# A Novel Competition between C–Se and C–Si Cleavages in Cyclization of β-Seleno-β-silyl-substituted Divinyl Ketones

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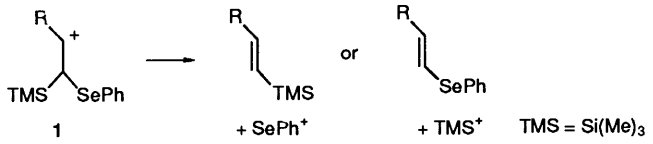
Reactions of β-seleno-β-silyl-substituted divinyl ketones **2–4** with Lewis acids at room temp. gave phenylseleno and/or trimethylsilyl functionalized cyclopentenones. The use of $TiCl_4$ or $SnCl_4$ results in C–Se cleavage leading to 5-(phenylseleno)-3-(trimethylsilyl)cyclopent-2-enones **9–11** as major products. In contrast, using $AgBF_4$–TMSCl (trimethylsilyl chloride) results in C–Si cleavage to give 3-(phenylseleno)cyclopenten-2-ones **12–14**. Lewis acid-dependent competitive cleavage between C–Se and C–Si bonds has been demonstrated.

Compounds containing selenium and silicon bonded to the same carbon are of synthetic and mechanistic interest. Selective transformations of β-hydroxy α-silyl selenides to vinyl selenides under basic conditions (Bu$^t$OK) and to vinylsilanes by treatment with a hydroxy activating reagent ($POCl_3$–$NEt_3$) have been reported.[1] In reactions of a carbonium ion **1**, there are two possible pathways, *i.e.* C–Se and C–Si cleavages (Scheme 1). It




**Scheme 1**

is well known that a silyl group is usually lost from a β-silyl cation,[2] and this property has been utilized in the silicon-directed Nazarov cyclization.[3] On the other hand, recently we reported that a β-seleno-substituted divinyl ketone underwent cyclization accompanied by selenophenyl migration in the presence of a Lewis acid.[4] Magnus has reported that Nazarov cyclization of β,β-silylthio divinyl ketones, presumed as intermediates, gave thioaryl substituted cyclopentenones, accompanied by loss of the TMS (trimethylsilyl) group.[5] Clearly, C–Si cleavage predominated over C–S cleavage. Since a C–Se bond is weaker than a C–S bond, cleavage of C–Se and C–Si bonds can potentially be competitive. It is of interest to examine selective cleavage of C–Se (*via* path **x**) or C–Si bonds (*via* path **y**) under various conditions (Scheme 2).

In this work, we focus our attention on the possibility of selective formation of 3-(phenylseleno)- or 5-(phenylseleno)-3-(trimethylsilyl)-cyclopent-2-enones, *i.e.* can Lewis acids be used to control C–Se or C–Si cleavage?

We report that Friedel–Crafts acylation of 1-(phenylseleno)-1-(trimethylsilyl)ethene **8**[6] gave β-seleno-β-silyl-substituted divinyl ketones **2–4**. The isolation of such type precursors for the Nazarov cyclization[7] has not yet been reported. It is also shown that the cyclization of **2–4** afforded phenylseleno and/or trimethylsilyl functionalized cyclopentenones in processes that could be affected by appropriate choice of Lewis acid.

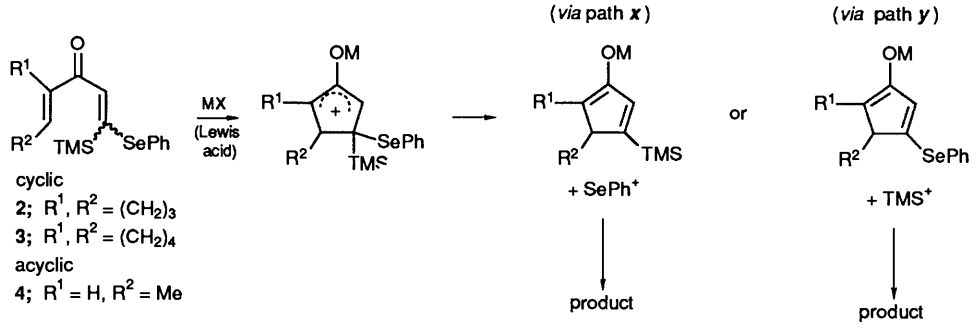
*Synthesis of β-Seleno-β-silyl Divinyl Ketones.*—β-Seleno-β-silyl divinyl ketones **2–4** were synthesized and isolated as follows. Treatment of 1-(phenylseleno)-1-(trimethylsilyl)ethene **8** with α,β-unsaturated acid chlorides **5–7** in the presence of $TiCl_4$ in $CH_2Cl_2$ at −78 °C for 3 h, gave the divinyl ketones **2–4** (33–96% yields; Scheme 3) in two isomeric forms **a** and **b**. These were readily separated by chromatography, but in $CDCl_3$ solution they isomerized slowly at room temp.† Spectral data failed to allow unequivocal *E* or *Z* assignments to the isomers **2–4 a** and **b**.

