Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron Letters
Tetrahedron Letters 48 (2007) 3349–3354

Stereoselective hetero Diels–Alder reaction of selenoaldehydes with pentavalent phosphole chalcogenides

Masahito Segi,* Katsuhiko Kawaai, Mitsunori Honda and Shuhei Fujinami

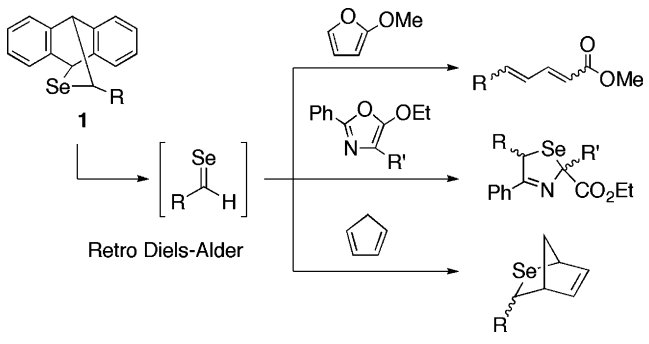
Division of Material Sciences, Graduate School of Natural Science and Technology, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan

Received 22 February 2007; revised 12 March 2007; accepted 15 March 2007
Available online 19 March 2007

Abstract—Stereoselective hetero Diels–Alder reaction of selenoaldehydes, generated by thermal retro Diels–Alder reaction of anthracene cycloadducts, with pentavalent 3,4-dimethylphosphole chalcogenides at 110 °C in toluene to give the corresponding [4+2] cycloadducts as a single diastereoisomer in good yields, accompanied by a slight scrambling of chalcogen atoms. Higher reaction temperature led to an increase of the scrambling between chalcogen atoms.

Hetero Diels–Alder reaction has been a potentially powerful synthetic tool and also a useful approach for the construction of heteroatom-containing cyclic ring system, which often results in high stereo- and regioselective observations.[1] Nitrogen, oxygen, or sulfur atom containing heterodienophiles such as imines, aldehydes, or thiocarbonyl compounds have been extensively developed in this hetero Diels–Alder methodology.[2] On the other hand, selenoaldehydes, being very reactive selenium analogues of aldehydes, have been considered to be highly reactive dienophiles in cycloaddition reactions[3] and have also recently been found to play an increasingly important role in the preparation of selenium-containing heterocycles.[4] In this context, we have already reported an efficient method for the synthesis of reactive selenocarbonyl compounds using $(Me_2Al)_2Se$ as a selenating agent,[5] and recently found that selenoaldehyde–anthracene cycloadducts **1** can serve as convenient and clean precursors of selenoaldehydes via thermal retro Diels–Alder reaction.[6] Cycloadducts **1** were easily prepared from reaction of the corresponding aldehydes with $(Me_2Al)_2Se$ in the presence of anthracene in good yields according to our previously reported procedure.[5e]

Utilizing this retro Diels–Alder reaction of **1**, we have already reported the reactions of selenoaldehydes with 2-methoxyfuran[7] and 5-ethoxyoxazoles[8] as shown in Scheme 1. In the reaction with 2-methoxyfuran, penta-2,4-dienoates were obtained in good yields along with the deposition of elemental selenium. On the other hand, the reaction with 5-ethoxyoxazoles gave the five-membered ring compounds having 3-selenazoline structure in good yields via the carbon–selenium bond cleavage in the [4+2] cycloadducts and the successive recyclization. Simple cyclopentadiene reacted with selenoaldehydes to give the [4+2] cycloadducts as a mixture of *endo* and *exo* isomers. Thus, the reactions of selenoaldehydes with five-membered ring cyclic dienes involving heteroatoms afforded interesting results, and these results prompted us to examine the reaction of selenoaldehydes with phosphorus-containing five-membered ring dienes,



Scheme 1.

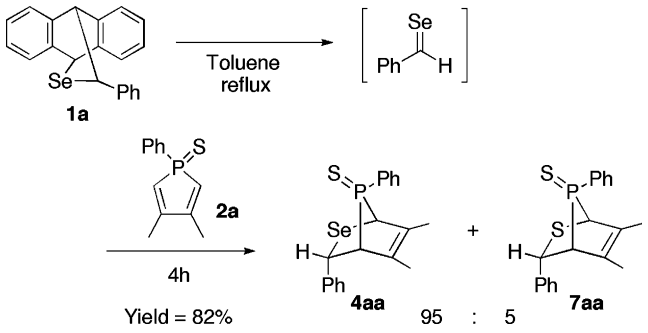
Keywords: Selenoaldehyde; Cycloaddition reaction; Phosphole sulfide; Phosphole selenide; Selenium-containing heterocycle.
* Corresponding author. Tel.: +81 76 234 4787; fax: +81 76 234 4800; e-mail: segi@t.kanazawa-u.ac.jp

