HETEROCYCLES, Vol. 86, No. 2, 2012, pp. 1253 - 1260. © 2012 The Japan Institute of Heterocyclic Chemistry
Received, 30th June, 2012, Accepted, 10th August, 2012, Published online, 24th August, 2012
DOI: 10.3987/COM-12-S(N)80

AZULENOPENTATHIEPIN: PREPARATION AND CONVERSION INTO AZULENES WITH SULFUR GROUPS AT THE 1- AND 2-POSITIONS

Ohki Sato,* Atsushi Sakai, Masami Aoki, Takaaki Kuramochi, and Juzo Nakayama

Department of Chemistry, Graduate School of Science and Engineering, Saitama University, Shimo-okubo 255, Sakura-ku, Saitama 338-8570, Japan; E-mail: ohkisato@chem.saitama-u.ac.jp

Abstract – Azulenopentathiepin was prepared by the reaction of azulene with elemental sulfur in boiling pyridine. Bis(thiolate) generated from the pentathiepin reacted with electrophiles such as iodomethane, methyl chloroformate, *N,N'*-carbonyldiimidazole and *N,N'*-thiocarbonyldiimidazole to afford the corresponding azulene derivatives. Desulfuration of the pentathiepin and the successive reaction with DMAD or a Pd(0) reagent afforded a 1,4-dithiin compound or Pd complexes.

INTRODUCTION

Azulenes are one of the most interesting classes in non-benzenoid aromatics and their chemical, physical and biological properties are of interest. Particularly, their electrochemical properties much attracted our attention and we had already reported azulene-based electron acceptors such as azulenequinones[1a] and tetracyanoazulenequinodimethanes.[1b,c] Our next interest is focused on azulene-based electron donors. For their construction, sulfur groups (*S*-groups) should be introduced into an azulene skeleton. However, synthetic methods for *S*-substituted azulene derivatives have not been much investigated,[2] and no method for direct introduction of *S*-groups at the 2-position is known so far as we are aware. [1,2,3,4,5]Pentathiepins[3] are stable seven-membered ring compounds with five sulfur atoms and a carbon-carbon double bond. Various pentathiepins fused to aromatics such as benzene,[4a] naphthalene,[4b] phenanthrene,[4b] thiophene,[4c] pyrrole[4c] and ferrocene[4d] etc. were prepared, and they could be converted to 1,2-bis(*S*-substituted) aromatics.

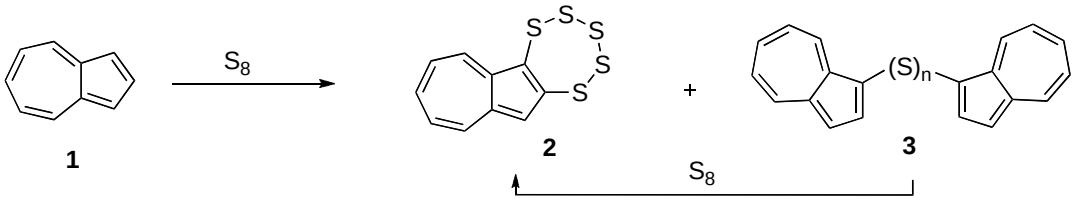
This paper is dedicated to Prof. Ei-ichi Negishi on the occasion of his 77th birthday.

We report herein the preparation of a new class of pentathiepin, azuleno[1,2-*f*][1,2,3,4,5]pentathiepin (**2**) by the sulfuration of azulene (**1**) with elemental sulfur in boiling pyridine, and its conversion into azulene derivatives with *S*-groups at the 1- and 2-positions.

