Palladium-Mediated Intramolecular Formation of a C–S Bond: Application to the Selective Syntheses of Six- and Seven-Membered Sulfur-Containing Heterocycles

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Received September 28, 1994[⊗]

Cyclopalladated complexes derived from benzylmethyl sulfide, *o*-iodo sulfides, or methyl-2-biphenyl sulfide react with alkynes to give stable organometallic compounds whereby the alkyne has inserted in the carbon–palladium bond. Activation of these complexes was effected by treatment with a silver salt, and resulting thermolysis led to a selective depalladation process, affording a series of both neutral and cationic 1*H*-2S-benzothiopyran derivatives. With dissymmetric alkynes this reaction displayed a high degree of regiocontrol. Under similar conditions, a new entry for the synthesis of derivatives of the rare family of dibenzo[*bd*]thiepins was acheived.

Introduction

Despite the plethora of firmly established transition metal-mediated syntheses of nitrogen-containing heterocycles in the literature, which invariably involve the selective formation of a C–N bond within the sphere of a transition metal,[1] it is rather disappointing to note that relatively few procedures have been developed for their corresponding sulfur counterparts. Many review articles[2] reflect the neglected aspect of this latter area, and a recent publication describing the synthesis of thiophenes, *via* a palladium catalyzed C–C bond formation,[3] commented on the lack of metal-mediated routes to S-heterocycles, suggesting that the thiophilicity of many transition metals may be a contributing factor to this "gap in the literature". Ironically, we can also note that much effort has been invested in the transition metal-mediated rupture of C–S bonds in heterocycles, namely in the study of the industrially important desulfurization process.[4]

Fortunately, however, there are some synthetically important contributions leading to S-heterocycles involving the selective formation of the carbon–heteroatom bond. Recent examples include the reactions of organometallic complexes with sulfur-containing reagents such as S_8, CS_2, PhNCS, and SCl_2 and subsequent C–S bond formation.[5] A Heck type reaction of norbornene with arylazoxy aryl sulfones afforded thiophene derivatives.[6] Rhodium-catalyzed intramolecular cyclizations of diazo mercaptans enabled the synthesis of many unusual five- to seven-membered rings.[7] We can add to these reactions novel rearrangements of thioepoxide derivatives which led to interesting S-heterocycles.[8]

In connection with studies on the application of the reactions of cyclometalated nitrogen-containing complexes with disubstituted alkynes in heteroannulation processes[9] we wished to apply this methodology for the formation of S-containing heterocycles. On the outset of this study little success had been acheived in this direction.[10–12]

Herein we describe the synthesis of a range of 1*H*-2-benzothiopyran and dibenzo[*bd*]thiepin derivatives start-

[⊗] Abstract published in *Advance ACS Abstracts,* January 15, 1995.

(1) Representative examples include: (a) Hegedus, L. S. *Angew. Chem. Int. Ed. Engl.* **1988,** *27,* 1113. (b) Vollhardt, K. P. C. *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 539. (c) Trost, B. M. *Angew. Chem. Int. Ed. Engl.* **1989**, 1173 (d) Knölker, H. J. *Synlett* **1992**, 371. (e) Bäckvall, J. E. *Pure Appl. Chem.* **1992,** *64,* 429. (f) Larock, R. C.; Yum, E. K. *J. Am. Chem. Soc.* **1991**, *113*, 6689. (g) Grellier, M.; Pfeffer, M.; van Koten, G. *Tetrahedron Lett.* **1994**, *35*, 2877. (h) Walsh, P. J.; Carney, M. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 6343. (i) West, F. G.; Naidu, B. N. *J. Am. Chem. Soc.* **1993**, *115*, 1177.

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(3) Arnau, N.; Moreno-Mañas, M.; Pleixats, R. *Tetrahedron* **1993**, *49*, 11019.

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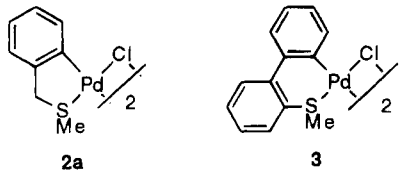
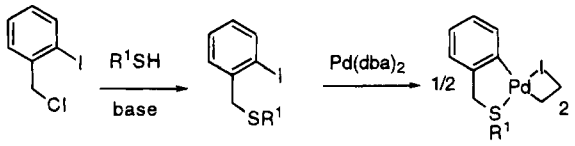
Chart 1



2a **3**

Scheme 1



1a: R^1=Me. **1b**: R^1=Et. **2a'**: R^1=Me. **2b**: R^1=Et.
1c: R^1=t-Bu. **1d**: R^1=Bn. **2c**: R^1=t-Bu. **2d**: R^1=Bn.
1e: R^1= allyl. **1f**: R^1= p-tolyl.

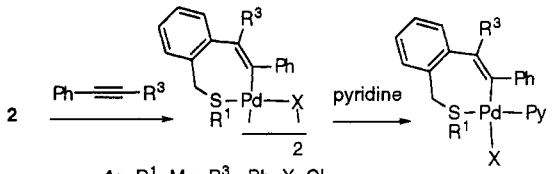
ing from cyclopalladated thioether complexes. The key feature of these reactions is the need to synthesize organometallic products resulting from the insertion of the alkyne in the Pd–C bond of the cyclopalladated complexes **2** and **3** (see Chart 1), prior to inducing the depalladation process. The resulting easy to handle air stable complexes, once suitably activated, can be selectively demetalated and, hence, afford the corresponding six- or seven-membered heterocycles by a cyclization process involving a novel intramolecular addition of a thioether group onto a palladated vinyl unit.

Results

2a and **3** were made by known C–H activation routes.[13] For reasons that will be discussed later, we required derivatives of **2** containing different substituents on the thioether group. The oxidative addition of aryl halides on palladium(0) compounds is another conceivable route to such complexes[14] and with this is mind we synthesized the *o*-iodo thioethers **1a–f** by employing a nucleophilic substitution of *o*-iodobenzyl chloride by a thiol under strongly basic conditions (Scheme 1).[15,16] Compounds **1** were obtained mainly as oils and used without further purification for the ensuing reactions.

Oxidative addition of these iodo thioethers on $Pd(dba)_2$ (dba = dibenzylidene acetone) enabled the ready access to the cyclopalladated compounds **2a'–2d**. These air stable solids were obtained in ca. 40–70% yields after Soxhlet extraction (to remove the dba liberated during the reaction) and gave correct elemental analyses. During these reactions a significant amount of metallic palladium was formed. The high yield of **2c** (68%) compared with its chloro-bridged analogue, formed by a C–H activation in ca. 30% yield, is worthy of note.[17] **2a'** gave an identical ^{1}H NMR spectrum to its chloro derivative **2a**. **2b** displayed the expected triplet for the methyl group, AB spin systems for the diastereotopic ethyl and benzyl CH_2 protons (albeit poorly resolved), due to coordination of the sulfur atom to palladium, and the aromatic region was extremely well resolved. In the ^{1}H NMR spectrum of **2c** a singlet for the *tert*-butyl group and an AB system for the benzylic methylene protons were observed. Similarly, for **2d** two AB systems were observed for the four benzylic CH protons. Therefore, although dimeric species, **2** gave relatively simple ^{1}H NMR spectra, which were indicative of the presence of a single *trans* isomer in solution for each of **2a'–2d**.