0040-4039/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2007.03.079

which would also be expected for the formation of new heterocyclic compounds involving selenium and phosphorus atoms. We selected pentavalent phosphole chalcogenides, 3,4-dimethylphosphole sulfides and selenides, as cyclic dienes having a phosphorus atom because of easy preparation and well-known reactivity of dienic system.[9] In this Letter, we describe stereoselective [4+2] cycloaddition of selenoaldehydes, generated by thermal retro Diels–Alder reaction of **1**, with pentavalent 3,4-dimethylphosphole chalcogenides to give the corresponding [4+2] cycloadducts as a single diastereoisomer.

Pentavalent 1-phenyl or 1-benzylphosphole chalcogenides (**2a**,**b** and **3a**,**b**) were prepared by treatment of the corresponding trivalent 3,4-dimethylphosphole[10] and elemental sulfur or selenium. The toluene solution of **1a** (R = Ph) and 3,4-dimethyl-1-phenylphosphole 1-sulfide (**2a**) was heated at reflux for 4 h to give two kinds of [4+2] cycloadducts with a 95:5 ratio in 82% yield. We, at first, thought that the obtained two cycloadducts were a relationship of diastereoisomers, but very interestingly, after the detail analysis of the spectral data, it turned out that the minor product was the [4+2] cycloadduct with the corresponding thioaldehyde as shown in Scheme 2. This result suggests that the reaction of selenoaldehyde with phosphole sulfide leads to the formation of the corresponding thioaldehyde in situ. On the other hand, the structure of major product (**4aa**) was supported by the analysis of NMR spectra and mass spectrum with a molecular ion peak at *m*/*z* 390.[11] Although the formation of four diastereoisomers is possible with respect to both asymmetric carbon originated from the selenoaldehyde and phosphorus centers in this cycloaddition, only one diastereoisomer was obtained with a complete stereoselectivity. The relative stereochemistry of this major product was finally confirmed by X-ray crystallography as depicted in Figure 1.[12] This shows clearly that two chalcogen atoms of sulfur and selenium are located in the same site and the pheny substituent originated from selenoaldehyde is situated in the *endo* position.

Several anthracene cycloadducts **1** (R = Ar) with an aromatic substituent were heated with phosphole sulfide **2a** (R′ = Ph) or **2b** (R′ = Bn) in toluene at reflux for 4 h to give mainly the corresponding [4+2] cycloadducts (**4**) of selenoaldehydes with phosphole sulfide in good yields as a single diastereoisomer. In all cases, minor products



Scheme 2.

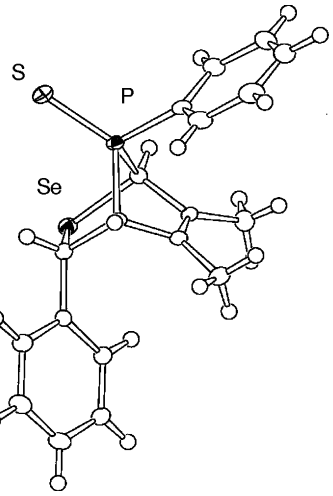
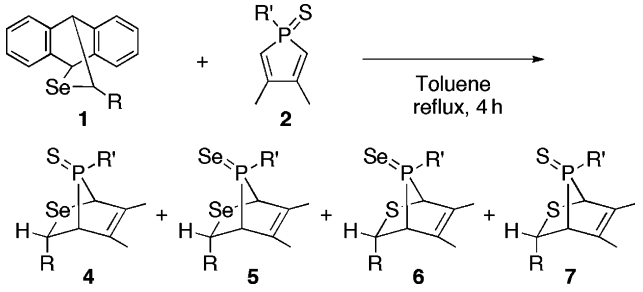


Figure 1. Crystal structure of cycloadduct **4aa**.

5–**7**, in which the combination of two chalcogen atoms in the cycloadducts is different, were obtained in small amounts as mentioned above. The results are shown in Table 1. The stereochemistry of major products was predicted to be same as that of adduct **4aa** by comparing with chemical shifts and coupling constants in NMR spectra.[13] Next, we have examined the reaction of aromatic selenoaldehydes with phosphole selenides **3a** (R′ = Ph) or **3b** (R′ = Bn) under similar reaction conditions. In this reaction, a scrambling of chalcogen atoms is of course impossible because of the same selenium atom in both reactants. As an expected result, a single diastereoisomer **5**, being identical with one of minor products in Table 1, in each entry was obtained in good yield with the above-mentioned complete stereoselectivity. The results are shown in Table 2.[14] Furthermore, to confirm the structure of other minor products **6** and **7** in Table 1, we independently conducted the reaction of the