RESULTS AND DISCUSSION

A reaction of azulene (**1**) with elemental sulfur in 1,2,4-trichlorobenzene (1,2,4-TCB) under thermal conditions afforded only bis(1-azulyl)sulfides (**3**) with an insoluble black solid and recovery of **1** (Table 1, Entry 1). **3** were a mixture of biazulenes connecting with one, two, three and more sulfur atoms (n = 1,[2d,e] 2,[2e] 3 and more) at a 1-position of both azulene moieties. The black solid might be a complex mixture of azulene oligomers and polymers networking with sulfur atoms at the 1-, 2- and/or 3-positions. In contrast, the reaction in boiling pyridine yielded a novel azulene-based cyclic pentasulfide, azulenopentathiepin (**2**) together with **3** and a black solid. The yield of **2** was improved owing to prevent intermolecular reactions in the diluted concentration (Entry 2: 6.0 x 10^{-2} M; Entry 3: 1.0 x 10^{-2} M). It is well known the low reactivity at a 2-position of azulenes[5] in electrophilic substitutions. Nevertheless, the surprising sulfration at the position would proceed on account of the generation of highly reactive species derived from S_8-pyridine. Activation of elemental sulfur by using pyridine was reported in preparation of a trisulfane from a cycloheptatriene.[6] **2** was also obtained by the reaction of **3** ($n_{ave.}$ = 4, determined by elemental analysis, from the reaction in Entry 3) with elemental sulfur in pyridine (Entry 4). Although the yield of **2** was still not enough, the supply by successive reactions under the conditions in Entries 3 and 4 was somewhat effective, so far (total yield from **1**: 28 %).

Table 1. Reaction of azulene (**1**) or bis(1-azulyl)sulfides (**3**) with elemental sulfur



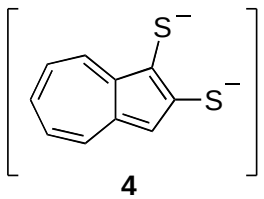
Entry	Substrate	S_8 / atoms	Solvent	Concentration / mol·L^{-1}	Temperature	Time	Yield 2	Yield 3	Yield 1
1	**1**	8	1,2,4-TCB	4.0 x 10^{-2}	130 °C	33 h	-	50 wt.%[a]	42 %
2	**1**	14	pyridine	6.0 x 10^{-2}	reflux	19 h	3 %	73 wt.%[a]	29 %
3	**1**	14	pyridine	1.0 x 10^{-2}	reflux	79 h	23 %	49 wt.%[a]	-
4	**3** ($n_{ave.}$ = 4)	15	pyridine	2.0 x 10^{-2}	reflux	63 h	23 wt.%[a]	75 wt.%[a]	-

[a] Percent by weight

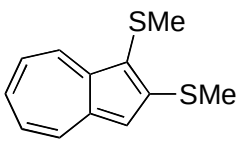
Azulenopentathiepin (**2**) was a bluish green powder [mp 142-143 °C (dec.)]. The ^{1}H NMR spectrum showed five protons at δ 7.42, 7.50, 7.77, 8.32 and 8.72 with an appropriate coupling constant (J = 9.8 Hz) as a seven-membered ring moiety of azulenes and a singlet proton at δ 7.60 as a five-membered one. The ^{13}C NMR spectrum showed ten carbons (two carbons were overlapped at δ 139.3) arising from an azulene skeleton. The longest wave-maximum of UV-VIS spectrum appeared at 605 nm (log ε 2.72) as a characteristic peak of azulene derivatives. MS spectra gave molecular ion and fragment ion peaks [FAB: *m/z* 287 (MH^+), 286 (M^+); EI: *m/z* 286 (M^+), 222 (M^+-2S)]. Together with the results of elemental analysis, those spectral data supported the proposed structure.

Electrochemical properties of **2** were investigated by CV measurement. The voltammogram showed an irreversible wave and the first reduction potential was nearly equal to that of azulene (**1**) [$(E_1^{red})_{pa}$: **2**; -2.03 V, **1**; -1.93 V]. On the other hand, its electron donation ability was slight smaller than that of **1** [$(E_1^{ox})_{pc}$: **2**; +0.97 V, **1**; +0.64 V]. These results indicated that the pentathiepin moiety would play a role of electron withdrawing group toward an azulene skeleton rather than that of donating one. ^{1}H NMR and UV-VIS spectra of **2** also suggested the withdrawing property; down field shifts of protons [**1**: δ 7.18 (t like, J = 9.9 Hz, 2H), 7.41 (d, J = 3.7 Hz, 2H), 7.60 (t like, J = 9.9 Hz, 1H), 7.92 (t, J = 3.7 Hz, 1H), 8.36 (d like, J = 9.9 Hz, 2H)] and a red shift of the longest wave-maximum [**1**: λ_{max} 580 nm (log ε 2.48)].

