Studies on tellurium-containing heterocycles. Part 18.[1] Preparation and structure of 2-benzotelluropyrylium salts and 2-benzoselenopyrylium salts

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Haruki Sashida,*[a] Kazuo Ohyanagi,[a] Mao Minoura[b] and Kin-ya Akiba[c]

[a] Faculty of Pharmaceutical Sciences, Hokuriku University, Kanagawa-machi, Kanazawa 920-1181, Japan. E-mail: h-sashida@hokuriku-u.ac.jp
[b] Department of Chemistry, School of Science, Kitasato University, 1-15-1 Kitasato, Sagamihara, Kanagawa 228-8555, Japan
[c] Advanced Research Center for Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan

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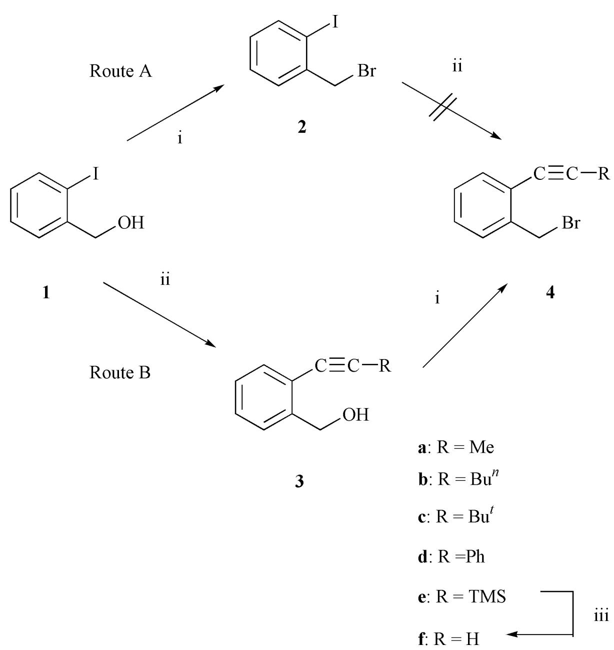
The regioselective and stereospecific intramolecular ring closure reactions of *o*-ethynylbenzyl tellurols **5A** and *o*-ethynylbenzyl selenols **5B**, which were readily generated by the reaction of the *o*-ethynylbenzyl bromides **4** with sodium hydrogen telluride (NaHTe) or sodium hydrogen selenide (NaHSe), produced the isotellurochromenes **6A** and isoselenochromenes **6B** together with (*Z*)-1-methylidene-2-telluraindans **7A** and (*Z*)-1-methylidene-2-selenaindans **7B**, respectively. The obtained isochromenes **6A** and **6B** were transformed into the corresponding 2-benzotelluropyrylium tetrafluoroborates **9A** and 2-benzoselenopyrylium tetrafluoroborates **9B** by treatment with triphenylcarbenium tetrafluoroborate ($Ph_3C^+BF_4^-$) in excellent yields, respectively. An X-ray structural analysis of the *tert*-butyl derivatives **9Ac** and **9Bc** is also described.

Introduction

The chemistry (syntheses, structure, physical properties, and reactions) of six-membered sulfur-containing heterocycles, thiopyrans,[2] thiopyrylium salts[3] and their benzo derivatives has been widely investigated and well established. Recently, extensive synthetic work on their tellurium[2–4] and selenium[2,3] analogs has been undertaken. The monocyclic pyrylium salts and 1-benzo derivatives containing a selenium[2] or tellurium atom[2,4] are known. However, no 2-benzotelluropyrylium salts,[5a] a theoretically possible structural isomer of the latter, have been prepared until now. With regard to the 2-benzoselenopyrylium salts, the synthesis of only the unsubstituted derivative was reported by Renson and Pirson more than 35 years ago.[6] Recently, we focused on the synthesis of various tellurium- or selenium-containing heterocycles[7] based on the successive intramolecular addition of the tellurols or selenols to an ethynyl group. We have previously succeeded in the general and facile two-step synthesis of the 1-benzotelluropyrylium salts[8] and 1-benzoselenopyrylium salts[9] from the corresponding telluro- or seleno-chromen-4-ones[7e] and also examined their reactions[10] with nucleophiles. As part of our continuing studies, we describe herein an extension of our synthetic strategy for the novel synthesis of the isotellurochromenes **6A** and isoselenochromenes **6B**, and their transformation into the corresponding title pyrylium salts **9**.



Scheme 1 *Reagents and conditions*: i, PBr_3, pyridine, $CHCl_3$, 0 °C to room temp., 6–10 h; ii, alkyne, $PdCl_2(Ph_3P)_2$, CuI, benzene–piperidine, room temp., 5–10 h; iii, K_2CO_3, MeOH, room temp., 1 h.

Results and discussion

Preparation of 2-benzotelluropyrylium and 2-benzoselenopyrylium salts

There are two possible routes for the preparation of the key starting *o*-ethynylbenzyl bromides **4** from *o*-iodobenzyl alcohol **1** as shown in Scheme 1. Route A through the *o*-iodobenzyl bromide **2** is more effective than route B due to the use of **2** as a mutual starting material for ethynylation. However, this path was eliminated because the ethynylation of **2** did not occur and only the homo-coupling products of the alkynes were obtained. *o*-Ethynylbenzyl alcohols **3** were easily prepared by Sonogashira's procedure.[11] The palladium-catalyzed coupling reaction of *o*-iodobenzyl alcohol **1** with 1-substituted alkynes in a mixed solvent of benzene and piperidine gave the desired ethynyl derivatives **3**, which were readily brominated with phosphorus tribromide to give the corresponding benzyl bromides **4** in good yields. The trimethylsilyl (TMS) group on