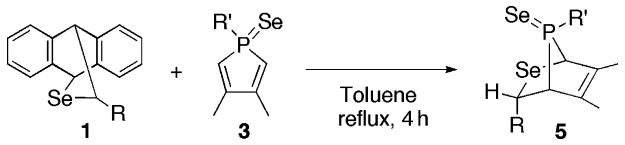
Table 1. Hetero Diels–Alder reaction of aromatic selenoaldehydes with 3,4-dimethylphosphole sulfides **2**



1 R	2 R′	Yield[a] (%)	Product ratio[b]
			4:**5**:**6**:**7**
Ph (**a**)	Ph (**a**)	82	95:—:—:5
p-NCC$_6$H$_4$ (**b**)	Ph (**a**)	97	99:—:—:1
p-MeOC$_6$H$_4$ (**c**)	Ph (**a**)	92	95:—:—:5
Ph (**a**)	Bn (**b**)	78	97:—:—:3
p-NCC$_6$H$_4$ (**b**)	Bn (**b**)	87	90:4:1:5
p-MeOC$_6$H$_4$ (**c**)	Bn (**b**)	91	91:4:1:4

[a] Isolated yield.
[b] Determined by ^{1}H NMR.

Table 2. Hetero Diels–Alder reaction of aromatic selenoaldehydes with 3,4-dimethylphosphole selenides **3**



1 **3** **5**

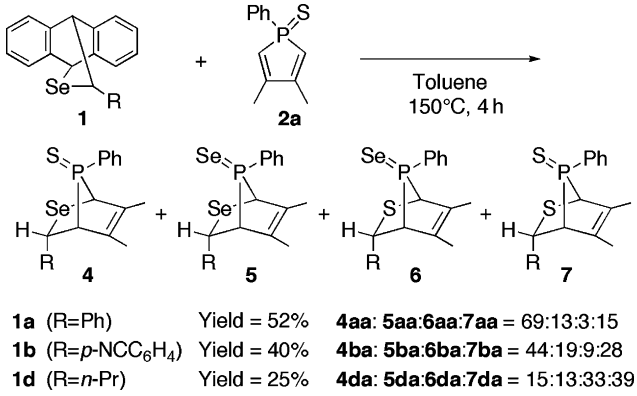
1 R	**3** R′	Cycloadduct	Yield[a] (%)
Ph (**a**)	Ph (**a**)	**5aa**	65
p-NCC_6H_4 (**b**)	Ph (**a**)	**5ba**	79
p-$MeOC_6H_4$ (**c**)	Ph (**a**)	**5ca**	69
Ph (**a**)	Bn (**b**)	**5ab**	71
p-NCC_6H_4 (**b**)	Bn (**b**)	**5bb**	89
p-$MeOC_6H_4$ (**c**)	Bn (**b**)	**5cb**	97

[a] Isolated yield.

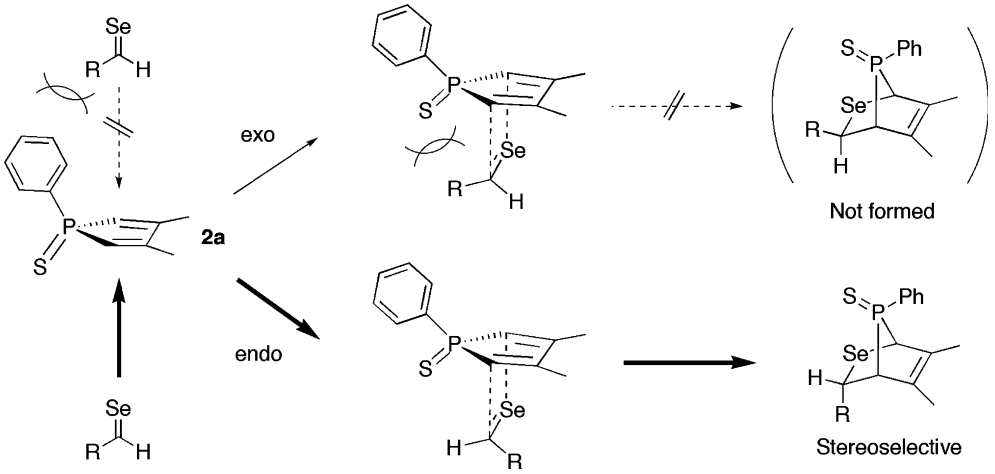
corresponding thioaldehydes[15] with phosphole sulfides **2** or selenides **3** in toluene under similar reaction conditions. All signals in ^1H and ^{13}C NMR spectra of the obtained cycloadducts were completely consistent with those of two minor products in Table 1.