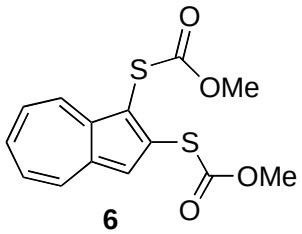
Various azulene derivatives with *S*-groups at the 1- and 2-positions could be presented by the conversion of azulenopentathiepin (**2**). Reduction of **2** with $NaBH_4$ in chlorobenzene/ethanol generated bis(thiolate) (**4**), which was methylated by iodomethane to give 1,2-bis(methylthio)azulene (**5**, a reddish violet viscous oil, 63 %). **4** generated with $LiAlH_4$ in THF was treated with methyl chloroformate to afford 1,2-bis(thiocarbonate) (**6**, a purple viscous oil, 80 %), whereas, in the case with a reactive carbonylation reagent, *N,N'*-carbonyldiimidazole to afford a cyclic compound, 2-oxo-1,3-dithiole [**7**, a blue solid, mp 136-137 °C (dec.), 99 %]. The similar reaction with *N,N'*-thiocarbonyldiimidazole afforded 2-thioxo-1,3-dithiole [**8**, green needles, mp 187-187.5 °C (dec.), 81 %]. Physical data of **5**, **6**, **7** and **8** were consistent with their proposed structures, respectively.



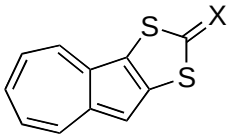
4



5



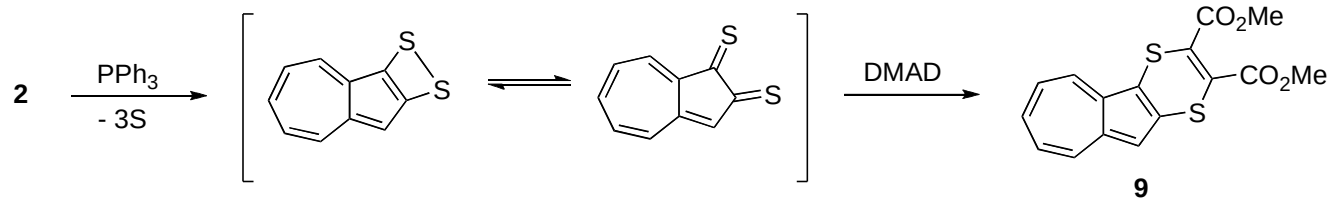
6



7: X = O
8: X = S

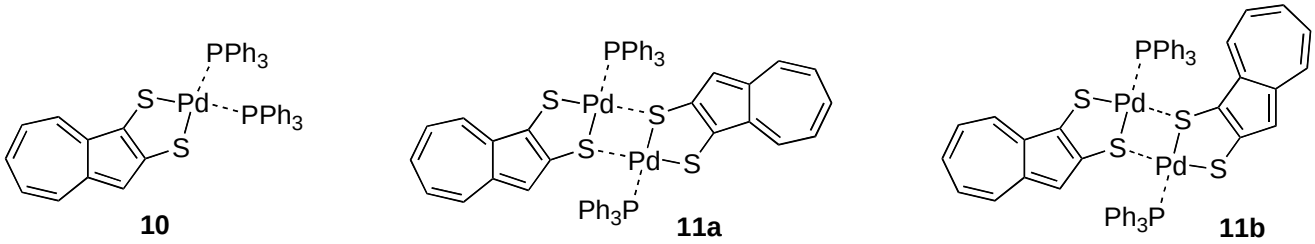
It is known that pentathiepins extruded three sulfur atoms to form intermediates dithiets and dithiones, which reacted with alkynes to give 1,4-dithiin compounds.[7] Treatment of azulenopentathiepin (**2**) with

PPh_3 in THF would generate azuleno-1,2-dithiet and -1,2-dithione as an equilibrium mixture (Scheme 1). The latter carried out a [4 + 2] cycloaddition with dimethyl acetylenedicarboxylate (DMAD) to produce azuleno-1,4-dithin (**9**, 56 %), which was a yellowish green powder (mp 90-91 °C). Its structure was confirmed by the measurement of instrumental analysis data (^{1}H and ^{13}C NMR, UV-VIS, IR and MS spectra and elemental analysis). In the case without DMAD, the reaction mixture was too complicated to define the structures.