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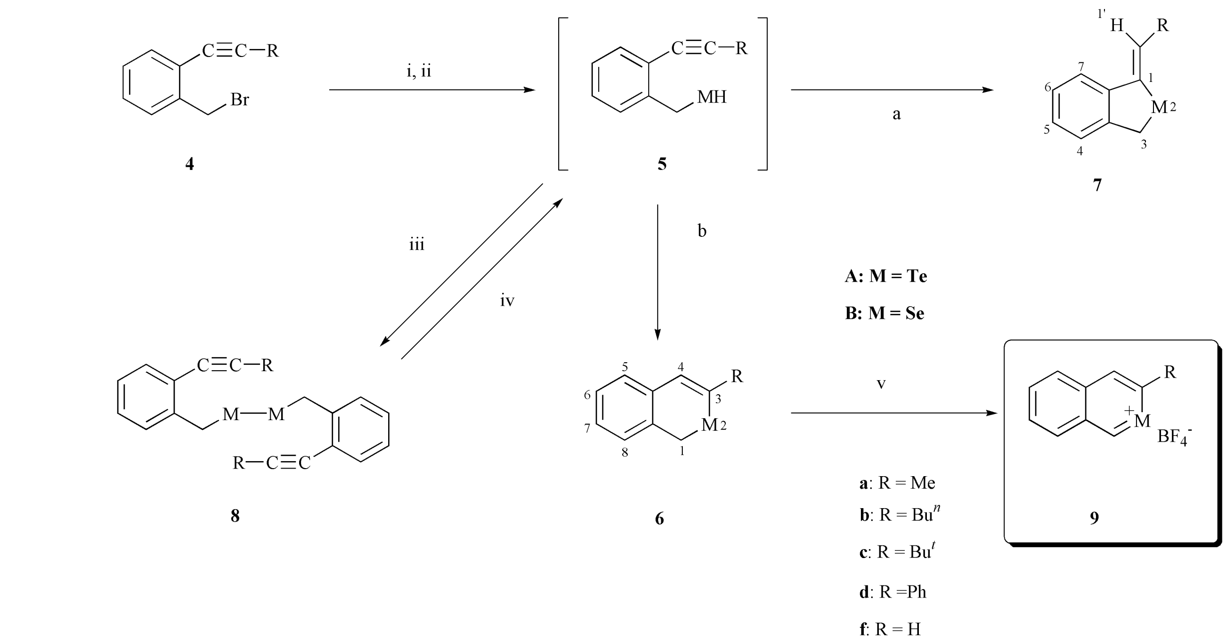


Scheme 2 *Reagents and conditions*: i, NaHTe or NaHSe (1.2 equiv.), DMF, 0 °C room temp., 1 h; ii, EtOH, 90 °C, 1–3 h; iii, $K_3Fe(CN)_6$, H_2O, room temp., 10 min; iv, $NaBH_4$, EtOH, room temp., 1 h; v, $Ph_3C^+BF_4^-$ (1.05 equiv.), $MeNO_2$, room temp., 30 min.

the triple bond of the benzyl bromide **4e** was easily removed to give the *o*-ethynylbenzyl bromide **4f** by treatment with potassium carbonate in methanol at room temperature.

The syntheses of the 2-benzotelluropyrylium salts **9A** and 2-benzoselenopyrylium salts **9B** are shown in Scheme 2. In order to obtain the isochromenes **6A** and **6B**, precursors for the preparation of the title compounds, we examined the conversion of the *o*-ethynylbenzyl bromides **4** into the *o*-ethynylbenzyl tellurols **5A** or *o*-ethynylbenzyl selenols **5B**. The treatment of the benzyl bromides **4** with sodium hydrogen telluride (NaHTe),[12] which was freshly prepared from tellurium dust and sodium borohydride in DMF, followed by the addition of ethanol, and then heating at 90 °C, resulted in the direct ring closure to afford the desired isotellurochromenes **6A**, together with the five-membered compounds, the (*Z*)-1-methylidene-2-telluraindans **7A**, *via* the specific tellurol intermediates **5A**. The isotellurochromenes **6A** were produced by the 6-*endo-dig* ring closure of **5A** at the sp carbon atom of the ethynyl group. The 2-telluraindans **7A** are the products of the 5-*exo-dig* reaction. The formation of compounds **5A** was characterized by the isolation of the bis(*o*-ethynylbenzyl) ditellurides **8A**, which were obtained by the potassium ferricyanide oxidation[13] of **5A** before heating in ethanol. The ditellurides **8A** reverted back to the tellurols **5A** by treatment with sodium borohydride in ethanol with reductive fission of the Te–Te bond. The trimethylsilylethynylbenzyl tellurol **5Ae** also gave the 3-unsubstituted isotellurochromene **6Af** directly with reductive removal of the TMS group under the reaction conditions, but in poor yield. The cyclization of ethynylbenzyl tellurol **5Af** proceeds to afford **6Af** in a higher, good yield. In this case, the 1-methylidene-2-telluraindan **7Af** was not obtained. It is well known and established that both intermolecular[7a,14] and intramolecular[7b–g] *trans*-additions of tellurols to a triple bond proceed stereospecifically to provide the *anti* Markovnikov-type products. The phenyl derivative **5Ad** gave the isotellurochromene **6Ad** and the telluraindans **7Ad** in 19 and 71% yields, respectively. In the ^1H NMR (400 MHz) spectra of the telluraindans **7A**, a nuclear Overhauser enhancement (NOE) was observed between the exocyclic methyne proton (1′-H) and the aromatic 7-H. Thus, the stereochemistry of the olefin moiety of **7A** was found to be the (*Z*)-form.

The isoselenochromenes **6B** and the (*Z*)-1-methylidene-2-selenaindans **7B** were similarly obtained using sodium hydrogen selenide (NaHSe). *o*-Ethynylbenzyl selenol **5Bf** regioselectively cyclized to afford isoselenochromene **6Bf** without producing the 2-selenaindan **7Bf**. In contrast, in the case of the phenyl derivative **5Bd**, only the 5-*exo-dig* reaction proceeded to form the benzylidene-2-selenaindan **7Bd** in 66% yield. Overall, the 6-*endo-dig* ring closure was the preferential reaction during the present intramolecular *trans*-addition of the tellurols or the selenols to an acetylenic moiety except for the phenyl derivative **5d**. These results are summarized in Table 1, and the ^1H NMR and MS spectral data for **6** and **7** are collected in Tables 2 and 3, respectively. All the isotellurochromenes **6A** and the isoselenochromenes **6B** except for the 3-unsubstituted isochromene **6Bf**[6] are hitherto unknown compounds.

Next, the transformation into the 2-benzotelluropyrylium salts **9A** and the 2-benzoselenopyrylium salts **9B** was carried out from the corresponding isochromenes **6A**, **6B** using the substrates obtained, except for the phenyl derivative **6Bd**. The 3-*tert*-butyl derivatives **6Ac**, **6Bc** and the 3-unsubstituted isochromenes **6Af**, **6Bf** were treated with triphenylcarbenium tetrafluoroborate ($Ph_3C^+BF_4^-$) in nitromethane at room temperature to give the desired corresponding 2-benzotelluropyrylium tetrafluoroborates **9Ac**, **9Af** and 2-benzoselenopyrylium tetrafluoroborates **9Bc**, **9Bf** as yellow or pale green prisms in high yields, respectively. These salts are quite stable and can be stored for several months even at room temperature under an argon atmosphere. However, they are instantaneously decomposed upon contact with water or a protic solvent such as an alcohol. In contrast, the 2-benzotelluropyrylium salts **9Aa**, **9Ab** and 2-benzoselenopyrylium salts **9Ba**, **9Bb** having another alkyl substituted group (methyl and *n*-butyl) on the C-3 position could not be obtained in a stable crystalline state from the corresponding isochromenes under the same conditions. They are too unstable to be isolated, and decompose even in solution in *ca.* 10–20 minutes. The reason why these pyrylium salts are not stable compared to the 3-*tert*-butyl and 3-unsubstituted derivatives might be the reaction shown in Scheme 3. A β-hydrogen from the heteroatom of the pyrylium salts **9** would be attacked and eliminated by the strong base, the tetrafluoroborate (BF_4^-) anion, to form the *o*-quinonoid compounds **10**, which would be unstable due to the destruction of the aromaticity of the benzene ring.