The mechanistic interpretation for the observed complete stereoselectivity is not clear at the present time. The following consideration based on steric effect is shown in Scheme 3, though the speculations. In the approach of selenoaldehyde to two faces of five-membered phosphole ring, a large steric repulsion between the R′ (R′ = Ph or Bn) substituent on phosphorus atom and the selenoaldehyde appears to be a significant factor. Accordingly, selenoaldehyde prefers the access to the site of sulfur atom selectively. On the other hand, regarding the face selectivity of selenoaldehyde, there exist a large steric repulsion between sulfur atom on phosphorus and the R group in an *exo* addition and/or a positive secondary orbital interaction in the *endo* transition state. As a result, the *endo* addition of selenoaldehyde proceeds selectively to afford only one diastereoisomer among possible four diastereomers. However, there are also other explanations for the face selectivity of phosphole ring. For example, the difference of HOMO orbital extension on two faces of the phosphole ring may lead to necessarily the observed high stereoselectivity. We are now investigating mechanistic interpretation based on the results of reaction using phosphole chalcogenides with another substituents.

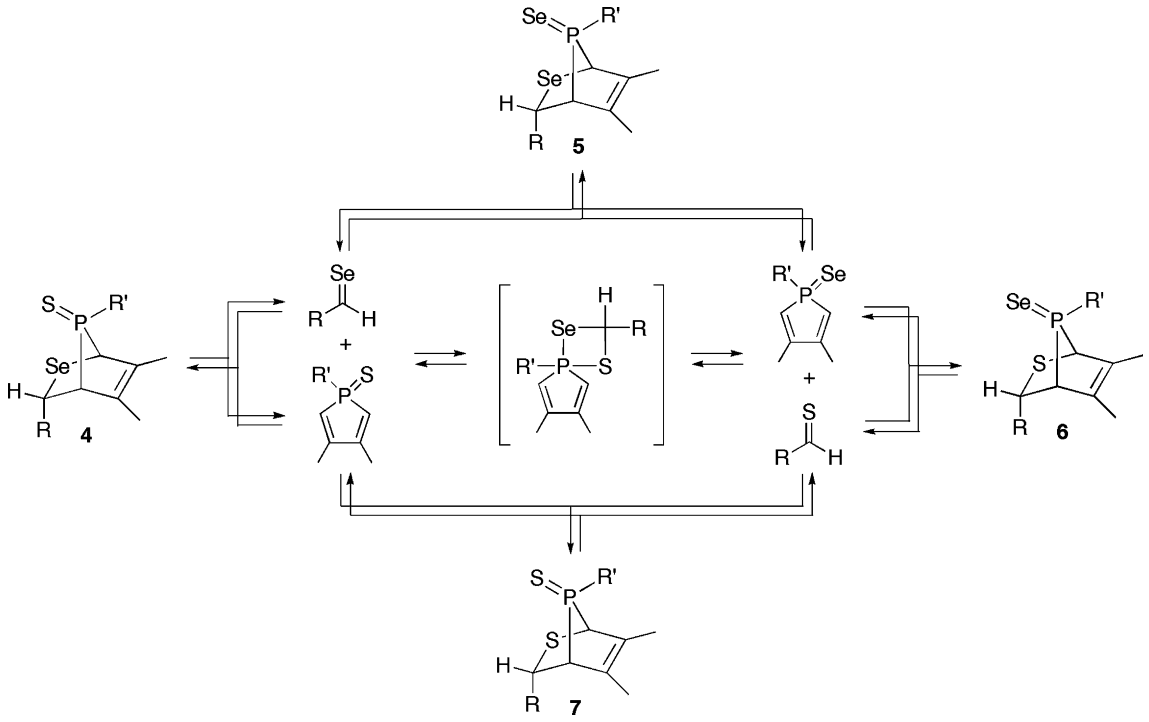
Next we tried the reaction of aliphatic selenoaldehydes with phosphole sulfide. Retro Diels–Alder reaction of **1** with an aliphatic substituent did not take place at a reflux temperature in toluene due to the stability, but the heating at over 150 °C resulted in an efficient regeneration of aliphatic selenoaldehydes in situ. Thus, **1d** (R = *n*-Pr) was heated with phosphole sulfide **2a** at 150 °C in toluene using a sealed stainless steel vessel to give a mixture of four cycloadducts **4da**, **5da**, **6da**, and **7da** with a 15:13:33:39 relative ratio in low total yield. This result indicates higher reaction temperature may cause an increase of scrambling of sulfur and selenium atoms. To make sure the temperature effect, we examined the reaction of aromatic selenoaldehydes with **2a** at 150 °C for 4 h in toluene, and as a result four cycloadducts **4**–**7** were obtained in moderate yields. The results at 150 °C summarized in Scheme 4. In addition, the heating of one cycloadduct **4ba** at 150 °C for 4 h in toluene resulted in the formation of a mixture of four cycloadducts **4ba**, **5ba**, **6ba**, **7ba** with a 42:24:5:29 ratio. This result indicates a thermal retro Diels–Alder reaction of



Scheme 4.