Scheme 1.

Azulenopentathiepin (**2**) should be a precursor for an azuleno-1,2-dithiolate ligand having coordination abilities toward soft metal ions such as Pd, Pt, Hg and so on. Treatment of **2** with $Pd(PPh_3)_4$ in CH_2Cl_2 produced mono Pd complex (**10**, a dark green solid, 6 %) and dinuclear complexes (**11a** and **11b**, dark brown needles, 27 %) as an inseparable mixture of regioisomers (**11a** : **11b** = 1 : 1). **10** was rather unstable and gradually converted into **11a** and **11b** in CH_2Cl_2 at rt. FAB-MS spectra of **10** and **11** gave each molecular ion peaks (**10**: *m/z* 821 (MH^+), 820 (M^+), M = $C_{46}H_{36}P_2{}^{106}PdS_2$; **11**: *m/z* 1117 ($MH^+$), 1116 ($M^+$), M = $C_{56}H_{42}P_2{}^{106}Pd_2S_2$) together with their isotopic peaks for ^{104}Pd, ^{105}Pd, ^{108}Pd and ^{110}Pd. In ^{31}P NMR spectra, **10** and the unsymmetrical isomer (**11b**) showed two peaks with a P-P coupling constant arising from different kinds of phosphines, respectively [**10**: δ 25.3 (d, J = 31.4 Hz), 27.6 (d, J = 31.4 Hz); **11b**: δ 33.2 (d, J = 7.2 Hz), 33.9 (d, J = 7.2 Hz)]. In contrast **11a** with a center of symmetry gave only one peak at δ 32.8 (s). This reaction involves the following steps: the extrusion of three sulfur atoms from **2** in the presence of PPh_3 arising from $Pd(PPh_3)_4$ (generation of azuleno-1,2-dithiet, see in Scheme 1), the oxidative addition of Pd(0) into a S-S bond of the dithiet (formation of **10**) and the successive dimerization of **10** with elimination of PPh_3 (formation of **11a** and **11b)**. It was reported that an oxidative addition of Pd(0) to a thiophene-fused 1,2-dithiin, which was dimerized to give a dinuclear Pd complex.[8]



In conclusion, we have succeeded in the preparation of a new azulene-fused pentathiepin, azulenopentathiepin, and found that it could be a useful precursor for the conversion into azulenes with *S*-groups at the 1- and 2-positions. Further work, aimed at the construction of novel azulene-based electron donors from *S*-substituted azulenes, is in progress.

EXPERIMENTAL

Mps were determined with a Mitamura air-bath apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra ($SiMe_4$ as the internal standard) were obtained with Bruker AV500, AM400, AV300, AC300 and/or AC200 spectrometers. IR spectra were obtained with a Perkin Elmer System 2000 FT instrument and electronic spectra (UV-VIS) with a JASCO V-560 spectrophotometer. MS spectra were obtained with a JEOL JMS700AM spectrometer and CV with an ALS-600 electrochemical measuring apparatus. Unless otherwise stated the spectra were taken in the following solvents/media: IR, KBr; UV-VIS, CH_2Cl_2; ^{1}HNMR (500, 400, 300 and 200 MHz), $CDCl_3$; MS spectra were taken at 70 eV by electron impact (EI) and/or fast atom bombardment (FAB) method; CV, V *vs.* Ag/Ag^+, GC, Pt wire, 0.1 M TEAP in acetonitrile. The progress of reactions was followed by TLC method using Merck Silica gel $60F_{254}$.