Similar β-hydrogen elimination behavior was observed in the case of the 1-benzyl-2-benzotelluropyrylium salt; the (*Z*)-1-benzylideneisotellurochromene[5a] was isolated. 3-Phenyl-2-benzotelluropyrylium salt **9Ad** was also moisture-sensitive

Table 1 Isotellurochromenes **6A**, isoselenochromenes **6B**, (*Z*)-1-methylidene-2-telluraindans **7A** and (*Z*)-1-methylidene-2-selenaindans **7B**

		6			7		
M	R	Yield (%)[a]	Appearance	Mp/°C	Yield (%)[a]	Appearance	Mp/°C
Te	Me	66	Yellow prisms[b]	59	25	Yellow prisms[b]	73–74
Te	Bu^n	66	Yellow oil	—	20	Pale yellow oil	—
Te	Bu^t	84	Yellow prisms[b]	63	0	—	—
Te	Ph	19	Yellow prisms[d]	51–52	71	Yellow prisms[c]	98–99
Te	H	64	Yellow prisms[d]	66–67	0	—	—
Se	Me	48	Pale yellow prisms[b]	43	33	Pale yellow prisms[b]	61–63
Se	Bu^n	49	Yellow oil	—	22	Yellow oil	—
Se	Bu^t	60	Yellow prisms[b]	69–71	14	Yellow oil	—
Se	Ph	0	—	—	66	Colorless prisms[c]	77–80
Se	H	56	Yellow oil	—	0	—	—

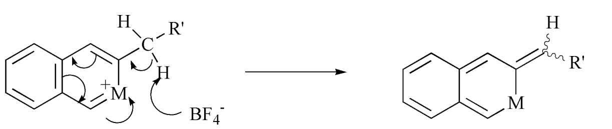
[a] Isolated yields. [b] From *n*-hexane. [c] From benzene–*n*-hexane. [d] From acetone–*n*-hexane.

Table 2 Spectral data for the isotellurochromenes **6A** and the isoselenochromenes **6B**

					δ_H (90 MHz, $CDCl_3$)			
Compd. no.	R	M	Formula	HRMS calcd (found)	1-H_2	4-H	Ph-H	R-H
6Aa	Me	Te	$C_{10}H_{10}Te$	259.9845 (259.9845)	3.90 (s)	6.59 (q, *J* 1.7)	7.01–7.26 (4H, m)	2.40 (3H, d, *J* 1.7, Me)
6Ab	Bu^n	Te	$C_{13}H_{13}Te$	302.0315 (302.0313)	3.86 (s)	6.59 (br s)	7.02–7.23 (4H, m)	0.93, 1.19–1.62, 2.59 (3H, t, *J* 6.2, 4H, m, 2H, br t, *J* 7.0, Bu^n)
6Ac	Bu^t	Te	$C_{13}H_{16}Te$	302.0315 (302.0313)	3.79 (s)	6.64 (s)	7.10–7.26 (4H, m)	1.29 (9H, s, Bu^t)
6Ad	Ph	Te	$C_{15}H_{12}Te$	322.0002 (321.9996)	3.98 (s)	7.09 (s)		7.17–7.64 (9H, m, Ph)
6Af	H	Te	C_9H_8Te	245.9689 (245.9693)	3.86 (s)	7.02 (d, *J* 10.3)	7.10–7.25 (4H, m)	7.22 (d, *J* 10.3, H)
6Ba	Me	Se	$C_{10}H_{10}Se$	209.9948 (209.9943)	3.85 (s)	6.63 (q, *J* 1.6)	6.92–7.30 (4H, m)	2.24 (3H, d, *J* 1.6, Me)
6Bb	Bu^n	Se	$C_{13}H_{16}Se$	252.0418 (252.0425)	3.85 (s)	6.71 (t, *J* 1.8)	6.97–7.34 (4H, m)	0.95, 1.22–1.83, 2.52 (3H, t, *J* 6.0, 4H, m, 2H, dt, *J* 1.8, 7.0, Bu^n)
6Bc	Bu^t	Se	$C_{13}H_{16}Se$	252.0418 (252.0414)	3.76 (s)	6.70 (s)	7.12–7.26 (4H, m)	1.29 (9H, s, Bu^t)
6Bf	H	Se	C_9H_8Se	195.9791 (195.9791)	3.84 (s)	6.79 (d, *J* 9.9)	7.09–7.25 (4H, m)	6.95 (d, *J* 9.9, H)

Table 3 Spectral data for (*Z*)-1-methylidene-2-telluraindans **7A** and (*Z*)-1-methylidene-2-selenaindans **7B**

					δ_H (90 MHz, $CDCl_3$)			
Compd. no.	R	M	Formula	HRMS calcd (found)	1′-H	3-H_2	Ph-H	R-H
7Aa	Me	Te	$C_{10}H_{10}Te$	259.9845 (259.9850)	6.76 (q, *J* 6.2)	4.65 (s)	7.05–7.76 (4H, m)	1.85 (3H, d, *J* 6.2, Me)
7Ab	Bu^n	Te	$C_{13}H_{16}Te$	302.0315 (302.0312)	6.67 (t, *J* 6.6)	4.62 (s)	7.05–7.71 (4H, m)	0.93, 1.26–1.62, 2.09 (3H, t, *J* 6.6, 4H, m, 2H, dt, *J* 6.6, 7.0, Bu^n)
7Ad	Ph	Te	$C_{15}H_{12}Te$	322.0002 (322.0005)	7.86 (s)	4.66 (s)		7.15–7.84 (9H, m, Ph)
7Ba	Me	Se	$C_{10}H_{10}Se$	209.9948 (209.9946)	6.44 (q, *J* 7.0)	4.38 (s)	7.03–7.70 (4H, m)	1.84 (3H, d, *J* 7.0, Me)
7Bb	Bu^n	Se	$C_{13}H_{16}Se$	252.0418 (252.0428)	6.36 (t, *J* 7.0)	4.38 (s)	7.03–7.69 (4H, m)	0.94, 1.17–1.78, 2.16 (3H, t, *J* 6.6, 4H, m, 2H, dt, *J* 6.6, 7.0, Bu^n)
7Bc	Bu^t	Se	$C_{13}H_{16}Se$	252.0418 (252.0417)	6.58 (s)	4.38 (s)	7.12–7.71 (4H, m)	1.26 (9H, s, Bu^t)
7Bd	Ph	Se	$C_{15}H_{12}Se$	272.0105 (272.0104)	7.51 (s)	4.50 (s)		7.23–7.79 (9H, m, Ph)



9

a: R = H

b: R = Pr^n

10

(unstable)

Scheme 3

and immediately decomposed upon contact with air. Thus, the deprotonation of these isochromenes by $Ph_3C^+BF_4^-$ to form the corresponding pyrylium salts was carried out in CD_3CN as a solvent, and the formation of **9Aa**, **9Ab**, **9Ad**, **9Ba** and **9Bb** was then monitored by ^1H NMR spectroscopy. The ^1H NMR spectral data of all the pyrylium salts **9A** and **9B** that have been prepared in the present study are listed in Table 4. The structures of these pyrylium salts **9** were elucidated from their ^1H and ^{13}C NMR spectra and elemental analyses and also from single-crystal X-ray studies in the case of the *tert*-butyl derivatives **9Ac** and **9Bc**.