Scheme 2



4a, R^1=Me, R^3= Ph, X=Cl.
4b, R^1=Me, R^3= CO_2Et, X=Cl. **4g**, R^1=Me, R^3= CHO, X=Cl.
4c, R^1=Me, R^3= CHO, X=Cl.
4d, R^1=Me, R^3= SO_2ptol, X=Cl. **4h**, R^1=Me, R^3= SO_2ptol, X=Cl.
4e, R^1=t-Bu, R^3= Ph, X=I.
4f, R^1=t-Bu, R^3= CO_2Et, X=I.

The attempted oxidative addition of other substrates (R^1 = H, allyl, *p*-tolyl) did not give satisfactory results. Moreover, the ^{1}H NMR spectra of the crude reaction mixtures prior to Soxhlet extraction were impossible to interpret due to the dba liberated during the reaction. The incompatibility of thiols and *S*-allyl thioethers with palladium complexes has already been encountered elsewhere for Pd^{II} complexes.[3] For example, benzenethiol was shown to react with $PdCl_2(MeCN)_2$ to give a polymeric species of the type $[PdCl(SPh)]_n$.

2a and **2c** reacted with disubstituted alkynes to afford the air stable sulfur chelated enlarged metallacyclic complexes **4** (Scheme 2), which in many instances were isolated and characterized by combustion analysis and by ^{1}H NMR spectroscopy.

Two general reaction conditions[11,12] were employed depending on the type of alkyne and cyclopalladated complex used. When the former contained strong electron-withdrawing groups the reaction often proceeded at rt; **4c** could be obtained by reacting phenylpropargyl aldehyde and **2a** in CH_2Cl_2 over a 2 h period at rt. The ^{1}H NMR spectrum of **4c** was simplified by the bridge-cleaving addition of pyridine, which afforded the corresponding monomeric pyridine complex **4g**. The iodo-bridged complex **4e** was formed in 81% yield as an orange solid by the reaction of **2c** with diphenylacetylene in refluxing 1,2 dichloroethane over a 1.5 h period. The ^{1}H NMR spectrum of **4e** or **4f** in $CDCl_3$ was rather complicated. For **4e** five singlets were observed for the t-Bu group, and the methylene protons were more complicated than a simple AB system. This complexity can be explained by the presence of several isomers of **4e** in solution. For example, the two thioether groups of the dimeric **4e** can be in a mutual *trans* and *cis* arrangement, and the two t-Bu groups can exist in both *syn* and *anti* positions[17] with respect to one another.

Reactions involving 4-phenyl-3-butyn-2-one as alkyne, or **2b**, for example, as starting material presumably led to complexes of the type **4**, although due to either their difficult characterization or for yield optimization purposes, these products were used for *in situ* demetalation reactions described below. Unfortunately, preliminary attempts at reacting **2d** with alkynes met with little success.

As expected, compounds **4** were very stable complexes and attempted depalladation reactions by employing

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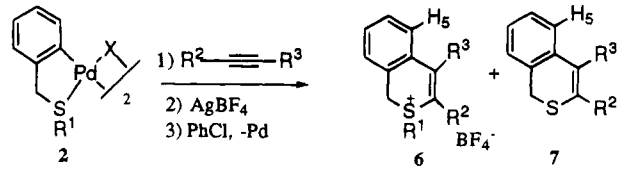
conventional techniques such as prolonged heating in refluxing chlorobenzene left the unchanged starting material. Another known method for the activation of these complexes is the formation of a cationic species[18] which often readily undergoes a depalladation reaction. Treatment of **4a**[11] with $AgBF_4$ in ether led to the immediate precipitation of silver choride and an orange solution. The latter was presumably the corresponding ether-bound cationic palladium complex, which for yield optimization purposes, was not isolated. Subsequent thermolysis in chlorobenzene led to the formation of metallic palladium and to a compound which could be precipitated from CH_2Cl_2/ether, identified as being the already known **6a**.[11] We were unable to identify the ether soluble filtrate due to its difficult purification. We were successful in applying this procedure to other derivatives. **2a** reacted with 4-phenyl-3-butyn-2-one followed by the usual demetalation procedure to give the ether insoluble **6c** in 48% yield, the filtrate once again being difficult to purify and characterize. With **4b**, under similar conditions, metallic palladium was formed along with a mixture of two distinct organic products in very similar yields which were separated either by precipitation or by column chromatography. The ether soluble oil **7b** gave relatively simple ^1H and ^{13}C NMR spectra. Apart from the characteristic ester and aromatic signals, a singlet at $\delta = 3.97$ ppm, superimposed on the quartet of the methylene protons of the ester, was attributed to the C-1 methylene protons, the corresponding carbon being found at $\delta = 32.7$ ppm in the ^{13}C spectrum. The ether insoluble heterocycle **6b** was shown to be cationic by IR (υ BF_4^- at 1080 cm^{-1}) and its relatively complex ^1H NMR spectrum was also most informative. A singlet at $\delta =$ 2.80 ppm (SMe), an ABX_3 pattern for the diastereotopic methylene protons of the ethoxy group at $\delta = 4.15$ ppm, and the AB spin system (CH_2) centered around 5 ppm (δ = 37.9 ppm for the corresponding carbon in the ^{13}C spectrum) all pointed to a heterocyclic system containing a trisubstituted sulfur as stereogenic center. Support for this formulation was provided by the fact that methylation of **7b** (MeI, $AgBF_4$, CH_2Cl_2/MeCN, rt, 0.5 h)[19] afforded **6b** in near quantitative yield. Other results are presented in Table 1 and pertinent analytical data can be found in the Experimental Section.

In many cases compounds **6** were rather unstable, hygroscopic compounds which could, however, be kept almost indefinitely at −20 °C. Attempted depalladation reactions involving **2a** with dimethyl acetylenedicarboxylate or *p*-(tolylsulfonyl)ethyne as alkyne were fruitless.

We were interested in studying the possible effect of changing the nature of the metalated thioether group (SR^1) in **2** on the selectivity in its reaction toward alkynes. Changing a methyl for an ethyl group had little effect, and hence **2b** afforded upon reaction with ethyl 3-phenylpropynoate a mixture of **6e** and **7b**. The ^1H NMR spectrum of **6e** was very similar to that of its methylated homologue **6b** although in this case an extra complexity arises in the fact that the diastereotopic methylene protons of the SEt group now appear as an ABX_3 pattern.

Using **2c** as starting material (entries 8–10, Table 1) led to much more selective reactions and compounds **7**

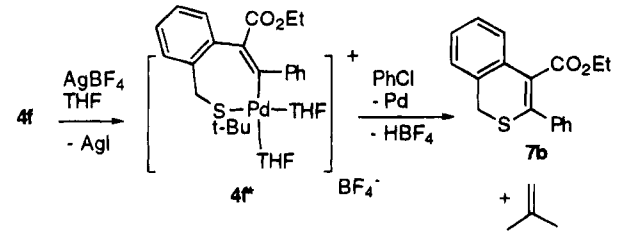
Table 1. Synthesis of 1*H*-2-Benzothiopyrans from 2 and Alkynes



entry	R^1	R^2	R^3	PhCl reflux time, h	products (yield)[a]
1	Me	Ph	Ph	1	**6a** (53)
2	Me	Ph	CO_2Et	1	**6b** (29),[c] **7b** (31)[c]
3	Me	Ph	COMe	0.5	**6c** (48)[c]
4	Me	Ph	CHO	1	**7c** (57)[c]
5	Et	Ph	Ph	1	**6d** (90)
6	Et	Ph	CO_2Et	1	**6e** (50)[b,c] **7b** (48)
7	Et	Ph	COMe	0.5	**6f** (69)[c]
8	t-Bu	Ph	Ph	0.5	**7a** (80%)
9	t-Bu	Ph	CO_2Et	1	**7b** (91)[c]
10	t-Bu	Ph	CHO	1	**7c** (78)

[a] Isolated yield; product gave satisfactory ^1H and ^{13}C spectra. [b] Product of limited purity. [c] Regiochemistry by ^1H NMR and by comparison with **7c**.