General procedure for the reaction of azulene (1) or bis(1-azulyl)sulfides (3) with elemental sulfur. A solution of **1** or **3** with elemental sulfur in the solvent was stirred for the time at the temperature under Ar. After removal of the solvent *in vacuo*, the residue was dissolved in CH_2Cl_2. The soluble component was purified by SiO_2 column chromatography to give azulenopentathiepin (**2**) and/or bis(1-azulyl)sulfides (**3**, an inseparable mixture of sulfides). Atoms of elemental sulfur, solvents, concentrations, times, temperatures and yields were indicated in Table 1.

Azulenopentathiepin (2): a bluish green powder; mp 142-143 °C (dec.); ^{1}H NMR δ 7.42 (t like, J = 9.8 Hz, 1H), 7.50 (t like, J = 9.8 Hz, 1H), 7.60 (s, 1H), 7.77 (t like, J = 9.8 Hz, 1H), 8.32 (d like, J = 9.8 Hz, 1H), 8.72 (d like, J = 9.8 Hz, 1H); ^{13}C NMR δ 123.5, 127.1, 127.2, 127.4, 139.3 (2C), 140.3, 141.3, 142.4, 151.3; UV-VIS (log ε) λ_{max} 605 (2.72), 293 (4.49), 232 (4.25), 223 (4.25); CV (V *vs.* Ag/Ag^+) $(E^{red})_{pa}$ -2.72, -2.40, -2.03, $(E^{ox})_{pc}$ +0.97, +1.29, +1.85, +2.05; MS (FAB, NBA) *m/z* 287 (MH^+), 286 (M^+); MS (EI) *m/z* 286 (M^+), 222 (M^+-2S). Anal. Calcd for $C_{10}H_6S_5$: C, 41.92; H, 2.11. Found: C, 41.73; H, 2.01.

Bis(1-azulyl)sulfides [3 ($n_{ave.}$ = 4), from Entry 3 in Table 1]: a green solid; Selected ^{1}H NMR of **3** (n = 1^{2d}) δ 7.15 (t like, J = 9.8 Hz, 2H), 7.22 (t like, J = 9.8 Hz, 2H), 7.28 (d, J = 4.1 Hz, 2H), 7.61 (t like, J = 9.8 Hz, 2H), 7.74 (d, J = 4.1 Hz, 2H), 8.24 (d like, J = 9.8 Hz, 2H), 8.78 (d like, J = 9.8 Hz, 2H); Selected ^{1}H NMR of **3** (n = 2) δ 6.80 (t like, J = 9.8 Hz, 2H), 7.16 (t like, J = 9.8 Hz, 2H), 7.32 (d, J = 4.1 Hz, 2H), 7.45 (t like, J = 9.8 Hz, 2H), 7.77 (d like, J = 9.8 Hz, 2H), 7.86 (d, J = 4.1 Hz, 2H), 8.26 (d like, J = 9.8 Hz, 2H); Selected MS (FAB, NBA) *m/z* 383 [MH^+ (n = 4)], 382 [M^+ (n = 4)], 351 [MH^+ (n = 3)], 350 [M^+

(n = 3)], 319 [MH^+ (n = 2)], 318 [M^+ (n = 2)], 287 [MH^+ (n = 1)], 286 [M^+ (n = 1)]. Anal. Calcd for $C_{20}H_{14}S_4$ (n = 4): C, 62.79; H, 3.69. Found: C, 62.71; H, 4.02.

The preparation of 1,2-bis(methylthio)azulene (5): To a solution of **2** (16 mg, 5.6 x 10^{-2} mmol) in dry chlorobenzene (4.5 mL) and *abs.* EtOH (4.5 mL), 10 mol *eq.* of $NaBH_4$ was added at rt under N_2. The solution was stirred for 15 min at rt and then 200 mol *eq.* of iodomethane was added and stirred for 1 h. The reaction mixture was quenched with 2 N HCl and the aqueous layer was extracted with ether. The organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by SiO_2 column chromatography to give **5** (7.8 mg, 63 %); a reddish violet viscous oil; ^{1}H NMR δ 2.31 (s, 3H), 2.68 (s, 3H), 7.13 (s, 1H), 7.24 (dd, *J* = 9.6, 9.2 Hz, 1H), 7.32 (dd, *J* = 9.8, 9.6 Hz, 1H), 7.51 (dd, *J* = 9.8, 9.6 Hz, 1H), 8.08 (d, *J* = 9.2 Hz, 1H), 8.54 (d, *J* = 9.6 Hz, 1H); UV-VIS (log ε) λ_{max} 535 (2.18), 405 (3.74), 388 (3.64), 317 (4.43), 253 (4.06); MS (FAB, NBA) *m/z* 221 (MH^+), 220 (M^+); MS (EI) *m/z* 220 (M^+); HRMS (EI) Calcd for $C_{12}H_{12}S_2$: 220.0380. Found: 220.0383.