The ^1H NMR spectral data for the monocyclic unsubstituted thiopyrylium,[15] selenopyrylium[15] and telluropyrylium cations[16] have been reported. However, no ^1H NMR data for the unsubstituted 2-benzothiopyrylium[17] and 2-benzoselenopyrylium salts[6] have been recorded in the literature, although they have been prepared; the 2-benzotelluropyrylium ring system was first constructed in this study. These ^1H NMR data (Table 4) and those of the 3-benzoyl-2-benzothiopyrylium cation reported by Shimizu and co-workers[18] indicate a remarkable fact about their chemical shifts. The chemical shifts of the aromatic protons of the pyrylium salts **9A** and **9B** appear at lower fields, in particular, both the proton signals of 1-H (δ 12.05–13.31) and those of 4-H (δ 8.75–9.30) resonate at much lower fields compared to the 2-benzothiopyrylium salts.[18] The chemical shift values of 1-H in these three pyrylium nuclei decrease in the order **9A** (Te) > **9B** (Se) > thiopyrylium salt (S, δ 11.29).[18] A similar tendency is observed for the 2-H protons of the five-membered heterocycles, the benzo[*b*]chalcogenophenes.[7d] In contrast, the proton signals of 4-H of **9A** and **9B** appear at almost the same chemical shifts (δ 8.75–9.30); that of the thiopyrylium salt is

Table 4 ^{1}H NMR spectral data for 2-benzotelluropyrylium **9A** salts and 2-benzoselenopyrylium salts **9B**

			δ_H (400 MHz, CD_3CN)			
Compd. no.	R	M	1-H	4-H	Ph-H	R-H
9Aa[a]	Me	Te	12.68 (br s)	8.75 (br s)	7.80–8.43 (4H, m)	3.14 (3H, br s, Me)
9Ab[a]	Bu^n	Te	12.96 (s)	8.85 (br s)	7.85–8.50 (4H, m)	0.98, 1.20–2.01, 3.54 (3H, t, *J* 7.6, 4H, m, 2H, t, *J* 7.9, Bu^n)
9Ac	Bu^t	Te	13.25 (s)	9.12 (s)	7.81–8.53 (4H, m)	1.68 (9H, s, Bu^t)
9Ad[a]	Ph	Te	13.11 (s)	9.20 (s)		7.77–8.55 (9H, m, Ph)
9Af	H	Te	13.31 (br d, *J* 2.9)	9.30 (d, *J* 11.0)	7.88–8.57 (4H, m)	10.48 (dd, *J* 11.0, 2.9, H)
9Ba[a]	Me	Se	11.82 (br s)	8.82 (br s)	7.94–8.53 (4H, m)	3.14 (3H, br s, Me)
9Bb[a]	Bu^n	Se	11.86 (s)	8.85 (br s)	7.98–8.55 (4H, m)	0.99, 1.20–2.07, 3.47 (3H, t, *J* 8.2, 4H, m, 2H, br t, *J* 8.6, Bu^n)
9Bc	Bu^t	Se	11.96 (s)	9.06 (s)	8.11–8.54 (4H, m)	1.70 (9H, s, Bu^t)
9Bf	H	Se	12.05 (d, *J* 2.9)	9.15 (br s)	8.08–8.64 (4H, m)	9.87 (dd, *J* 9.5, 2.9, H)

[a] Not isolated.

Table 5 Selected bond lengths (Å) and angles (°) of **9Ac**

Te(1)–C(1)	2.003(7)	Te(1)–C(2)	2.042(5)
C(1)–C(9)	1.392(7)	C(2)–C(3)	1.374(8)
C(3)–C(8)	1.429(7)	C(8)–C(9)	1.439(8)
C(1)–Te(1)–C(2)	95.4(3)	Te(1)–C(1)–C(9)	125.2(4)
Te(1)–C(2)–C(3)	120.5(5)	C(2)–C(3)–C(8)	129.9(5)
C(3)–C(8)–C(9)	124.6(5)	C(1)–C(9)–C(8)	124.4(5)

Table 6 Selected bond lengths (Å) and angles (°) of **9Bc**

Se(1)–C(1)	1.806(5)	Se(1)–C(2)	1.853(4)
C(1)–C(9)	1.394(7)	C(2)–C(3)	1.363(6)
C(3)–C(8)	1.425(6)	C(8)–C(9)	1.418(7)
C(1)–Se(1)–C(2)	101.0(2)	Se(1)–C(1)–C(9)	124.8(3)
Se(1)–C(2)–C(3)	120.3(3)	C(2)–C(3)–C(8)	128.2(4)
C(3)–C(8)–(9)	122.4(4)	C(1)–C(9)–C(8)	123.2(4)

observed somewhat more downfield (δ 9.50) because it has a benzoyl group as an electron-withdrawing substituent at the C-3 position.

X-Ray analysis

The structure of the 2-benzotelluropyrylium salt **9A**, which is a previously unknown heterocyclic ring system, was characterized by X-ray crystallographic analysis of a single crystal obtained by recrystallization from dichloromethane.

Fig. 1 shows the molecular structure of the 3-*tert*-butyl derivative **9Ac**, and selected bond lengths and angles of **9Ac** are listed in Table 5. To our knowledge, this is the first crystal structure of benzotelluropyrylium, although the structure of one monocyclic telluropyrylium has been reported.[19] The benzopyrylium ring system in **9Ac** is planar and the cation and anion lie on mirror planes. The tellurium atom has no significant interaction with the counter anion. The closest distance from tellurium to the nearest fluorine in the borate is 3.790(3) Å, which is longer than the sum of the van der Waals radii (3.55 Å).[20] It is noteworthy that the carbon (C-1)–tellurium bond length (2.003 Å) in the telluropyrylium ring is significantly shorter than the typical covalent bond length of Te–C (2.12 Å). The shortness of the carbon–tellurium bond in **9Ac** is rather comparable to the values of the carbon (sp^2)–tellurium double bond lengths that have been reported in the range of 1.987–2.298 Å with an average of 2.06 Å.[21] Although the precise details of the resonance structures in the telluropyrylium are not clear, it is likely that the localized double bond that forms around the tellurium provides an important contribution to the overall description.