Scheme 3



were obtained exclusively after alkyne insertion/depalladation. During the formation of **7b** we were able to detect isobutene by gas-phase chromatography (Scheme 3).

One major asset of these reactions is the high degree of regioselectivity associated with the formation of **6** and **7** starting from dissymmetric alkynes (Table 1, entries 2–4, 6, 7, 9, 10), and in line with many previous results the phenyl group ends up in the 3-position of the final heterocycle. This was evident from the ^1H NMR spectrum of **7b**; the aromatic proton observed as a doublet at $\delta = 7.95$ ppm is obviously the H_5 proton due to the deshielding effect of the adjacent ester group. In **7c** a doublet can similarly be found at $\delta = 8.26$ ppm and, hence, the regioselectivity was assigned such that the carbonyl group was in the 4-position. Conversely, in **7a** where a phenyl group flanks the H_5 proton, the latter is shielded and can be found as a doublet at $\delta = 6.5$ ppm.

An X-ray crystal structure of **7c**, of crystals formed from a CH_2Cl_2/acetonitrile solution, was undertaken and showed that a new C–S bond has been formed between the previously palladated carbon (C5 in ORTEP plot, see Figure 1) and the palladium-bound sulfur atom. **7c** adopts a half-boat conformation in the solid state, and bond lengths and angles are similar to those of reported thiopyrans.[20] The methylene protons of **7c** appeared as a singlet in the ^1H NMR spectrum at rt and even at −90 °C (in CD_2Cl_2), suggesting that there is a low energy barrier to ring inversion. The phenyl group, as predicted by ^1H NMR, is in the 3-position of the heterocycle.

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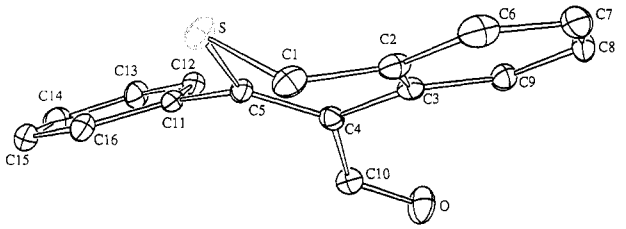
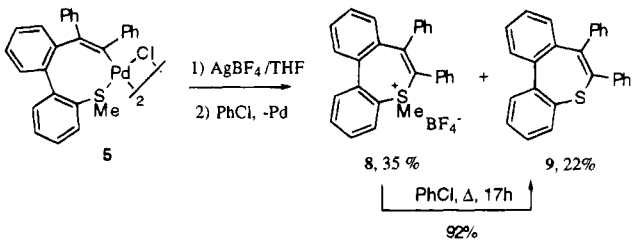


Figure 1. ORTEP plot of **7c** using the adopted numbering scheme.

Scheme 4



We were interested in exploiting the above alkyne insertion/demetalation procedure for the synthesis of thiepin derivatives. **3** was an ideal starting point for these reactions and was readily obtained by the C−H activation of the corresponding thioether derivative using $Pd(OAc)_2$ in acetic acid followed by chromatographic purification.[13] When we treated **5** (synthesized from **3** and diphenylacetylene in refluxing PhCl for 0.5 h, followed by solvent evaporation and crystallization from CH_2Cl_2/ hexane[12]) with $AgBF_4$, followed by thermolysis in PhCl, a palladium mirror was deposited and a mixture of compounds was obtained from which **8** could be precipitated by ether addition (Scheme 4).

The ether soluble fraction of the above reaction consisted of seemingly two distinct products which we were unable to separate although the absence of a υ BF_4^- showed that these were unlikely to be cationic. One of the products was identified as **9** which was prepared separately by the demethylation of **8** in refluxing PhCl overnight.

The ^1H NMR spectrum of **8** displayed a singlet at δ = 2.96 ppm and a shielded aromatic doublet at δ = 6.15 ppm (in **9** a similar doublet can be found at δ = 8.82 ppm), along with other aromatic signals. Attempts in forming other derivatives of **8** or **9** with the other alkynes employed above gave unsatisfactory results.

The structure of **8** was unequivocally established by a single crystal X-ray diffraction study of crystals obtained from CH_2Cl_2/hexane.[38] The ORTEP plot of the cationic part of one enantiomer of **8** is shown in Figure 2. It is once again apparent that a new C−S bond has been formed between S1 and C1 in the boat shaped seven-membered ring. To the best of our knowledge this is the first X-ray determination of a derivative of the dibenzo-[*bd*]thiepin family.[21] Bond alternation in **8** is apparent and, hence, there is minimal congugation in the thiepin ring in accord with calculations[22] and crystal structure determinations of similar thiepin systems.[23,24]

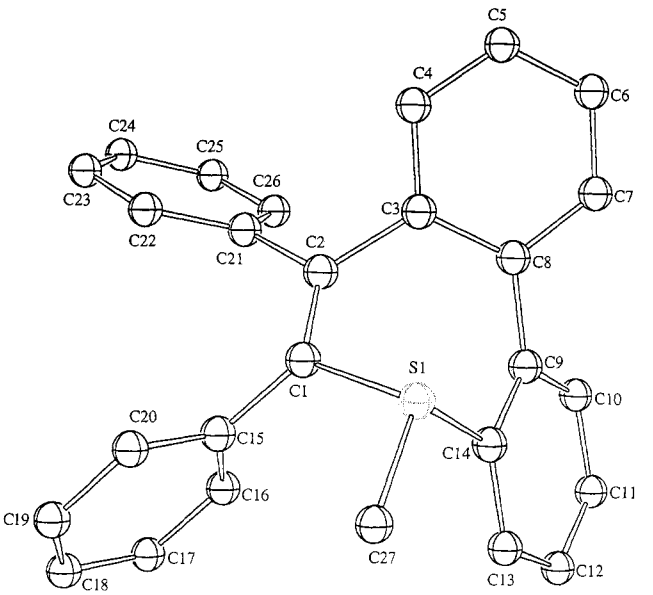


Figure 2. ORTEP plot of the cationic part of one of the enantiomers of **8** using the adopted numbering scheme.

