1}H NMR δ 3.51 (2H, d, *J* = 8.24 Hz), 4.15 (5H, s), 4.21 (2H, t, *J* = 1.84 Hz), 4.32 (2H, t, *J* = 1.83 Hz), 6.34 (1H, dt, *J* = 15.78, 8.20 Hz), 7.1–7.3 (5H, m). ^{13}C NMR δ 11.55 (t), 44.65 (s, C-ferrocene), 69.14 (d), 71.36 (d), 79.69 (d), 126.06 (d), 126.96 (d), 137.24 (s, C-phenyl). Anal. Found: C, 50.87; H, 4.10. $C_{19}H_{18}FeTe$ calc. C, 53.10; H, 4.22%.

Although we failed to isolate the following three compounds, we confirmed their structure by ^{1}H-NMR after removal of the solvent from the reaction mixture.

Ferrocenyl 3-methyl-2-butenyl telluride (**16**): ^{1}H NMR δ 3.37 (2H, d, *J* = 8.79 Hz), 4.15 (5H, s), 4.20 (2H, t, *J* = 1.79 Hz), 4.32 (2H, t, *J* = 1.79 Hz).

Ferrocenyl geranyl telluride (**17**): ^{1}H NMR δ 3.37 (2H, d, *J* = 8.51 Hz), 4.14 (5H, s), 4.19 (2H, t, *J* = 1.79 Hz), 4.32 (2H, t, *J* = 1.79 Hz).

2-Cyclohexenyl ferrocenyl telluride (**18**): ^{1}H NMR δ 1.55–2.15 (6H, m), 3.91 (1H, m), 4.15 (5H, s), 4.20 (2H, t, $J = 1.79$ Hz), 4.32 (2H, t, $J = 1.79$ Hz).

Ferrocenyl (E)-styryl telluride (**19**): To a solution of diferrocenyl ditelluride (0.62 g, 1.00 mmol) in ethanol (10 ml) was added a solution of $NaBH_4$ (0.10 g, 2.50 mmol) in ethanol (20 ml) at room temperature under N_2. After a while the solution turned from orange to pale yellow. A solution of phenylacetylene (0.24 g, 2.20 mmol) in ethanol (10 ml) was then added to the pale yellow solution and the mixture was stirred under reflux for 20 h. After it had cooled, the mixture was treated with brine and extracted with CH_2Cl_2 (50 ml × 3). The extract was dried over $MgSO_4$ and evaporation of the solvent from the extract left a red solid which was subjected to column chromatography on SiO_2 (hexane as eluent) to give an orange solid (1.90 mmol, 95%) of **19** in a pure form; mp 97–98°C. ^{1}H NMR δ 4.18 (5H, s), 4.27 (2H, t, $J = 1.35$ Hz), 4.42 (2H, t, $J = 1.35$ Hz), 6.98 (1H, 10.53 Hz), 7.2–7.4 (5H, m). ^{13}C NMR δ 47.83 (s, C-ferrocene), 69.74 (d), 71.76 (d), 78.98 (d), 111.80 (d), 127.79 (d), 127.97 (d), 128.95 (d), 135.90 (d), 139.62 (s, C-phenyl). Anal. Found: C, 52.04; H, 3.86. $C_{18}H_{16}FeTe$ calc. C, 52.00; H, 3.88%.

Ferrocenyl phenylethynyl telluride (**20**): To a solution of diferrocenyl ditelluride (1.52 g, 2.43 mmol) in benzene (10 ml) was added bromine (0.41 g, 2.53 mmol) at 0°C under N_2. Separately, phenylacetylene (0.53 g, 5.20 mmol) was dissolved in 10 ml THF (distilled on $LiAlH_4$ under N_2) at 0°C and n-butyllithium (2.8 ml of 1.8 N n-hexane solution; 5.40 mmol) was then slowly added at 0°C and the resulting solution was stirred for 30 min. This solution was slowly added to the above benzene solution of ferrocenetellurenyl bromide at 0°C with a syringe, and then it was warmed up to room temperature and stirred for 1.5 h. The mixture was treated with brine (200 ml) then extracted with CH_2Cl_2 (3 × 50 ml), and the extract dried over $MgSO_4$. Removal of the solvent under reduced pressure left a yellow residue which was subjected to column chromatography on SiO_2(CH_2Cl_2 as eluent) providing **20** as a yellow solid (4.33 mmol, 89%); mp 164–165°C. ^{1}H NMR δ 4.21 (5H, s), 4.30 (2H, t, $J = 1.89$ Hz), 4.52 (2H, t, $J = 1.89$ Hz), 7.2–7.4 (5H, m). ^{13}C NMR δ 45.55 (s, C-ferrocene), 69.32 (d), 71.54 (d), 78.43 (d), 78.93 (s), 100.29 (s), 109.66 (s). Anal. Found: C, 52.44; H, 3.31. $C_{18}H_{14}FeTe$ calc. C, 52.25; H, 3.41%.

3.2. General procedure for telluroxide elimination by oxidation of alkyl ferrocenyl telluride in the presence of an additive

To a two-necked round bottom flask (25 ml) containing the telluride (1 mmol), triethylamine (1–2 mmol) or TCNE(TCNQ) (1–2 mmol), and diethyl ether (5 ml) was added solid metachloroperbenzenzoic acid (MCPBA, purity 80%, 1–2 mmol as pure MCPBA) by portions at 25°C and the mixture was stirred with a magnetic stirrer for 2 h. It was poured into saturated aqueous Na_2CO_3 solution (100 ml) containing hydrazine (10 ml) and the mixture was stirred for 30 min to remove the resulting meta-chlorobenzoic acid (MCBA) and also to reduce the remaining MCPBA and the telluroxide or its analogue to MCBA and the telluride, respectively. The solution was extracted with diethyl ether (3 × 50 ml) and the extract was dried over $MgSO_4$ and analyzed by GLC using a suitable internal standard.

3.3. ^{1}H-NMR analysis of a charge-transfer complex between diferrocenyl ditelluride or alkyl ferrocenyl telluride and TCNE

The $CDCl_3$ solution (1 ml) of diferrocenyl ditelluride or alkyl ferrocenyl telluride (0.05 mmol) and TCNE (0.05 mmol) was analysed at 25°C in a ^{1}H-NMR tube. The degree of TCNE-complex formation was determined by the integral ratio of protons. Analysis of the complex formation between the tellurides and TCNQ was carried out similarly.

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