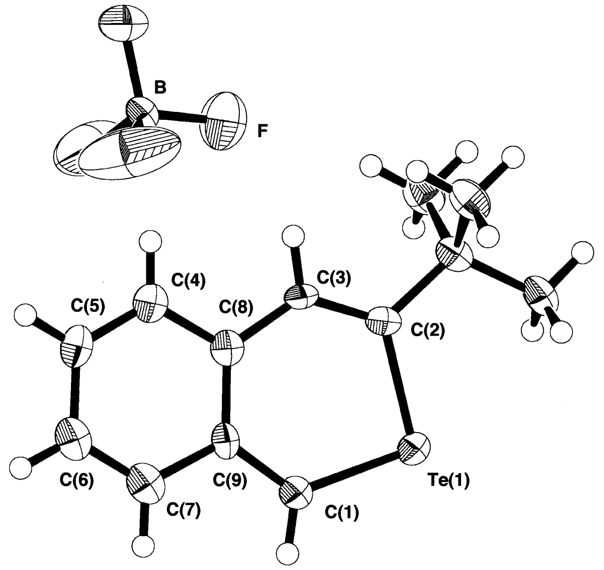


Fig. 1 ORTEP drawing of **9Ac** with 50% probability level.

The structure of the corresponding 2-benzoselenopyrylium **9Bc** was determined for comparison. The molecular structure of **9Bc** and selected bond lengths and angles are given in Fig. 2 and Table 6, respectively.

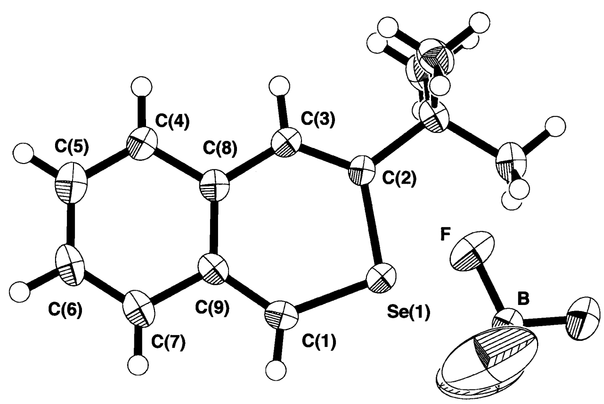


Fig. 2 ORTEP drawing of **9Bc** with 50% probability level.

The selenopyrylium **9Bc** showed an isomorphous structure to that of **9Ac** and also has mirror planes through the cation and anion. The C(1)–Se bond length [1.806(5) Å] is noticeably shorter than those usually observed for carbon–selenium single bond lengths (average 1.970 Å),[22] being close to the C=Se double bond lengths that have been observed in selenoketones (1.774,[23a] and 1.790 Å[23b]).

Conclusion

In the present work, general preparations have been achieved for the isotellurochromenes and isoselenochromenes together with the (Z)-1-methylidene-2-indanes containing tellurium and selenium atoms by an intramolecular cyclization reaction with a triple bond. The isochromenes were transformed into the corresponding novel 2-benzotelluropyrylium and 2-benzoselenopyrylium salts. The structure of these pyrylium salts has been found to be quite flat based on the X-ray analyses of the *tert*-butyl derivatives. Examination of the reactivities of these pyrylium salts is in progress and will be reported in the near future.

Experimental

Melting points were measured on a Yanagimoto micro melting point hot stage apparatus and are uncorrected. IR spectra were recorded on a Hitachi 270-30 spectrometer. Mass spectra (MS) and HRMS were recorded on a JEOL JMS-DX300 instrument. ^{1}H NMR spectra were recorded on a JEOL PMX-60 SI (60 MHz), a JEOL EX-90A (90 MHz) or a JEOL JNM-GSX 400 (400 MHz) spectrometer in $CDCl_3$ or CD_3CN using tetramethylsilane as the internal standard; J values are given in Hz. ^{13}C NMR spectra and NOE spectra were measured on a JEOL JNM-GSX 400 spectrometer. ^{125}Te NMR spectra were recorded on a JEOL EX-400 spectrometer at 126.1 MHz, and samples were referenced to $^{125}TeMe_2$ as an external standard. ^{77}Se NMR spectra were recorded on a JEOL EX-400 spectrometer at 76.2 MHz, and samples were referenced to Me_2Se as an external standard.

General procedure for the preparation of *o*-ethynylbenzyl alcohols 3a–e

To a mixture of alkyne (**b**: hex-1-yne, **c**: *tert*-butylacetylene, **d**: phenylacetylene, **e**: trimethylsilylacetylene, 0.11 mol) and *o*-iodobenzyl alcohol **1** (23.4 g, 0.1 mol)† in benzene (200 mL) and piperidine (200 mL) were added $PdCl_2(Ph_3P)_2$ (702 mg, 1 mmol) and CuI (400 mg, 2.1 mmol). The mixture was stirred at room temperature under argon for 6–10 h. Cold water (300 mL) was added to the mixture, and the resulting aqueous mixture was extracted with benzene (200 mL × 3). The combined organic extract was washed with water (200 mL × 4), 5% H_2SO_4 (200 mL × 3), sat. $NaHCO_3$ (200 mL × 2) and brine (200 mL × 2), and then dried ($MgSO_4$).

The benzene was removed *in vacuo*. The red residual oil was purified by silica gel chromatography using *n*-hexane–CH_2Cl_2 (1 : 1) as eluent to give pure **3**. In the case of **3a**, a slow stream of methylacetylene, which was prepared from 1,2-dibromopropane and KOH in refluxing *n*-BuOH, was immediately passed through the reaction mixture without isolation.

***o*-Prop-1-ynylbenzyl alcohol 3a.** Yield 88%, pale yellow prisms, mp 71–72 °C (from benzene–*n*-hexane); ν_{max} (KBr)/cm^{-1} 3332 (OH), 2240 (C≡C); δ_H ($CDCl_3$, 60 MHz) 2.08 (3H, s, Me), 2.35 (1H, s, OH), 4.80 (2H, s, Ph-CH_2-OH), 7.2–7.5 (4H, m, Ph-H) (HRMS *m*/*z*: M$^+$ calcd for $C_{10}H_{10}O$: 146.0732; found: 146.0741).