Discussion

We have shown that it is possible to form S-heterocycles by the formal intramolecular addition of a thioether onto a vinyl group.[25] The formation of **6-9** adds to the relatively small number of intramolecular C−S bond-forming syntheses of six- and seven-membered rings. Similar derivatives to **6** have been formed mainly by the *intermolecular* formation of a C−S bond,[26] including a most remarkable, albeit limited to one alkyne, reaction which yielded a 1*H*-2-benzothiopyran in high yield and in the absence of palladium.[26a]

The syntheses of seven-membered derivatives via a C−S bond formation have been mainly applied to saturated thiepane derivatives.[27] The synthetic scope of our reactions for the thiepin derivatives **8** and **9** was unfortunately much more limited than that for **6** or **7**. At this point we can, however, seek consolation in the fact that a relatively limited number of synthetic approaches to these 8π systems exist due to their instability and facile sulfur extrusion.[28] Sophisticated methods have been employed for the synthesis of the particularly unstable

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monocyclic thiepins and both steric stabilization[29] as well as metal complexation[30] have been used to permit their isolation. Other stable systems are known in which the sulfur atom is alkylated[31] and oxidized [23] and where the thiepin ring is part of a fused system.[32] The stability of **8** may very well reside in two of the above criteria: the sulfur is alkylated and the thiepin system is part of a fused aromatic system.

The heterocyclization reactions of **5** and **4** are very similar. The cationic and neutral heterocycles **8** and **9** are formed in similar amounts from **5** (see Scheme 4). **2a** affords a ca. 1:1 mixture of **6b** and **7b** after reaction with ethyl 3-phenylpropynoate (see Table 1). Both reactions require 1 h thermolysis of the palladium-containing precursors. The neutral heterocycle **7c** is the sole product of the depalladation of **4c** under similar conditions.

In order to explain the formation of the neutral heterocycles, using **2a** or **3** as starting materials, one might be tempted to invoke the initial formation of a cationic heterocycle which, during the reflux period, is demethylated *in situ*.[33] This is quite unlikely; the cationic derivatives **6a**, **6b**, and **8** were all stable to PhCl reflux over a 1 h period. **8** required overnight reflux before furnishing **9** (see Scheme 4). **6a** afforded **7a**, and **6b** gave **7b**, both after over 30 h reflux in PhCl.

Participation of the Pd(0) liberated during the reaction, that might catalyze or induce demethylation of the cationic heterocycle, is also unlikely. When we treated **8** with 1 equiv of $Pd(dba)_2$ (PhCl reflux, 1 h) no significant demethylation was obvious from the ^1H NMR spectrum of the product mixture, although this result is not totally conclusive in so far as the Pd(0) liberated from the demetalation of **5** ought to be significantly different to $Pd(dba)_2$.

A remaining possibility for these reactions is participation of the palladium in the demethylation process *prior to the formation of the heterocyclic products*. Our reaction is in some respects reminiscent of a nucleophilic type attack on an activated metal bound thioether[34] although this suggestion remains very speculative as we have insufficient evidence to establish whether this type of process is responsible for our demethylation reactions. Water present in the reaction from the solvent or $AgBF_4$ may be the nucleophile that provokes the partial or total demethylation of the thioether group, as in the formation of **7c** (Scheme 5).

We have already shown that the heterocyclization reactions involving **2c** and alkynes are particularly selective affording neutral heterocyclic products **7** and exclusively isobutene, with no other gaseous product being detected in the gas phase. Therefore, it is quite reasonable to rule out a radical mechanism for the formation of **7** from **2c**. A cationic pathway would be much more likely but whether this process involves the dealkylation of an unstable *tert*-butylated thiopyrilium salt (i.e. **6** with R^1= t-Bu) or loss of the t-Bu group by

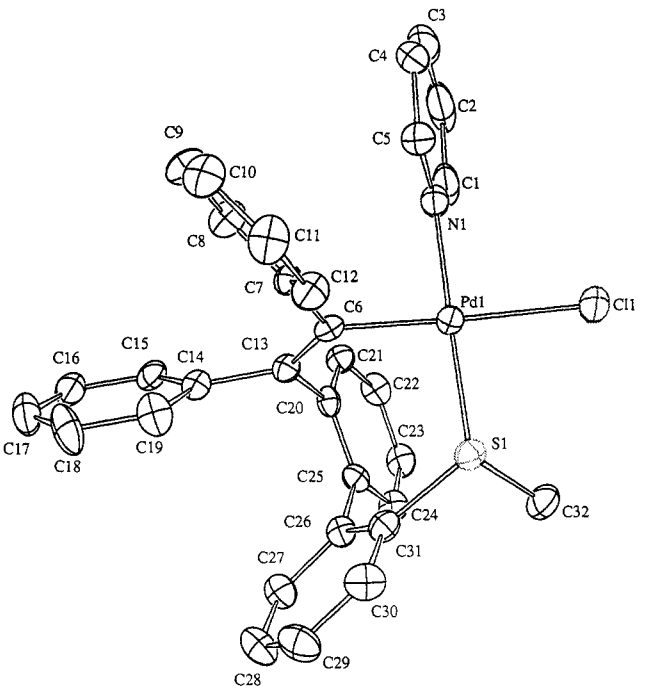
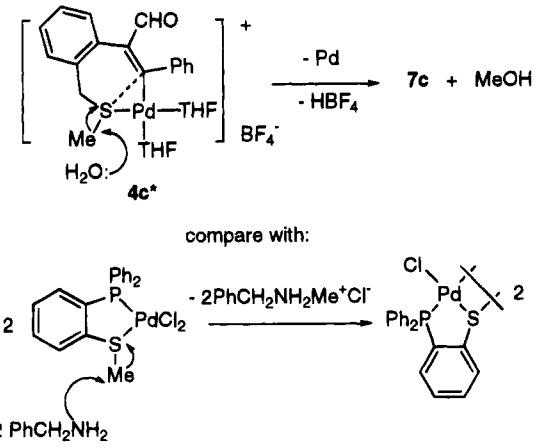


Figure 3. ORTEP plot of **5′** using the adopted numbering scheme.

Scheme 5



activation of the thioether group by the metal prior to the heterocycle formation, as in Scheme 5, has not been clarified at present.

The mechanism of the formation of the C−S bond during these demetalation reactions can be attributed to a reductive elimination type process in line with what we have proposed for the related C−N bond-forming reactions. A crystal structure determination of a derivative of **5**, **5′**, sheds some light upon this cyclization process. Crystals of **5′** were formed from a CH_2Cl_2/pyridine solution (ca. 2 mL:0.1 mL) into which hexane was diffused slowly at rt. The thioether (S1) and vinyl groups (C6 according to the adopted numbering scheme) in a mutual *cis* position in the square planar complex with a C6 to S1 distance of 3.073 Å (see Figure 3). The structures of similar alkyne-incorporated palladium complexes have been determined by X-ray methods.[35]

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Conclusion

We have shown that otherwise stable organometallic complexes resulting from the selective insertion of disubstituted alkynes in the Pd–C bond of cyclopalladated thioether complexes can be selectively depalladated to yield cationic and neutral S-heterocycles. These reactions represent a new addition to the existing dearth of examples involving the intramolecular formation of a C–S bond mediated by a transition metal and demonstrate that the thiophilicity of these metals should not be an obstacle in these processes. It is hoped that these results might stimulate interest amongst synthetic chemists toward developing new transition metal mediated routes to S-heterocycles.