The preparation of bis(thiocarbonate) (6), 2-oxo-1,3-dithiole (7) or 2-thioxo-1,3-dithiole (8). To a solution of **2** in dry THF (concentration: 1.8 x 10^{-2} mM), 10 mol *eq.* of $LiAlH_4$ was added at 0 °C under Ar. The solution was stirred for 30 min at rt and then 20 mol *eq.* of methyl chloroformate, *N,N'*-carbonyldiimidazole or *N,N'*-thiocarbonyldiimidazole was added and stirred for 10 min at rt. The reaction mixture was quenched with 2 N HCl and the aqueous layer was extracted with ether. The organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The resulting residue was purified by SiO_2 column chromatography to give **6** (80 %), **7** (99 %) or **8** (81 %), respectively.

Bis(thiocarbonate) (6): a purple viscous oil; ^{1}H NMR δ 3.81 (s, 3H), 3.91 (s, 3H), 7.38 (t like, *J* = 9.6 Hz, 1H), 7.42 (t like, *J* = 9.6 Hz, 1H), 7.73 (t like, *J* = 9.6 Hz, 1H), 7.89 (s, 1H), 8.39 (d like, *J* = 9.6 Hz, 1H), 8.55 (d like, *J* = 9.6 Hz, 1H); UV-VIS (log ε) λ_{max} 555 (2.18), 375 (3.58), 345 (3.70), 310 (4.45), 299 (4.45); IR ν 1727; MS (FAB, NBA) *m/z* 309 (MH^+), 308 (M^+); MS (EI) *m/z* 308 (M^+); HRMS (EI) Calcd for $C_{14}H_{12}O_4S_2$: 308.0177. Found: 308.0181.

2-Oxo-1,3-dithiole (7): a blue solid; mp 136-137 °C (dec.); ^{1}H NMR δ 7.26 (t like, *J* = 9.8 Hz, 2H), 7.45 (s, 1H), 7.65 (t like, *J* = 9.8 Hz, 1H), 8.04 (d like, *J* = 9.8 Hz, 1H), 8.25 (d like, *J* = 9.8 Hz, 1H); UV-VIS (log ε) λ_{max} 585 (2.11), 386 (3.08), 372 (3.40), 355 (3.36), 312 (4.29), 303 (4.23), 251 (3.71); IR ν 1708; MS (FAB, NBA) *m/z* 219 (MH^+), 218 (M^+). Anal. Calcd for $C_{11}H_6OS_2$: C, 60.52; H, 2.77. Found: C, 60.31; H, 2.89.

2-Thioxo-1,3-dithiole (8): green needles; mp 187-187.5 °C (dec.); ^{1}H NMR δ 7.30 (t like, *J* = 9.8 Hz, 2H), 7.38 (s, 1H), 7.71 (t like, *J* = 9.8 Hz, 1H), 8.10 (d like, *J* = 9.8 Hz, 1H), 8.32 (d like, *J* = 9.8 Hz, 1H); UV-VIS (log ε) λ_{max} 602 (2.60), 436 (3.68), 415 (4.36), 399 (4.30), 355 (4.07), 344 (4.08), 325 (4.30), 278 (4.28), 253 (4.01); IR ν 1074; MS (FAB, NBA) *m/z* 235 (MH^+), 234 (M^+). Anal. Calcd for $C_{11}H_6S_3$: C, 56.37; H, 2.58. Found: C, 56.39; H, 2.57.