***o*-*n*-Hex-1-ynylbenzyl alcohol 3b.** Yield 92%, yellow oil; ν_{max} (neat)/cm^{-1} 3360 (OH), 2228 (C≡C); δ_H ($CDCl_3$, 60 MHz): 0.96, 1.3–1.8, 2.46 (3H, t, J 6, 4H, m, 2H, t, J 7, Bu^n), 2.25 (1H, s, OH), 4.82 (2H, s, Ph-CH_2-OH), 7.2–7.6 (4H, m, Ph-H) (HRMS *m*/*z*: M$^+$ calcd for $C_{13}H_{16}O$: 188.1201; found: 188.1197).

***o*-(3,3-Dimethylbut-1-ynyl)benzyl alcohol 3c.** Yield 88%, yellow oil; ν_{max} (neat)/cm^{-1} 3368 (OH), 2236 (C≡C); δ_H ($CDCl_3$, 60 MHz) 1.36 (9H, s, Bu^t), 2.47 (1H, s, OH), 4.80 (2H, s, Ph-CH_2-OH), 7.2–7.5 (4H, m, Ph-H) (HRMS *m*/*z*: M$^+$ calcd for $C_{13}H_{16}O$: 188.1201; found: 188.1197).

***o*-Phenylethynylbenzyl alcohol 3d.** Yield 90%, pale yellow prisms, mp 70–72 °C (from benzene–*n*-hexane); ν_{max} (KBr)/cm^{-1} 3264 (OH), 2240 (C≡C); δ_H ($CDCl_3$, 60 MHz) 2.38 (1H, s, OH), 4.93 (2H, s, Ph-CH_2-OH), 7.2–7.7 (9H, m, Ph-H) (HRMS *m*/*z*: M$^+$ calcd for $C_{15}H_{12}O$: 208.0888; found: 208.0888).

***o*-Trimethysilylethynylbenzyl alcohol 3e.** Yield 92%, yellow oil; ν_{max} (neat)/cm^{-1} 3352 (OH), 2156 (C≡C); δ_H ($CDCl_3$, 60 MHz) 0.28 (9H, s, TMS), 2.45 (1H, s, OH), 4.85 (2H, s, Ph-CH_2-OH), 7.2–7.6 (4H, m, Ph-H) (HRMS *m*/*z*: M$^+$ calcd for $C_{12}H_{16}OSi$: 204.0970; found: 204.0975).

General procedure for the preparation of *o*-ethynylbenzyl bromides 4a–e

To a stirred solution of *o*-ethynylbenzyl alcohol **3** (50 mmol) and pyridine (5.14 g, 65 mmol) in chloroform (50 mL) at 0 °C was slowly added phosphorus tribromide (14.9 g, 55 mmol). The mixture was stirred at room temperature for 6–12 h, and then poured into ice–water. The resulting aqueous mixture was extracted with CH_2Cl_2 (200 mL × 3), and the combined organic extract was washed with 5% H_2SO_4 (200 mL × 2), sat. $NaHCO_3$ (200 mL × 2) and brine (200 mL × 2), and then dried ($MgSO_4$). After removal of the organic solvent *in vacuo*, the residual oil was purified by silica gel chromatography using *n*-hexane as eluent to give the pure benzyl bromide **4**. The following compounds were thus prepared.

***o*-Prop-1-ynylbenzyl bromide 4a.** Yield 85%, colorless oil; ν_{max} (neat)/cm^{-1} 2252, 2220 (C≡C); δ_H ($CDCl_3$, 60 MHz) 2.12 (3H, s, Me), 4.67 (2H, s, Ph-CH_2-Br), 7.2–7.5 (4H, m, Ph-H) (HRMS *m*/*z*: M$^+$ calcd for $C_{10}H_9Br$: 207.9888, 209.9868; found: 207.9881, 209.9866).

***o*-*n*-Hex-1-ynylbenzyl bromide 4b.** Yield 78%, colorless oil; ν_{max} (neat)/cm^{-1} 2228 (C≡C); δ_H ($CDCl_3$, 60 MHz) 0.97, 1.3–1.8, 2.49 (3H, t, J 6, 4H, m, 2H, t, J 7, Bu^n), 4.70 (2H, s, Ph-CH_2-Br), 7.2–7.6 (4H, m, Ph-H) (HRMS *m*/*z*: M$^+$ calcd for $C_{13}H_{15}Br$: 250.0357, 252.0338; found: 250.0329, 252.0337).

***o*-(3,3-Dimethybut-1-ynyl)benzyl bromide 4c.** Yield 80%, colorless oil; ν_{max} (neat)/cm^{-1} 2240 (C≡C); δ_H ($CDCl_3$, 60 MHz) 1.39 (9H, s, Bu^t), 4.67 (2H, s, Ph-CH_2-Br), 7.2–7.5 (4H, m, Ph-H) (HRMS *m*/*z*: M$^+$ calcd for $C_{13}H_{15}Br$: 250.0357, 252.0338; found: 250.0350, 252.0347).

***o*-Phenylethynylbenzyl bromide 4d.** Yield 94%, colorless oil; ν_{max} (neat)/cm^{-1} 2216 (C≡C); δ_H ($CDCl_3$, 60 MHz) 4.72 (2H, s, Ph-CH_2-Br), 7.2–7.7 (9H, m, Ph-H) (HRMS *m*/*z*: M$^+$ calcd for $C_{15}H_{11}Br$: 270.0044, 272.0025; found: 270.0038, 272.0021).

***o*-Trimethylsilylethynylbenzyl bromide 4e.** Yield 76%, colorless oil; ν_{max} (neat)/cm^{-1} 2160 (C≡C); δ_H ($CDCl_3$, 60 MHz) 0.30 (9H, s, TMS), 4.70 (2H, s, Ph-CH_2-Br), 7.2–7.7 (4H, m, Ph-H) (HRMS *m*/*z*: M$^+$ calcd for $C_{12}H_{15}BrSi$: 266.0126, 268.0107; found: 266.0121, 268.0114).

***o*-Ethynylbenzyl bromide 4f.** To a stirred solution of *o*-trimethylsilylethynylbenzyl bromide **4e** (8.01 g, 30 mmol) in methanol (60 mL) at room temperature was added K_2CO_3 (0.35 g). After the reaction mixture had been stirred for 1 h, it was poured into ice–water. The resulting aqueous mixture was extracted with with CH_2Cl_2 (100 mL × 3), and the combined organic extract was washed with brine (100 mL × 2) and dried ($MgSO_4$). The organic solvent was evaporated *in vacuo* to give almost pure *o*-ethynylbenzyl bromide **4f** (5.21 g, 89%) as a

† This compound **1** is commercially available, but easily obtained quantitatively by diborane reduction of *o*-iodobenzoic acid on a large scale.

colorless oil; ν_{max} (neat)/cm^{-1} 2108 (C≡C); δ_H ($CDCl_3$, 60 MHz) 3.48 (1H, s, C≡C*H*), 4.74 (2H, s, Ph-CH_2-Br), 7.3–7.7 (4H, m, Ph-H) (HRMS *m*/*z*: M^+ calcd for C_9H_7Br: 193.9731, 195.9711; found: 193.9733, 195.9712).