Experimental Section

General Comments. Experimental procedures are as reported elsewhere.[9g] Most reactions were performed in air using distilled (CH_2Cl_2 over P_2O_5, THF, *n*-hexane, and *n*-pentane over sodium) or commercial grade solvents (chlorobenzene, 1,2-dichloroethane). Silver halide abstractions, using $AgBF_4$, were performed under N_2 using conventional Schlenk techniques. NMR spectra were recorded in $CDCl_3$. *J* values are given in hertz. Alkynes, thiols, and other starting materials were used as obtained from commercial sources. **2a**,[13] **3**,[13] and (*p*-tolylsulfonyl)ethyne[36] were made using the given procedures.

Methyl 2-Iodobenzyl Sulfide (1a). This orange oil (60%) was made by a slight adaptation of a general procedure:[13] ^{1}H NMR δ 2.05 (s, 3H), 3.78 (s, 2H), 6.93 (dt, 1H, $^3J_{HH}$ = 6.6, $^4J_{HH}$ = 1.2), 7.30 (m, 2H), 7.83 (d); ^{13}C δ 15.6, 43.6, 101.4, 128.4, 128.9, 130.2, 139.9, 140.7.

Ethyl 2-Iodobenzyl Sulfide (1b). 2-Iodobenzyl chloride (IBnCl) (2.5 g, 10 mmol) and ethanethiol (0.60 g, 10 mmol) were stirred at rt in toluene (30 mL), in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (1.5 g, 10 mmol). After overnight stirring, the DBU·Cl precipitate was removed by filtration, and the organic filtrate was separated, washed with water (5 mL), and then dried over $MgSO_4$. After removal of the latter by filtration, the filtrate was evaporated to afford a yellow liquid (2.6 g, 93%) which was slightly contaminated with IBnCl: ^{1}H NMR δ 1.26 (t, 3H, $^3J_{HH}$ = 7.4), 2.51 (q, 2H), 3.82 (s, 2H), 6.92 (dt, 1H, $^3J_{HH}$ = 5.8, $^4J_{HH}$ = 1.9), 7.24–7.36 (m, 2H), 7.82 (d); ^{13}C δ 14.8, 25.9, 41.3, 100.9, 128.4, 128.7, 130.0, 139.8, 141.2.

***tert*-Butyl 2-Iodobenzyl Sulfide (1c).** IBnCl (2.5 g, 10 mmol) and 2-methyl-2-propanethiol (0.900 g, 10 mmol) were stirred at rt in a mixture of toluene and water (10 mL/10 mL), in the presence of NaOH (0.900 g, 22.5 mmol) and Adogen (0.050 g). After 1 h stirring, the organic phase was separated, washed with water (5 mL) and then dried over $MgSO_4$. After removal of the latter by filtration, the yellow filtrate was evaporated to afford a yellow liquid (2.98 g) which upon slow evaporation yielded a yellow waxy solid: yield 2.62 g (88%): ^{1}H NMR δ 1.39 (s, 9H), 3.86 (s, 2H), 6.90 (dt, 1H, $^3J_{HH}$ = 6, $^4J_{HH}$ = 1.6), 7.28 (dt, 1H), 7.43 (dd,$^3J_{HH}$ = 7.6), 7.80 (dd); ^{13}C NMR δ 31.1, 38.8, 43.2, 100.7, 128.5, 128.7, 130.4, 139.7, 141.1. Anal. Calcd for $C_{11}H_{15}IS$: C, 43.15; H, 4.94. Found: C, 43.66; H, 5.06.

Benzyl 2-Iodobenzyl Sulfide (1d). This orange liquid was made as for **1c** from IBnCl (1.248 g, 4.96 mmol) and benzenethiol (0.617 g, 4.96 mmol): yield 1.548 g (92%): ^{1}H NMR δ 3.71, 3.73 (2s, 4H), 6.92–7.35 (m, 8H), 7.86 (d, 1H, $^3J_{HH}$ = 7.9); ^{13}C δ 36.4, 41.2, 101.1, 127.2, 128.4, 128.7, 128.8, 129.2, 130.1, 138.0, 139.9, 140.7; *m/z* 340 (M^+), 249 (69%, M^+ – benzyl), 212 (100%, M^+ – HI).

Allyl 2-Iodobenzyl Sulfide (1e). This yellow oil was made by the same route as **1c** starting from IBnCl (1.25 g, 4.96 mmol) and 2-propene-1-thiol (0.515 g, 80% commercial grade): yield 1.3 g (90%); ^{1}H NMR δ 3.10 (dd, 2H, $^3J_{HH}$ = 7.0, $^4J_{HH}$ = 0.9), 3.75 (s, 2H), 5.17 (m, 2H), 5.80 (1H, m), 6.93, 7.30 (2m, 3H), 7.84 (d, $^3J_{HH}$ = 7.7); ^{13}C δ 34.7, 40.4, 101.1, 117.7, 128.3, 128.8, 130.1, 134.3, 139.9, 140.8; *m/z* 290 (M^+, 40%), 217 (100%, M^+– *S*-allyl).

***p*-Tolyl 2-Iodobenzyl Sulfide (1f).** This orange oil was made by the above method from IBnCl (2.58 g, 10.23 mmol) and *p*-toluenethiol (1.27 g, 10.23 mmol): yield 2.30 g (66%): ^{1}H NMR δ 2.31 (s, 3H), 4.15 (s, 2H), 6.90–7.25 (m, 7H), 7.83 (d, 1H, $^3J_{HH}$ = 7.1); ^{13}C δ 21.5, 45.5, 101.1, 128.4, 128.8, 129.0, 129.9, 130.1, 130.3, 131.7, 132.2, 137.0, 139.8, 140.4.

2-Iodobenzenethiol (1g). This oil was made from I-BnCl (2.52 g, 10 mmol) and thiourea (0.76 g, 10 mmol), followed by NaOH hydrolysis using the procedure described for benzenethiol:[37] yield 2.42 g (74%): ^{1}H NMR δ 1.99 (t, 1H, $^3J_{HH}$ = 8.1), 3.80 (d, 2H), 6.91 (dt, 1H, $^3J_{HH}$ = 7.2, $^4J_{HH}$ = 1.5), 7.24–7.36 (m, 2H), 7.82 (d); ^{13}C δ 34.8, 99.8, 129.0, 129.0, 129.4, 139.9, 143.8; *m/z* 250 (M^+), 217 (100%, M^+ – SH).

[$C_6H_4CH_2$-2-SMePdI]$_2$ (2a′). This was obtained as an orange solid: yield 0.420 g (56%) according to the method for **2c**, using **1a** (0.597 g, 2.26 mmol) and Pd(dba)$_2$ (1.17 g, 2.04 mmol). Its ^{1}H NMR spectra is identical to that of its chloro analogue.[13]

[$C_6H_4CH_2$-2-SEtPdI]$_2$ (2b). This was obtained as an orange solid: yield 0.505 g (67%), from **1b** (0.615 g, 2.21 mmol) and Pd(dba)$_2$ (1.13 g, 1.97 mmol) by the same method given for **2c**: ^{1}H NMR δ 1.48 (t, 3H, $^3J_{HH}$ = 6.0), 3.02 (m, 2H), 3.92, 4.35 (2d (AB), 2H), 6.84 (t, 1H, $^3J_{HH}$ = 7.6), 6.95 (d, $^3J_{HH}$ = 7.2), 7.08 (d), 7.90 (d). Anal. Calcd for $C_9H_{11}IPdS$: C, 28.11; H, 2.88. Found: C, 28.01; H, 2.48.