Scheme 3.



Scheme 5. Plausible mechanism for exchange of chalcogen atoms.

cycloadducts **4** proceeded easily at 150 °C and the exchange of chalcogen atoms occurred somewhere under these conditions.

Based on the above results, the most likely pathway for the scrambling of sulfur and selenium atoms in the cycloadducts may be as follows. It seems that selenoaldehydes undergo a [4+2] hetero Diels–Alder reaction with phosphole sulfide, whereas can also cause an exchange of chalcogen atoms at over 110 °C via a probable four-membered ring intermediate[16] to give the corresponding thioaldehydes and phosphole selenide. Thus, four compounds, selenoaldehyde, thioaldehyde, phosphole sulfide, and phosphole selenide, coexist in the reaction mixture and four combinations are possible for hetero Diels–Alder reaction to afford cycloadducts **4**–**7**. Furthermore, these cycloadducts undergo reversibly a retro Diels–Alder reaction at over 110 °C. A plausible mechanism for exchange of chalcogen atoms is shown in Scheme 5.

In conclusion, we have demonstrated that the reaction of selenoaldehydes with pentavalent 3,4-dimethylphosphole chalcogenides at 110 °C proceeded efficiently to give new bicyclic [4+2] cycloadducts involving both selenium and phosphorus atoms as a single diastereoisomer with complete stereoselectivity in good yields. At higher reaction temperature (>110 °C), a significant exchange of chalcogen atoms between selenoaldehyde and phosphole sulfide occurred, resulting in the formation of a mixture of four cycloadducts **4**–**7**. This result suggests these phosphole chalcogenides can serve as a new chalcogenating reagent for carbonyl compounds. We are currently investigating about the possibility and will report the results of our findings in due course.

Acknowledgement

This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture, Japan.

References and notes

1. For review, see Boger, D. L.; Weinreb, S. N. *Hetero Diels–Alder Methodology in Organic Synthesis*; Academic Press: London, 1987.
2. For reviews, see (a) Danishefsky, S. J.; DeNinno, M. P. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 15–23; (b) Waldmann, H. *Synthesis* **1994**, 535–551; (c) Jorgensen, K. A. *Angew. Chem., Int. Ed.* **2000**, *39*, 3558–3588.
3. For reviews on synthetic studies of selenoaldehydes, see (a) Okazaki, R. *Yuki Gosei Kagaku Kyokaishi* **1988**, *46*, 1149–1163; (b) Tokitoh, N.; Okazaki, R. *Pol. J. Chem.* **1998**, *72*, 971–1000; (c) Guziec, L. J.; Guziec, F. S., Jr. In *Comprehensive Organic Functional Group Transformations 2*; Katritzky, A. R., Taylor, R. J. K., Eds.; Elsevier: Amsterdam, 2005; pp 397–417; For theoretical studies, see (d) Rohr, U.; Schatz, J.; Sauer, J. *Eur. J. Org. Chem.* **1998**, 2875–2883; (e) Bachrach, S. M.; Jiang, S. *J. Org. Chem.* **1999**, *64*, 8248–8355; (f) Liao, H.-Y.; Su, M.-D.; Chu, S.-Y. *Chem. Phys.* **2000**, *261*, 275–287; (g) Orlova, G.; Goddard, J. D. *J. Org. Chem.* **2001**, *66*, 4026–4035.
4. (a) Renson, M. In *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1986; Vol. 1, pp 399–516; (b) Litvinov, V. P.; Dyachenko, V. D. *Russ. Chem. Rev.* **1997**, *66*, 923–951.
5. (a) Segi, M.; Koyama, T.; Nakajima, T.; Suga, S.; Murai, S.; Sonoda, N. *Tetrahedron Lett.* **1989**, *30*, 2095–2098; (b) Segi, M.; Kojima, A.; Nakajima, T.; Suga, S. *Synlett* **1991**,

105–106; (c) Li, G. M.; Segi, M.; Nakajima, T. *Tetrahedron Lett.* **1992**, *33*, 3515–3518; (d) Segi, M.; Takahashi, T.; Ichinose, H.; Li, G. M.; Nakajima, T. *Tetrahedron Lett.* **1992**, *33*, 7865–7868; (e) Segi, M.; Nakajima, T. *Yuki Gosei Kagaku Kyokaishi* **1995**, *53*, 678–686; (f) Li, G. M.; Zingaro, R. A.; Segi, M.; Reibenspies, J. H.; Nakajima, T. *Organometallics* **1997**, *16*, 756–762; (g) Li, G. M.; Niu, S.; Segi, M.; Zingaro, R. A.; Yamamoto, H.; Watanabe, K.; Nakajima, T.; Hall, H. B. *J. Org. Chem.* **1999**, *64*, 1565–1575.