General procedure for the treatment of the benzyl bromides 4 with NaHTe: formation of isotellurochromenes 6Aa–f and 1-methylidene-2-telluraindan 7Aa–f

A solution of *o*-ethynylbenzyl bromide **4** (10 mmol) in DMF (10 mL) was slowly added to a solution of NaHTe (12 mmol), which was freshly prepared from tellurium dust (1.53 g) and $NaBH_4$ (0.54 g) in DMF (40 mL) at 0 °C under an argon atmosphere. The reaction mixture was stirred under the conditions for 1 h. EtOH (40 mL) was added to the reaction mixture, and then the whole mixture was heated at 90 °C with stirring for 1–3 h. After addition of water (200 mL), the aqueous mixture was extracted with benzene (100 mL × 3). The organic extract was washed with water (200 mL × 3) and brine (200 mL × 3), dried ($MgSO_4$), and concentrated *in vacuo*. The resulting residue was purified by silica gel chromatography using *n*-hexane as eluent to give pure **6A** and **7A**. The results and spectral data are given in Tables 1–3.

General procedure for the treatment of benzyl bromides 4 with NaHSe: formation of isoselenochromenes 6Ba–f and 1-methylidene-2-selenaindan 7Ba–f

A solution of **3** (10 mmol) in DMF (10 mL) was treated with sodium hydrogen selenide (12 mmol), prepared from selenium dust (0.96 g) and sodium borohydride (0.54 g), and worked up to give **6B** and **7B**. The results and spectral data are given in Tables 1–3.

General procedure for the preparation of 2-benzotelluropyrylium tetrafluoroborates 9A and 2-benzoselenopyrylium tetrafluoroborates 9B

$Ph_3C^+BF_4^-$ (1.88 g, 5.5 mmol) was added to a stirred solution of the isochromenes **6** (1.51 g, 5 mmol) in dry $MeNO_2$ (10 mL) and the mixture was stirred at room temperature for 30 min. To the reaction mixture was added dry Et_2O to precipitate the pyrylium salts **9**. The following compounds were thus obtained. (^{1}H NMR spectral data are listed in Table 4.)

3-*tert*-Butyl-2-benzotelluropyrylium tetrafluoroborate 9Ac. Yield 89%, pale green prisms (CH_2Cl_2–$CHCl_3$), mp 101 °C (decomp.); ν_{max} (KBr)/cm^{-1} 1054 (BF_4^-); δ_C (CD_3CN, 100 MHz) 33.3 (q), 43.8 (s), 131.4 (d), 132.1 (d), 135.40 (d), 137.8 (d), 139.6 (d), 139.9 (s), 143.7 (s), 182.9 (s), 188.8 (d); δ_{Te} (CD_3CN) 1257.5 (Anal. calcd for $C_{13}H_{15}BF_4Te$: C, 40.49; H, 3.92. Found: C, 40.35; H, 3.75%).

2-Benzotelluropyrylium tetrafluoroborate 9Af. Yield 89%, pale green prisms (CH_2Cl_2–$CHCl_3$); mp 109–113 °C (decomp.); ν_{max} (KBr)/cm^{-1} 1056 (BF_4^-); δ_C (CD_3CN, 100 MHz) 132.0 (d), 132.5 (d), 135.3 (d), 139.5 (d), 141.0 (s), 142.3 (d), 142.4 (s), 146.7 (d), 193.2 (d) (Anal. calcd for $C_9H_7BF_4Te$: C, 32.80; H, 2.14. Found: C, 32.27; H, 2.20%).

3-*tert*-Butyl-2-benzoselenopyrylium tetrafluoroborate 9Bc. Yield 89%, pale green prisms (CH_2Cl_2–$CHCl_3$), mp 182–184 °C (decomp.); ν_{max} (KBr)/cm^{-1} 1056 (BF_4^-); δ_C (CD_3CN, 100 MHz) 32.3 (q), 42.4 (s), 132.4 (d), 132.8 (d), 133.5 (d), 134.4 (d), 135.3 (s), 141.6 (d), 142.2 (s), 177.8 (s), 181.2 (d); δ_{Se} (CD_3CN) 890.0 (Anal. calcd for $C_{13}H_{15}BF_4Se$: C, 46.33; H, 4.49. Found: C, 46.21; H, 4.46%).

2-Benzoselenopyrylium tetrafluoroborate 9Bf. Yield 85%, pale green prisms (CH_2Cl_2–$CHCl_3$), mp 127 °C (decomp.); ν_{max} (KBr)/cm^{-1} 1052 (BF_4^-); δ_C (CD_3CN, 100 MHz) 133.1 (d), 133.4 (d), 133.5 (d), 136.6 (s), 138.4 (d), 140.7 (s), 141.7 (d), 145.4 (d), 184.0 (d) (Anal. calcd for $C_9H_7BF_4Se$: C, 38.48; H, 2.51. Found: C, 38.53; H, 2.32%).

X-Ray data collection for 9Ac and 9Bc ‡

Single crystals suitable for X-ray diffraction study of **9Ac** and **9Bc** were obtained from a dichloromethane solution of the compound at room temperature.

Crystal data for 9Ac. $C_{13}H_{15}BF_4Te$, M = 385.67, orthorhombic, *Pnma*, a = 14.2630(5), b = 6.7450(2), c = 14.3100(5) Å, V = 1376.68(7) Å^3, Z = 4, ρ_{calcd} = 1.861 g cm^{-3}. R_w = 0.060 (R = 0.100) and GOF = 1.356 for 1572 observed reflections [109 parameters, $I > 3.00\sigma(I)$].

Crystal data for 9Bc. $C_{13}H_{15}BF_4Se$, M = 337.03, orthorhombic, *Pnma*, a = 13.8420(4), b = 6.7860(1), c = 14.2960(5) Å, V = 1342.85(5) Å^3, Z = 4, ρ_{calcd} = 1.667 g cm^{-3}. R = 0.060 (R_w = 0.108) and GOF = 1.475 for 1528 observed reflections [109 parameters, $I > 3.00\sigma(I)$]. All data were collected at 190 K on a MAC Science DIP2030 imaging plate with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The structure was solved using the teXsan (Rigaku) system and all nonhydrogen atoms were refined anisotropically. The hydrogen atoms were included at calculated positions but not refined. Atomic coordinates, bond lengths and angles, and other important parameters have been deposited at the Cambridge Crystallographic Data Centre. ‡

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‡ CCDC reference numbers 175478 and 175479. See http://www.rsc.org/suppdata/p1/b1/b111045b/ for crystallographic files in .cif or other electronic format.