[$C_6H_4CH_2$-2-StBuPdI]$_2$ (2c). **1c** (1.29 g, 4.2 mmol) and Pd(dba)$_2$ (2.03 g, 3.5 mmol) were stirred overnight in toluene (50 mL) at rt. After filtration over Celite, to remove traces of metallic palladium formed, CH_2Cl_2 (100 mL) was added to wash the product through, and the combined filtrates were evaporated. The resulting yellow solid was placed in a Soxhlet apparatus and the excess dba removed by overnight extraction with hexane. The extracts were discarded and after drying and washing with ether (ca. 40 mL), a yellow solid was obtained: yield 0.990 g (68%); ^{1}H NMR δ 1.42 (s, 9H), 3.86, 4.41 (2bs, 2H), 6.80 (t, 1H, $^3J_{HH}$ = 6.0), 6.91 (t, 1H), 7.03 (d, $^3J_{HH}$ = 8.0), 7.87 (m). Anal. Calcd for $C_{11}H_{15}IPdS$: C, 32.02; H, 3.66. Found: C, 32.38; H, 3.67.

[$C_6H_4CH_2$-2-SCH$_2C_6H_4$PdI]$_2$ (2d). This was obtained as a green solid: yield 0.340 g (44%) from **1d** (0.670 g, 1.97 mmol) and Pd(dba)$_2$ (1.0 g, 1.74 mmol) by the above method: ^{1}H NMR δ 3.77, 4.36 (2m (AB), 2H), 4.09 (m (AB), 2H), 6.85–7.40 (m, 8H), 7.93 (d, $^3J_{HH}$ = 7.7). Anal. Calcd for $C_{14}H_{13}IPdS$: C, 37.65; H, 2.93. Found: C, 37.73; H, 2.95.

[Pd{C(Ph)=(CHO)C_6H_4-2-SMe}(μ-Cl)]$_2$ (4c). **2a** (0.170 g, 0.61 mmol) and phenylpropargyl aldehyde (PPA) (0.080 g, 0.61 mmol), in CH_2Cl_2 (20 mL), were stirred for 2 h at rt. After solvent concentration to ca. 2 mL and hexane addition (20 mL), a yellow solid was collected by filtration and dried: yield 0.180 g (73%). A small sample was transformed into its pyridine monomer **4g** in order to simplify its NMR spectrum[11,12] and for analytical purposes: ^{1}H NMR δ 2.71 (s, 3H), 3.37, 3.97 (2d, 2H, $^2J_{HH}$ = 13.0), 6.82 (d, 1H, $^3J_{HH}$ = 4.8), 7.15–7.57 (m, 10H); 7.72 (dt, 1H, $^3J_{HH}$ = 7.7), 8.26 (d, 2H, $^3J_{HH}$ = 4.6), 9.34 (s, 1H). Anal. Calcd for $C_{22}H_{20}ClNOPdS$: C, 54.10; H, 4.13. Found: C, 53.73; H, 3.84.

[Pd{C(Ph)=C(SO$_2$-*p*-tol)C_6H_4-2-SMe} (μ-Cl)]$_2$ (4d). This yellow solid was formed in 90% yield from **2a** and (*p*-tolylsulfonyl)ethyne with overnight stirring using the method used for **4c**: ^{1}H NMR δ ($CDCl_3$ and pyridine-d_5): 2.31 (s, 3H), 2.52 (s, 3H), 2.93, 3.27 (AB, 2H, $^3J_{HH}$ = 13.3), 6.54 (m, 1H), 6.98–7.26 (m, 10H); 7.41 (t, 1H, $^3J_{HH}$ = 7.3), 7.58 (t, 1H), 8.02 (d, 1H, $^3J_{HH}$ = 7.4). Anal. Calcd (for **4h**) $C_{22}H_{20}ClNOPdS$: C, 51.60; H, 3.96. Found: C, 52.07; H, 3.96.

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(38) The authors have deposited experimental details concerning the crystal structure determination of compounds **5′**, **7c**, and **8**, atomic coordinates, thermal parameters, lists of bond distances and angles at the Cambridge Crystallographic Data Centre. These data can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

[Pd{C(Ph)=C(Ph)C_6H_4-2-St-Bu}(μ-I)]$_2$ (4e). This was obtained as an orange solid: yield 0.196 g (81%) by heating **2c** (0.170 g, 0.41 mmol) and diphenylacetylene (DPA) (0.085 g, 0.48 mmol) according to the method given for **4f**. ^{1}H NMR δ 1.16, 1.20, 1.21, 1.25, 1.29, (m, 9H), 3.71, 4.19 (2m, 2H), 6.83−7.82 (m, 14H). Anal. Calcd for $C_{25}H_{25}IPdS$: C, 49.55; H, 4.20. Found: C, 49.79; H, 4.18.

[Pd{C(Ph)=(CO_2Et)C_6H_4-2-St-Bu}(μ-I)]$_2$ (4f). A solution of **2c** (0.216 g, 0.52 mmol) and ethyl 3-phenylpropynoate (EPP) (0.100 g, 0.57 mmol) in 1,2-dichloroethane (20 mL) was heated under reflux for 1.5 h. After solvent evaporation, washing with hexane (20 mL), and drying *in vacuo*, an orange solid was obtained: yield 0.245 g (80%); ^{1}H NMR δ 0.82 (m, 3H), 1.30 (m, 9H), 3.57, 4.02 (m, 2H), 3.87 (m, 2H), 7.2−7.69 (m, 9H). Anal. Calcd for $C_{22}H_{25}IO_2PdS$: C, 45.03; H, 4.29. Found: C, 45.05; H, 4.39.

1*H*-2-*S*-Methyl-3,4-diphenylbenzothiopyrilium Tetrafluoroborate (6a). To **4a**[11] (0.525 g, 1.14 mmol) in a mixture of CH_2Cl_2/ether (60 mL/10 mL) was added $AgBF_4$ (0.30 g, 1.5 mmol). After 0.5 h stirring at rt, the AgCl filtrate was removed by filtration over Celite. The resulting red filtrate was evaporated to afford a brown solid. The latter was heated for 1 h in refluxing chlorobenzene (PhCl) (40 mL) during which metallic palladium was formed. After cooling and Celite filtration, the filtrate was evaporated *in vacuo* yielding an orange oil. The latter was dissolved in CH_2Cl_2 (ca. 5 mL) and a beige solid **6a** was precipitated by pentane addition (ca. 40 mL), collected by filtration, and dried: yield 0.245 g (53%); ^{1}H NMR δ 2.99 (s, 3H), 5.03, 5.15 (AB, 2H, $^2J_{HH}$ = 16.0), 7.05−7.67 (m, 14H); ^{13}C NMR δ 21.9, 38.6, 119.5, 122.1, 128.5, 128.9, 129.1, 129.8, 130.1, 130.3, 130.7, 131.7, 132.1, 132.9, 135.3, 148.6; IR (cm^{-1}) 1080 (BF_4^-). Anal. Calcd for $C_{22}H_{19}BF_4S$ (+0.25 CH_2Cl_2): C, 63.10; H, 4.61. Found: C, 62.99; H, 4.64.