The preparation of azuleno-1,4-dithiin (9): Into a mixture of **2** (20 mg, 7.0 x 10^{-2} mmol) and 130 mol *eq.* of DMAD in dry THF (7.0 mL), 5.0 mol *eq.* of PPh_3 was added by potions over a 2 h period at rt under N_2. The solvent was removed *in vacuo* and the residue was purified by SiO_2 column chromatography to give **9** (13 mg, 56 %); a yellowish green powder; mp 90-91 °C; ^{1}H NMR δ 3.84 (s, 3H), 3.87 (s, 3H), 7.04 (s, 1H), 7.05 (t like, J = 9.8 Hz, 1H), 7.07 (t like, J = 9.8 Hz, 1H), 7.40 (t like, J = 9.8 Hz, 1H), 7.73 (d like, J = 9.8 Hz, 1H), 7.89 (d like, J = 9.8 Hz, 1H); ^{13}C NMR δ 53.3, 53.4, 109.3, 113.8, 125.0, 126.0, 127.2, 131.9, 132.1, 133.0, 134.7, 137.6, 137.7, 143.5, 163.1, 163.9; UV-VIS (log ε) λ_{max} 620 (2.74), 340 (4.62), 270 (4.59); IR ν 1735, 1716; MS (FAB, NBA) *m/z* 333 (MH^+), 332 (M^+). Anal. Calcd for $C_{16}H_{12}O_4S_2$: C, 57.81; H, 3.64. Found: C, 57.64; H, 3.56.

The reaction of azulenopentathiepin (2) with $Pd(PPh_3)_4$: To a solution of **2** (15 mg, 5.2 x 10^{-2} mmol) in dry CH_2Cl_2 (3.0 mL), 1.0 mol *eq.* of $Pd(PPh_3)_4$ was added at 0 °C under Ar and stirred for 15 min at the same temperature. The reaction mixture was quenched with saturated aqueous NH_4Cl and the aqueous layer was extracted with CH_2Cl_2. The organic layer was removed under reduced pressure and the residue was purified by short SiO_2 column chromatography to give **10** (2.4 mg, 6 %) and an inseparable mixture of regioisomers, **11a** and **11b** (16 mg, **11a** : **11b** = 1 : 1, 27 %). **10** was rather unstable and gradually converted to **11a** and **11b** in CH_2Cl_2 (concentration: 10^{-2}-10^{-3} mM) at rt.

Mononuclear Pd complex (10): a dark green solid; ^{1}H NMR δ 6.69 (t like, J = 9.8 Hz, 1H), 6.71 (t like, J = 9.8 Hz, 1H), 6.82 (s, 1H), 7.07 (t like, J = 9.8 Hz, 1H), 7.13-7.38 (m, 18H), 7.42-7.60 (m, 13H), 7.62 (d like, J = 9.8 Hz, 1H); ^{31}P NMR δ 25.3 (d, J = 31.4 Hz, 1P), 27.6 (d, J = 31.4 Hz, 1P); UV-VIS (log ε) λ_{max} 641 (1.95), 446 (3.28), 428 (3.43), 369 (4.20), 352 (4.20), 294 (3.89); MS (FAB, NBA) *m/z* 825 (MH^++4), 824 (M^++4), 823 (MH^++2), 822 (M^++2), 821 (MH^+), 820 (MH^+-1, M^+), 819 (MH^+-2, M^+-1) 818 (M^+-2), M = $C_{46}H_{36}P_2{}^{106}PdS_2$.