References

1 For part 17, see ref. 10*b*.
2 J. Kuthan, P. Sebek and S. Bohm, *Adv. Heterocycl. Chem.*, 1994, **59**, 179–244.
3 G. Doddi and G. Ercolani, *Adv. Heterocycl. Chem.*, 1994, **60**, 65–195.
4 (*a*) I. D. Sadekov and V. Minkin, *Adv. Heterocycl. Chem.*, 1995, **63**, 1–60; (*b*) M. R. Detty and (in part) M. B. O'Regan, *The Chemistry of Heterocyclic Compounds: Telluropyrylium Compounds*, ed. E. C. Taylor, John Wiley & Sons, Inc., New York, 1994, vol. 53, pp. 219–291.
5 A part of this work has been appeared in a preliminary communication: (*a*) H. Sashida and K. Ohyanagi, *J. Chem. Soc., Perkin Trans. 1*, 1998, 2123; (*b*) H. Sashida and K. Ohyanagi, *Heterocycles*, 1999, **51**, 17.
6 M. Renson and P. Pirson, *Bull. Soc. Chim. Belg.*, 1966, **75**, 456.
7 (*a*) H. Sashida, H. Kurahashi and T. Tsuchiya, *J. Chem. Soc., Chem. Commun.*, 1991, 802; (*b*) H. Sashida, K. Ito and T. Tsuchiya, *J. Chem. Soc., Chem. Commun.*, 1993, 1493; (*c*) H. Sashida, K. Ito and T. Tsuchiya, *Chem. Pharm. Bull.*, 1995, **43**, 19; (*d*) H. Sashida, K. Sadamori and T. Tsuchiya, *Synth. Commun.*, 1998, **28**, 713; (*e*) H. Sashida, *Synthesis*, 1998, 745; (*f*) H. Sashida and A. Kawamukai, *J. Heterocycl. Chem.*, 1998, **35**, 165; (*g*) H. Sashida and S. Yasuike, *J. Heterocycl. Chem.*, 1998, **35**, 725; (*h*) H. Sashida, A. Kuroda and T. Tsuchiya, *Chem. Commun.*, 1998, 767; (*i*) H. Sashida, *Heterocycles*, 1998, **48**, 631; (*j*) H. Sashida, *Synthesis*, 1999, 1866; (*k*) H. Sashida, *Heterocycles*, 2000, **51**, 49.
8 H. Sashida and H. Minamida, *J. Chem. Soc., Perkin Trans. 1*, 1999, 1665.
9 H. Sashida and H. Minamida, *J. Chem. Res. (S)*, 2000, 569.

10 (*a*) H. Sashida, H. Minamida and K. Yamamoto, *J. Chem. Res. (S)*, 2000, 572; (*b*) H. Sashida, M. Yoshida, H. Minamida and M. Teranishi, *J. Heterocycl. Chem.*, in the press.
11 K. Sonogashira, Y. Tohda and N. Hagihara, *Tetrahedron Lett.*, 1975, 4467.
12 J. Liu, M. Qiu and X. Zhou, *Synth. Commun.*, 1990, **20**, 2759.
13 L. Engman and J. Persson, *J. Organomet. Chem.*, 1990, **388**, 71.
14 (*a*) M. V. Lakshmikanthan, M. P. Cava, M. Albeck, L. Engman, P. Carroll, J. Bergman and F. Wudl, *Tetrahedron Lett.*, 1981, **22**, 4199; (*b*) S. Uemura and S. Fukuzawa, *Tetrahedron Lett.*, 1982, **23**, 1181; (*c*) S. Uemura, S. Fukuzawa and S. R. Patil, *J. Organomet. Chem.*, 1983, **243**, 9; (*d*) M. J. Dabdoub and V. B. Dabdoub, *Tetrahedron*, 1995, **51**, 9839.
15 (*a*) I. Degani, L. Lunazzi and F. Taddei, *Boll. Sci. Fac. Chim. Ind. Bologna*, 1965, **23**, 131; (*b*) P. Sandor and L. Radics, *Org. Magn. Reson*, 1981, **16**, 148.
16 M. R. Detty, W. C. Lenhart, P. G. Gassman and M. R. Callstrom, *Organometallics*, 1989, **8**, 861.
17 C. C. Price, M. Hori, T. Parasaran and M. Polk, *J. Am. Chem. Soc.*, 1963, **85**, 2278.
18 H. Shimizu, S. Miyazaki, T. Kataoka, M. Hori and O. Muraoka, *J. Chem. Soc., Perkin Trans. 1*, 1994, 3129.
19 M. R. Detty, J. M. McKelvey and H. R. Luss, *Organometallics*, 1988, **7**, 1131.
20 L. Pauling, *The Nature of The Chemical Bond*, 3rd edn., Cornell University Press, New York, 1960.
21 The experimental C=Te double bond lengths were taken from the following references: (*a*) V. V. Tkachev, L. O. Atovmyan, I. D. Sadekov, A. I. Usachev and V. I. Minkin, *Zh. Strukt. Khim.*, 1978, **19**, 679; (*b*) M. F. Lappert, T. R. Martin and G. M. McLaughlin, *J. Chem. Soc., Chem. Commun.*, 1980, 635; (*c*) M. R. Detty and H. R. Luss, *J. Org. Chem.*, 1983, **48**, 5149; (*d*) G. R. Clark, K. Marsden, C. E. F. Rickard, W. R. Roper and L. J. Wright, *J. Organomet. Chem.*, 1988, **338**, 393; (*e*) M. R. Detty, J. M. McKelvey and H. R. Luss, *Organometallics*, 1988, **7**, 1131; (*f*) N. Kuhn, G. Henkel and T. Kratz, *Chem. Ber.*, 1993, **126**, 2047; (*g*) M. Minoura, T. Kawashima, N. Tokitoh and R. Okazaki, *Chem. Commun.*, 1996, 123; (*h*) G. M. Li, R. A. Zingaro, M. Segi, J. H. Reibenspies and T. Nakajima, *Organometallics*, 1997, **16**, 756; (*i*) A. J. Arduengo, F. Davidson, H. V. R. Dias, J. R. Goerlich, D. Khasnis, W. J. Marshall and T. K. Prakasha, *J. Am. Chem. Soc.*, 1997, **119**, 12742.
22 F. H. Alle, O. Kennard, D. G. Watoson, L. B. Brammer, A. G. Orpen and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1987, S1.
23 (*a*) P. R. Brooks, J. A. Counter, R. Bishop and E. R. T. Tiekink, *Acta Crystallogr., Sect. C*, 1991, **47**, 1939; (*b*) K. Okuma, K. Kojima, I. Kaneko, Y. Tsujimoto, H. Ohta and Y. Yokomori, *J. Chem. Soc., Perkin Trans. 1*, 1994, 2151.