6. (a) Segi, M.; Yamamoto, H.; Hori, T.; Nakajima, T. *Phosphorus, Sulfur Silicon Relat. Elem.* **1998**, *136–138*, 599–602; (b) Tomoda, S.; Zhang, J.; Kaneno, D.; Segi, M.; Zhou, A. *Tetrahedron Lett.* **2000**, *41*, 4597–4601; (c) Segi, M. *Yuki Gosei Kagaku Kyokaishi* **2003**, *61*, 661–669.
7. Zhou, A.; Segi, M.; Nakajima, T. *Tetrahedron Lett.* **2003**, *44*, 1179–1182.
8. Segi, M.; Zhou, A.; Honda, M. *Phosphorus, Sulfur, and Silicon* **2005**, *180*, 1045–1049.
9. For review on phosphole chemistry, see (a) Mathey, F. *Chem. Rev.* **1988**, *88*, 429–453; For the reaction of thiocarbony compounds with phosphole sulfide, see (b) Kashman, Y.; Wagenstein, I.; Rudi, A. *Tetrahedron* **1976**, *32*, 2427–2431; (c) Qin, Y.; Selvaratnam, S.; Vittal, J. J.; Leung, P.-H. *Organometallics* **2002**, *21*, 5301–5306.
10. Breque, A.; Mathey, F.; Savignac, P. *Synthesis* **1981**, 983–985.
11. Cycloadduct **4aa**: mp 184–186 °C, ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.21 (s, 3H), 1.86 (s, 3H), 3.19 (br s, 1H), 4.05 (br d, $J = 3.5$ Hz, 1H), 5.80 (br s, 1H), 7.22–7.62 (m, 10H); ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 13.45 (d, $J = 5.1$ Hz), 16.44 (d, $J = 5.6$ Hz), 48.74 (d, $J = 46.8$ Hz), 53.37 (d, $J = 13.4$ Hz), 60.77 (d, $J = 53.6$ Hz), 127.28, 128.15, 128.35 (d, $J = 11.2$ Hz), 129.19, 129.76 (d, $J = 8.9$ Hz), 130.58, 130.67, 132.01 (d, $J = 77.2$ Hz), 137.75 (d, $J = 12.8$ Hz), 138.85 (d, $J = 11.1$ Hz); Mass (EI mode): *m*/*z* (relative intensity) 115 (13.2), 143 (16.8), 149 (19.5), 188 (19.8), 205 (45.9), 220 (100), 249 (33.0), 277 (19.7), 309 (24.2), 388 (25.5), 390 (M^+, 50.8); HRMS calcd for $C_{19}H_{19}PSSe$ (M^+) 390.0110. Found: 390.0103.
12. Crystal data for **4aa**: $C_{19}H_{19}PSSe$, colourless crystalline solid, $0.35 \times 0.25 \times 0.10$ mm^3; formula weight = 389.35. Triclinic, space group: *P*1. Unit cell dimensions: $a = 10.8449(9)$, $b = 11.1393(8)$, $c = 16.9388(9)$, $\alpha = 90.860(7)$, $\beta = 97.655(6)$, $\gamma = 119.077(6)$ at 123 K, $V = 1764.9(2)$, $Z = 4$, $R = 0.031$ and $R_W = 0.052$ for 7466 reflections ($I > 3.00\sigma(I)$), GOF = 1.29.
13. *Selected spectral data of cycloadducts* **4**. Compound **4ba**: mp 186–187 °C, ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.20 (s, 3H), 1.88 (s, 3H), 3.19 (br s, 1H), 4.11 (br d, $J = 3.2$ Hz, 1H), 5.79 (br s, 1H), 7.39–7.61 (m, 9H); ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 13.58 (d, $J = 5.0$ Hz), 16.46 (d, $J = 5.0$ Hz), 49.23 (d, $J = 46.8$ Hz), 53.06 (d, $J = 14.5$ Hz), 59.77 (d, $J = 53.6$ Hz), 111.17, 118.32, 128.50 (d, $J = 11.7$ Hz), 129.83 (d, $J = 11.2$ Hz), 130.13, 130.91, 130.95, 131.94, 132.05, 138.55 (d, $J = 12.3$ Hz), 145.06 (d, $J = 11.1$ Hz); Mass (EI mode): *m*/*z* (relative intensity) 188 (48.7), 205 (25.0), 220 (100), 302 (930.9), 335 (21.4), 413 (18.5), 415 (M^+, 37.5); HRMS