Dinuclear Pd complexes (11a and 11b, a mixture of regioisomers): dark brown needles; Selected ^{1}H NMR of **11a** δ 6.10 (t like, J = 9.8 Hz, 2H), 6.39 (s, 2H), 6.72 (t like, J = 9.8 Hz, 2H), 6.91 (d like, J = 9.8 Hz, 2H), 7.15-7.38 (m, 20H), 7.49-7.66 (m, 14H); Selected ^{1}H NMR of **11b** δ 6.10 (t like, J = 9.8 Hz, 1H), 6.39 (s, 1H), 6.49 (t like, J = 9.8 Hz, 1H), 6.60 (t like, J = 9.8 Hz, 1H), 6.74 (t like, J = 9.8 Hz, 1H), 6.87-6.93 (m, 3H), 7.10 (t like, J = 9.8 Hz, 1H), 7.11 (t like, J = 9.8 Hz, 1H), 7.15-7.38 (m, 18H), 7.46 (d like, J = 9.8 Hz, 1H), 7.49-7.66 (m, 13H); Selected ^{31}P NMR of **11a** δ 32.8 (s, 2P); Selected ^{31}P NMR of **11b** δ 33.2 (d, J = 7.2 Hz, 1P), 33.9 (d, J = 7.2 Hz, 1P); UV-VIS (log ε) λ_{max} 606 (2.90), 441 (3.76), 363 (3.80), 337 (3.89), 228 (4.05); MS (FAB, NBA) *m/z* 1125 (MH^++8), 1124 (M^++8), 1123 (MH^++6), 1122 (M^++6), 1121 (MH^++4), 1120 (M^++4), 1119 (MH^++2) 1118 (MH^++1, M^++2), 1117 (MH^+, M^++1), 1116 (MH^+-1, M^+), 1115 (MH^+-2, M^+-1), 1114 (MH^+-3, M^+-2), 1113 (MH^+-4, M^+-3), 1112 (M^+-4), M = $C_{56}H_{42}P_2{}^{106}Pd_2S_4$. Anal. Calcd for $C_{56}H_{42}P_2Pd_2S_4$: C, 60.16; H, 3.79. Found: C, 60.57; H, 4.15.

REFERENCES

1. a) O. Sato, N. Matsuda, S. Yoshioka, A. Takahashi, Y. Sekiguchi, J. Tsunetsugu, and (the late) T. Nozoe, *J. Chem. Res. (M)*, 1998, 635; and *J. Chem. Res. (S)*, 1998, 108; b) O. Sato, Y. Koizumi, Y. Sekiguchi, S. Yoshioka, J. Tsunetsugu, Y. Z. Yan, A. Mori, H. Takeshita, and T. Nozoe, *Chem. Lett.*, 2000, 1078; c) O. Sato, M. Sato, H. Sugimoto, T. Kuramochi, T. Shirahata, and K. Takahashi, *J. Sulfur Chem.*, 2009, **30**, 360.
2. a) A. G. Anderson, Jr. and R. N. McDonald, *J. Am. Chem. Soc.*, 1959, **81**, 5669; b) K. Hafner, H. Patzelt, and H. Kaiser, *Ann.*, 1962, **656**, 24; c) L. L. Replogle, R. M. Arluck, and J. R. Maynard, *J. Org. Chem.*, 1965, **30**, 2715; d) L. L. Replogle, G. C. Peters, and J. R. Maynard, *J. Org. Chem.*, 1969, **34**, 2022; e) T. Asao, S. Ito, and N. Morita, *Tetrahedron Lett.*, 1989, **30**, 6345.
3. L. S. Konstantinova and O. A. Rakitin, *Chem. Rev.*, 2004, **104**, 2617; and cited references in this review.
4. a) F. Fehér and M. Langer, *Tetrahedron Lett.*, 1971, 2125; b) A. Alam, M. Kon-no, S. Ogawa, and R. Sato, *Tetrahedron*, 2007, **63**, 927; c) L. S. Konstantinova, O. A. Rakitin, and C. W. Rees, *Chem. Commun.*, 2002, 1204; d) H. Muraoka, S. Ogawa, N. Nagahora, Y. Kawai, and R. Sato, *Bull. Chem. Soc. Jpn.*, 2005, **78**, 2026.
5. R. D. Brown, *Trans. Faraday Soc.*, 1948, **44**, 984.
6. H. Fritz and C. D. Weis, *Tetrahedron Lett.*, 1974, **18**, 1659.
7. a) R. Sato, K. Chino, and M. Saito, *Sulfur Lett.*, 1990, **10**, 233; b) S. A. Amelichev, L. S. Konstantinova, N. V. Obruchnikova, O. A. Rakitin, and C. W. Rees, *Org. Lett.*, 2006, **8**, 4529.
8. K. Kudo, T. Okamoto, and S. Yamaguchi, *Organometallics*, 2006, **25**, 2374.