1*H*-2-*S*-Methyl-3-phenyl-4-carbethoxybenzothiopyrilium Tetrafluoroborate (6b). To **4b**[11] (0.580 g, 1.28 mmol) in THF (20 mL) was added $AgBF_4$ (0.290 g, 1.5 mmol). After 1 h stirring at rt, filtration over Celite to remove the AgCl precipitate, and evaporation of the filtrate, a yellow solid was obtained. The latter was heated for 1 h in refluxing PhCl (40 mL). After cooling and solvent evaporation, the black residue was extracted with CH_2Cl_2 (ca. 50 mL) and filtered over a silica column. The first yellow band, **7b**, was obtained as an oil: yield 0.116 g (31%) after solvent evaporation. Elution with CH_2Cl_2/acetone (30 mL/70 mL) afforded an oil **6b** which partially crystallised upon slow evaporation of the solvent *in vacuo*: yield 0.148 g (29%): (**6b**) ^{1}H NMR δ 0.97 (t, 3H, $^3J_{HH}$ = 7.1), 2.80 (s, 3H), 4.15 (dq, (ABX_3), 2H, $^2J_{HH}$ = 14.2), 4.92, 5.23 (2d, 2H, $^2J_{HH}$ = 16.6), 7.55−7.71 (m, 9H); ^{13}C NMR δ 13.6, 20.7, 37.9, 63.0, 120.9, 123.5, 126.6, 128.2, 128.0, 129.6, 129.8, 130.7, 131.2, 131.6, 132.9, 140.2, 144.5, 164.4; IR (cm^{-1}) 1063 (BF_4^-), 1717 (CO); *m*/*z* 311 (M^+), 295 (10%, $M^+ - CH_3$).

1*H*-2-*S*-Methyl-3-phenyl-4-acetylbenzothiopyrilium Tetrafluoroborate (6c). **2a** (0.215 g, 0.85 mmol) and 4-phenyl-3-butyn-2-one (0.113 g, 0.8 mmol) were stirred at rt for 1 h in CH_2Cl_2 (20 mL). After solvent evaporation, the residue was stirred in THF (20 mL) with $AgBF_4$ (0.160 g, 0.8 mmol) for 1 h. After removal of the AgCl over Celite and evaporation of the filtrate, the resulting yellow solid was heated for 0.5 h in refluxing PhCl (40 mL). The resulting black suspension was filtered over Celite, and after solvent evaporation, a brown solid could be obtained by precipitation from CH_2Cl_2/pentane and drying *in vacuo*: yield 0.140 g (48%); ^{1}H NMR δ 2.12 (s, 3H), 2.67 (3H, s), 5.06, 5.32 (AB, 2H, $^2J_{HH}$ = 15.0), 7.25−7.65 (m, 9H); ^{13}C NMR δ 20.2, 30.9, 37.6, 120.7, 121.2, 123.6, 125.9, 127.4, 129.7, 130.5, 131.1, 131.7, 132.6, 134.6, 147.1; 201.3; IR (cm^{-1}) 1080 (BF_4^-), 1700 (CO); *m*/*z* (EI): 266 (M^+ − Me). Anal. Calcd for $C_{18}H_{17}BF_4OS$: C, 58.72; H, 4.65. Found: C, 58.98; H, 4.74.

1*H*-2-*S*-Ethyl-3,4-diphenylbenzothiopyrilium Tetrafluoroborate (6d). **2b** (0.190 g, 0.49 mmol) and DPA (0.105 g, 0.59 mmol) were heated in refluxing 1,2-dichloroethane (30 mL) for 1 h. After solvent evaporation, $AgBF_4$ (0.120 g, 0.61 mmol) was added in THF (30 mL). Removal of the AgI precipitate over Celite, solvent evaporation, and PhCl reflux following the procedure for **6a** afforded a red oil. The latter was dissolved in CH_2Cl_2 (5 mL) and a pink solid was precipitated by pentane addition (20 mL), collected by filtration, and dried: yield 0.185 g (90%); ^{1}H NMR δ 1.42 (t, 3H $^3J_{HH}$ = 7.4), 3.45 (dq (ABX_3), 2H, $^2J_{HH}$ = 14.2), 5.12 (bs (AB), 2H), 7.01−7.64 (m, 14H); ^{13}C NMR δ (poor solubility) 9.8, 35.1, 36.7, 128.7, 129.1, 129.7, 130.1, 130.4, 131.9, 132.8, 133.4; IR (cm^{-1}) 1060 (BF_4^-); *m*/*z* (FAB) 329.1 (M^+). Anal. Calcd for $C_{23}H_{21}BF_4S$ (+0.25 H_2O): C, 64.95; H, 5.21. Found: C, 65.33; H, 5.20.

1*H*-2-*S*-Ethyl-3-phenyl-4-carbethoxybenzothiopyrilium Tetrafluoroborate (6e). **2b** (0.205 g, 0.53 mmol) and EPP (0.105 g, 0.6 mmol) were stirred in dichloromethane (20 mL) for 2 h at rt. An orange oil was obtained after solvent evaporation. Stirring with $AgBF_4$ (0.120 g, 0.62 mmol) in THF (30 mL) for 1 h at rt, subsequent filtration over Celite, and solvent evaporation afforded an orange oil/solid. Reflux in PhCl (40 mL) for 1 h gave a black suspension, and this was followed by cooling. Celite filtration and solvent evaporation afforded an oil. A rather unstable, difficult to purify, brown solid **6e** was precipitated from CH_2Cl_2/pentane (2 mL : 25 mL): yield 0.112 g (50%) and an orange filtrate **7b** was obtained from the evaporated filtrate: yield 0.075 g (48%); ^{1}H NMR δ 0.96 (t, 3H, $^3J_{HH}$ = 7.1), 1.25 (t, 3H, $^3J_{HH}$ = 7.1), 3.25, 3.37 (dq (ABX_3), 2H, $^2J_{HH}$ = 13.2), 4.13 (dq (ABX_3)), 4.95, 5.23 (2d (AB), 2H, $^2J_{HH}$ = 16.9), 6.8−7.75 (m, 9H); ^{13}C NMR δ 9.5, 13.4 (2 CH_3), 35.0, 36.8, 63.0 , 121.6, 121.8, 126.5, 127.0, 127.8, 128.4, 129.5, 129.8, 130.5, 131.0, 131.4, 132.4, 132.8, 140.8, 164.3; IR (cm^{-1}) 1080 (BF_4^-), 1720 (CO); *m*/*z* (FAB) 325.1 (M^+).