calcd for $C_{20}H_{18}NPSSe$ (M^+) 415.0063. Found: 415.0061. Compound **4ab**: ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.38 (s, 3H), 1.98 (s, 3H), 2.76 (br s, 1H), 3.44–3.62 (m, 3H), 5.63 (br s, 1H), 7.23–7.31 (m, 10H); ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 13.38 (d, $J = 5.6$ Hz), 16.58 (d, $J = 6.2$ Hz), 34.79 (d, $J = 43.5$ Hz), 48.61 (d, $J = 42.9$ Hz), 53.81 (d, $J = 11.7$ Hz), 59.39 (d, $J = 49.1$ Hz), 127.03 (d, $J = 3.4$ Hz), 127.25, 128.11, 128.36 (d, $J = 2.8$ Hz), 129.08, 129.18, 130.13 (d, $J = 6.1$ Hz), 132.78 (d, $J = 8.4$ Hz), 137.42 (d, $J = 12.8$ Hz), 138.87 (d, $J = 10.6$ Hz); Mass (EI mode): *m*/*z* (relative intensity) 91 (43.4), 143 (100), 201 (27.2), 234 (19.5), 249 (17.6), 402 (23.8), 404 (M^+, 47.4); HRMS calcd for $C_{20}H_{21}PSSe$ (M^+) 404.0267. Found: 404.0259. Compound **4cb**: ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.42 (s, 3H), 1.98 (s, 3H), 2.72 (br s, 1H), 3.38–3.59 (m, 3H), 3.77 (s, 3H), 5.60 (br s, 1H), 6.76 (d, $J = 8.6$ Hz, 2H), 7.15 (d. $J = 8.6$ Hz, 2H), 7.26–7.31 (m, 5H); ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 13.47 (d, $J = 5.6$ Hz), 16.75 (d, $J = 6.2$ Hz), 34.97 (d, $J = 43.5$ Hz), 48.68 (d, $J = 42.9$ Hz), 53.35 (d, $J = 11.7$ Hz), 55.27, 59.52 (d, $J = 49.1$ Hz), 113.61, 127.15 (d, $J = 3.3$ Hz), 128.49 (d, $J = 2.8$ Hz), 129.25 (d, $J = 5.0$ Hz), 130.31, 130.85 (d, $J = 10.6$ Hz), 132.94 (d, $J = 8.3$ Hz), 137.56 (d, $J = 12.3$ Hz), 158.77; Mass (EI mode): *m*/*z* (relative intensity) 91 (70.9), 143 (100), 200 (30.3), 231 (42.2), 234 (22.2), 279 (31.8), 432 (23.9), 434 (M^+, 46.9); HRMS calcd for $C_{21}H_{23}OPSSe$ (M^+) 434.0372. Found: 434.0374.
14. Selected spectral data of cycloadducts **5**. Compound **5aa**: mp 174–176 °C, ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.19 (s, 3H), 1.85 (s, 3H), 3.27 (br s, 1H), 4.13 (br d, $J = 4.0$ Hz, 1H), 5.86 (br s, 1H), 7.24–7.59 (m, 10H); ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 13.60 (d, $J = 5.0$ Hz), 16.48 (d, $J = 5.0$ Hz), 49.06 (d, $J = 38.5$ Hz), 53.37 (d, $J = 15.1$ Hz), 59.98 (d, $J = 46.3$ Hz), 127.39, 128.24, 128.39 (d, $J = 11.7$ Hz), 129.28, 129.66 (d, $J = 8.9$ Hz), 130.69 (d, $J = 2.2$ Hz), 131.05 (d, $J = 4.5$ Hz), 132.90 (d, $J = 67.5$ Hz), 138.04 (d, $J = 11.7$ Hz), 138.69 (d, $J = 11.7$ Hz); Mass (EI mode): *m*/*z* (relative intensity) 178 (41.4), 188 (25.9), 205 (22.2), 266 (48.7), 268 (100), 277 (52.1), 436 (30.9), 438 (M^+, 34.4); HRMS calcd for $C_{19}H_{19}PSe_2$ (M^+) 437.9555. Found: 437.9554. Compound **5ba**: mp 171–172 °C, ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.19 (s, 3H), 1.87 (s, 3H), 3.26 (br s, 1H), 4.17 (br d, $J = 4.0$ Hz, 1H), 5.85 (br s, 1H), 7.38–7.59 (m, 9H); ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 13.74 (d, $J = 4.5$ Hz), 16.54 (d, $J = 5.0$ Hz), 49.57 (d, $J = 38.0$ Hz), 53.12 (d, $J = 