In the first step of Scheme 3, the nucleophilic olefin **8** adds to acylium ion to give a carbonium ion stabilized by the PhSe group. Loss of a proton leads to the divinyl ketones **2–4**. A similar pathway has been suggested for the reaction of 1-(phenylthio)-1-(trimethylsilyl)ethene **24** and acid chlorides in the presence of Lewis acids.[5] Through the present isolation of precursors **2–4**, the addition–deprotonation scheme has now been established.

*Nazarov Cyclization of β-Seleno-β-silyl Divinyl Ketones* **2–4**.—*Lewis acid:* $TiCl_4$ *or* $SnCl_4$. A reaction mixture containing pure **2a** or **2b**, and $TiCl_4$ in $CH_2Cl_2$ at −78 °C when allowed to warm to room temp. gave 1-(phenylseleno)-4-(trimethylsilyl)bicyclo-[3.30]oct-3-en-2-one **9**‡ as the major product in 67 and 57.4%

† A similar isomerization was observed in 1-(dimethylamino)-2-(phenylseleno)maleate and fumarate.[8]

‡ The assignment of the TMS substituent position for **9** was established by conversion to **15** using $Bu_3SnH$, AIBN (azoisobutyronitrile) in benzene (80 °C, 1 h, 100% yield).




**Scheme 2**

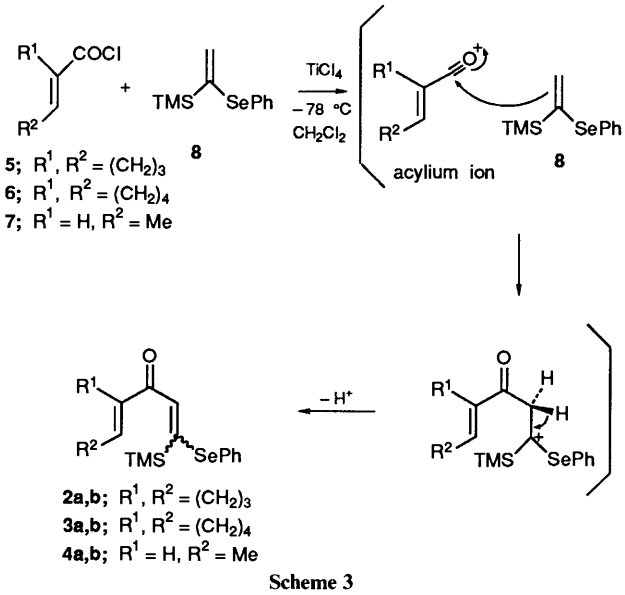
**Table 1** Isolated yield of reactions of **2**–**4** with Lewis acids in Scheme 4[a,b,c]