1*H*-2-*S*-Ethyl-3-phenyl-4-acetylbenzothiopyrilium Tetrafluoroborate (6f). A CH_2Cl_2 solution (20 mL) of **2b** (0.350 g, 0.91 mmol) and 4-phenyl-3-butyn-2-one (0.145 g, 1 mmol) was stirred at rt for 2.5 h. After solvent evaporation, an orange solid was obtained. To the latter, in THF (20 mL), was added $AgBF_4$ (0.210 g, 1.08 mmol). After 1 h stirring and removal of the AgI precipitate by filtration over Celite (the latter was washed with a further 20 mL CH_2Cl_2), an orange filtrate was obtained which was evaporated to dryness. The resulting orange solid was placed in PhCl (40 mL) and heated at reflux temperature for 0.5 h. After the usual workup, a brown solid was obtained from CH_2Cl_2/pentane, collected by filtration, and dried: yield 0.240 g (69%); ^{1}H NMR δ 1.21 (t, 3H, $^3J_{HH}$ = 7.5), 2.10 (s, 3H), 3.45 (2dq (ABX_3), 2H), 5.12, 5.32 (AB, 2H, $^2J_{HH}$ = 16.5), 7.30−7.69 (m, 9H); ^{13}C NMR δ 9.4, 30.7, 34.4, 36.6, 119.2, 122.0, 125.9, 126.0, 127.3, 129.6, 130.3, 131.0, 131.5, 132.1, 132.5, 139.5, 147.8, 201.4; IR (cm^{-1}) 1080 (BF_4^-), 1706 (CO); *m*/*z* (FAB) 295.1 (M^+). Anal. Calcd for $C_{19}H_{19}BF_4OS$: C, 59.70; H, 5.01. Found: C, 60.27; H, 5.06.

1*H*-2-*S*-3, 4-Diphenylbenzothiopyran (7a). To **4e** (0.169 g, 0.285 mmol) in a mixture of CH_2Cl_2/ether (10 mL: 10 mL) was added $AgBF_4$ (0.080 g, 0.41 mmol). After 0.5 h stirring at rt, filtration over Celite to remove the AgI precipitate, and evaporation of the red filtrate, an orange solid was obtained. The latter was heated for 0.5 h in refluxing PhCl (40 mL). After cooling, the dark solution was filtered over Celite to remove the metallic palladium formed and the filtrate was evaporated *in vacuo*. A yellow oil was obtained using the workup for **7c**: yield 0.070 g (80%); ^{1}H NMR δ 4.02 (s, 2H), 6.85 (d, 1H, $^3J_{HH}$ = 7.4), 7.05−7.70 (m, 13H); ^{13}C NMR δ 32.5, 126.4, 126.8, 127.1, 127.3, 127.9, 128.7, 128.9, 129.1, 131.4, 131.4, 135.2, 136.5, 139.0, 139.8; *m*/*z* 300 (M^+).

1*H*-2-*S*-3-Phenyl-4-carbethoxybenzothiopyran (7b). **4f** (0.245 g, 0.42 mmol) was treated with $AgBF_4$ (0.110 g, 0.57 mmol) in THF (20 mL), followed by PhCl reflux using the same conditions as for the formation of **6b**. An orange oil was obtained: yield 0.113 g (91%); ^{1}H NMR δ 0.86 (t, 3H,$^3J_{HH}$ = 7.1), 3.94 (q, 2H), 3.97 (s, 2H), 7.18−7.57 (m, 8H), 7.93 (dd, 1H, $^3J_{HH}$ = 5.1, $^4J_{HH}$ = 2.9); ^{13}C NMR δ 13.6, 32.7, 61.0, 125.2, 126.7, 127.8, 128.2, 128.4, 129.6 132.1, 138.4, 145.1, 168.0; IR (cm^{-1}) 1195 (CO), 1716 (CO); *m*/*z* 296 (M^+).

1*H*-2-*S*-3-Phenyl-4-formylbenzothiopyran (7c). **2c** (0.210 g, 0.51 mmol) and PPA (0.080 g, 0.61 mmol) were refluxed in 1,2-dichloroethane (20 mL) for 1 h. An orange solid was obtained after solvent concentration, hexane addition (30 mL), and evaporation of the combined solvents. Stirring a THF solution (40 mL) of this solid with $AgBF_4$ (0.120 g, 0.6 mmol) for 0.75 h was followed by AgI filtration and filtrate evaporation. Following 1 h PhCl reflux (40 mL) and CH_2Cl_2 (60 mL) extraction, Celite filtration afforded a dark solution. Concen-

tration of this solution, followed by hexane addition, and filtration to remove impurities gave **7c** as an orange oil: yield 0.095 g (78%) after solvent evaporation. Crystals suitable for X-ray diffraction could be obtained from slow evaporation of a $CHCl_3$/acetonitrile solution: ^1H NMR δ 3.94 (s, 2H), 7.20–7.62 (m, 8H), 8.26 (d, 1H, $^3J_{HH} = 6.0$), 9.97 (s, 1H); ^{13}C NMR δ 33.4, 119.8, 121.7, 123.7, 124.6, 125.2, 126.2, 127.2, 127.4, 127.5, 128.4, 128.7, 128.8, 130.0, 131.2, 131.4, 131.5, 131.9, 133.2, 134.9, 165.8, 187.6; IR (cm^{-1}) 1669 (CO); *m/z* 252 (M^+). Anal. Calcd for $C_{16}H_{12}OS$ (+0.5 H_20): C, 73.53; H, 5.01. Found: C, 74.02; H, 4.56.

6,7-Diphenyl-*S*-methyldibenzo[*bd*]thiepinium Tetrafluoroborate (8). **5** (0.190 g, 0.37 mmol) and $AgBF_4$ (0.090 mg, 0.46 mmol) were stirred in CH_2Cl_2/THF (20 mL/5 mL) for 1 h at rt. After the usual AgCl filtration and evaporation of the filtrate, the resulting orange solid was heated in refluxing PhCl (30 mL) for 1.25 h. After cooling, Celite filtration, and solvent evaporation according to the above procedures, a crude beige solid was obtained from CH_2Cl_2/hexane (2 mL: 20 mL), collected by filtration, and dried. The filtrate was evaporated to afford an orange solid (0.060 g). The beige solid was filtered over silica (acetone eluant) to yield an oil **8**: yield 0.060 g (35%). X-ray quality crystals were obtained by slow diffusion of hexane into a CH_2Cl_2 solution of **8**: ^1H NMR δ 2.96 (s, 3H), 6.15 (d, 1H, $^3J_{HH} = 7.4$), 6.83–7.97 (m, 17H); IR 1080 (BF_4^-);(cm^{-1}); *m/z* 376 (M^+, 9%), 362 ($M^+ - CH_3$, 100%). Anal. Calcd for $C_{27}H_{20}BF_4S$: C, 69.84; H, 4.56. Found: C, 69.86; H, 4.77.

6,7-Diphenyldibenzo[*bd*]thiepin (9). **8** (0.098 g, 0.21 mmol) was heated in PhCl (20 mL) for 17 h. After solvent evaporation *in vacuo* and filtration of the residue over alumina (CH_2Cl_2 eluant), a yellow paste was obtained, after solvent evaporation, which was reextracted with hexane. Evaporation of the latter extracts yielded a pale yellow paste: yield 0.070 g (92%); ^1H NMR δ 7.09–7.67 (m, 17H), 8.82 (d, 1H, $^3J_{HH} = 8.6$); *m/z* 362 ($M^+ + H$, 32%), 330 ($M^+ + H - S$, 100%).

Acknowledgment. A. Dégremont and S. Libs are gratefully thanked for their valuable technical assistance. The Commission of the European Communities is thanked for financial support of this project (grant no. ERBSCC*CT000011).

Supplementary Material Available: Figure 4 showing the X-ray crystal structures of the two enantiomers of **8** (both present in the asymmetric unit of the unit cell) respectively.[38] Copies of ^1H and ^{13}C NMR spectra of compounds for which elemental analyses were not obtained (i.e. **1a,b,d–f, 6b,e, 7a,b**, and **9**) (21 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of this journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO941877H