16.2$ Hz), 60.04 (d, $J = 46.8$ Hz), 111.38, 118.39, 128.57 (d, $J = 11.7$ Hz), 129.76 (d, $J = 8.9$ Hz), 130.22, 130.57 (d, $J = 4.5$ Hz), 131.02 (d, $J = 2.2$ Hz), 132.08, 132.38 (d, $J = 68.6$ Hz), 138.88 (d, $J = 11.7$ Hz), 144.92 (d, $J = 11.7$ Hz); Mass (EI mode): *m*/*z* (relative intensity) 58 (47.7), 187 (35.6), 188 (32.9), 205 (29.9), 266 (49.3), 268 (100), 302 (48.9), 459 (11.5), 461 (20.1), 463 (M^+, 22.4); HRMS calcd for $C_{20}H_{18}NPSe_2$ (M^+) 462.9507. Found: 462.9491. Compound **5ab**: mp 172–174 °C, ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.36 (s, 3H), 1.96 (s, 3H), 2.83 (br s, 1H), 3.56–3.76 (m, 3H), 5.68 (br s, 1H), 7.22–7.30 (m, 10H); ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 13.43 (d, $J = 5.6$ Hz), 16.58 (d, $J = 6.2$ Hz), 36.54 (d, $J = 35.1$ Hz), 48.89 (d, $J = 35.2$ Hz), 54.10 (d, $J = 12.8$ Hz), 59.62 (d, $J = 43.0$ Hz), 127.19 (d, $J = 3.3$ Hz), 127.34, 128.18, 128.41 (d, $J = 3.4$ Hz), 129.16 (d, $J = 5.0$ Hz),129.27, 130.43 (d, $J = 4.5$ Hz), 132.79 (d, $J = 8.3$ Hz), 137.62 (d, $J = 11.1$ Hz), 138.69 (d, $J = 10.6$ Hz); Mass (EI mode): *m*/*z* (relative intensity) 91 (100), 191 (41.6), 201 (38.3), 280 (22.3), 282 (45.7), 449 (17.5), 451 (M^+, 18.9); HRMS calcd for $C_{20}H_{21}PSe_2$ (M^+) 451.9711. Found: 451.9695. Compound **5cb**: ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.41 (s, 3H), 1.96 (s, 3H), 2.79 (br s, 1H), 3.46–3.83 (m, 3H), 3.76 (s, 3H), 5.65 (br s, 1H), 6.76 (d, $J = 8.9$ Hz, 2H), 7.15 (d. $J = 8.9$ Hz, 2H), 7.30–7.58 (m, 5H); ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 13.41 (d, $J = 5.0$ Hz), 16.64 (d, $J = 5.6$ Hz), 36.56 (d, $J = 35.1$ Hz), 48.82 (d, $J = 35.2$ Hz), 53.49 (d, $J = 13.9$ Hz), 55.19, 59.56 (d, $J = 41.8$ Hz), 113.53, 127.16 (d, $J = 3.3$ Hz), 128.39 (d, $J = 2.8$ Hz), 129.15 (d, $J = 5.0$ Hz), 130.25, 130.44 (d, $J = 18.9$ Hz), 130.55, 132.80 (d, $J = 8.3$ Hz), 137.61 (d, $J = 11.1$ Hz), 158.68; Mass (EI mode): *m*/*z* (relative intensity) 91 (100),

191 (48.0), 200 (95.2), 202 (53.4), 231 (64.6), 280 (33.9), 282 (61.2), 321 (97.2), 480 (20.7), 482 (M^+, 22.3); HRMS calcd for $C_{21}H_{23}OPSe_2$ (M^+) 481.9817. Found: 481.9854.

15. Thioaldehydes were similarly generated in situ by retro Diels–Alder reaction of thioaldehyde–anthracene cycloadducts, which were prepared by reaction of the corresponding aldehydes with $(Me_2Al)_2S$[17] in the presence of anthracene at reflux in toluene.
16. Oxygen–selenium exchange reactions via a similar four-membered ring intermediate using pentavalent phosphorus compound with a P=Se group ($PhP(Se)Cl_2$) have been already reported; Michael, J. P.; Reid, D. H.; Rose, B. G.; Speirs, R. A. *J. Chem. Soc., Chem. Commun.* **1988**, 1494–1496.
17. Li, G. M.; Niu, S.; Segi, M.; Tanaka, K.; Nakajima, T.; Zingaro, R. A.; Reibenspies, J. H.; Hall, M. B. *J. Org. Chem.* **2000**, *65*, 6601–6612.