| Starting material | Lewis acid | Products (%) | | | | |
|---|---|---|---|---|---|---|
| **2a** | $TiCl_4$ | **9** (67) | **12** (0) | **15** (1.4) | | |
| **2b** | $TiCl_4$ | **9** (57.4) | **12** (0) | **15** (0) | | |
| **2a** | $SnCl_4$ | **9** (72) | **12** (6) | **15** (0.9) | | |
| **2b** | $SnCl_4$ | **9** (57) | **12** (0) | **15** (0) | | |
| **2a** | $AgBF_4$[d] | **9** (0) | **12** (35) | **15** (0) | | |
| **2b** | $AgBF_4$[e] | **9** (0) | **12** (0) | **15** (0) | | |
| **2b** | $AgBF_4$–TMSCl | **9** (0) | **12** (52) | **15** (0) | | |
| **2a:2b** = 2:1 | TMSCl[f] | **9** (0) | **12** (0) | **15** (0) | | |
| **3a** | $TiCl_4$ | Complex mixture | | | | |
| **3b** | $TiCl_4$ | Complex mixture | | | | |
| **3a** | $SnCl_4$ | **10** (38) | **13** (0) | | | |
| **3b** | $SnCl_4$ | **10** (50) | **13** (0) | | | |
| **3a** | $AgBF_4$–TMSCl[g] | **10** (0) | **13** (56) | | | |
| **3b** | $AgBF_4$–TMSCl[h] | **10** (0) | **13** (25) | | | |
| **3b** | $AgOSO_2CF_3$ | **10** (0) | **13** (47) | | | |
| **4a** | $TiCl_4$ | **11** (31) | **14** (11.6) | **16** (4.8) | **17** (7.6) | **18** (0) |
| **4b** | $TiCl_4$ | **11** (55) | **14** (3.7) | **16** (9.7) | **17** (0) | **18** (0) |
| **4a** | $SnCl_4$ | **11** (35) | **14** (13) | **16** (9) | **17** (0) | **18** (9.5) |
| **4b** | $SnCl_4$ | **11** (29) | **14** (6) | **16** (15) | **17** (0) | **18** (0) |
| **4a** | $AgBF_4$–TMSCl[i] | **11** (0) | **14** (35) | **16** (0) | **17** (0) | **18** (0) |
| **4b** | $AgBF_4$–TMSCl[j] | **11** (0) | **14** (26) | **16** (0) | **17** (0) | **18** (0) |

[a] The product ratios of isolated products are the same as those from the crude $^1H$ NMR spectra within experimental errors. [b] The bicyclo compounds **9**, **10**, **12**, **13** and **15** are single diastereoisomers by NMR spectroscopy, and assigned to *cis* ring junction stereochemistry on the basis of thermodynamic expectation. [c] The compounds **11** and **17** are single diastereoisomers and assigned to *trans* stereochemistry for 4,5-substituents. [d] **2b** (45%) was obtained. [e] No reaction. [f] **2a:2b** = 1 : 1 was recovered. [g] **3b** (13%) was obtained. [h] **3b** (47%) was recovered. [i] **4b** (26%) was obtained. [j] **4b** (37%) was recovered.

isolated yields, respectively. Pure **3a** or pure **3b** when treated with $TiCl_4$ in $CH_2Cl_2$ under the same condition gave a complex mixture. Pure **4a** or pure **4b** when treated with $TiCl_4$ in $CH_2Cl_2$ at −78 °C to room temp. gave 4-methyl-5-(phenylseleno)-3-(trimethylsilyl)cyclopent-2-enone **11** as the major product in 31 and 55% yields, respectively. Warming of **2**–**4** in the presence of $SnCl_4$ from −78 °C to room temperature gave compounds **9**, **10** and **11** as the main products in 29–72% yields (Scheme 4 and Table 1).

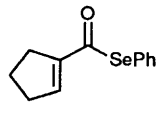
*Lewis acid:* $AgBF_4$ *and/or* TMSCl *or* $AgOSO_2CF_3$. Treatment of **2a** in the presence of $AgBF_4$ in $CH_2ClCH_2Cl$–$CH_2Cl_2$ at −50 °C to room temp. gave 4-(phenylseleno)bicyclo[3.3.0]oct-3-en-2-one **12** (35%) and **2b** (45%); **2b** remained unchanged upon treatment with $AgBF_4$. When *ca.* 1 equiv. of chlorotrimethylsilane (TMSCl) was added to $AgBF_4$ as an activating reagent, **2b** afforded **12** in 52% yield. Treatment of **3** and **4** in the presence of $AgBF_4$–TMSCl at room temperature gave 3-(phenylseleno)cyclopent-2-enones **13** and **14**, respectively. The cyclized products **12**–**14** with the SePh group are of the same type as the sulphur analogues, which were reported by Magnus.[5] Compounds **3a** and **4a** produced the isomers **3b** (13%) and **4b** (26%), respectively, in addition to the cyclized products **13** (56%) and **14** (35%) in the presence of $AgBF_4$–TMSCl. Reaction of a 2:1 mixture of **2a** and **2b** with TMSCl in $CH_2Cl_2$ gave no cyclized products. Reaction of **3b** with $AgOSO_2CF_3$ in $CH_2Cl_2$ gave **13** (47%) (Scheme 4 and Table 1). In all cases, the pure geometrical isomers **a** and **b** of the starting divinyl ketones gave similar cyclization product ratios.*



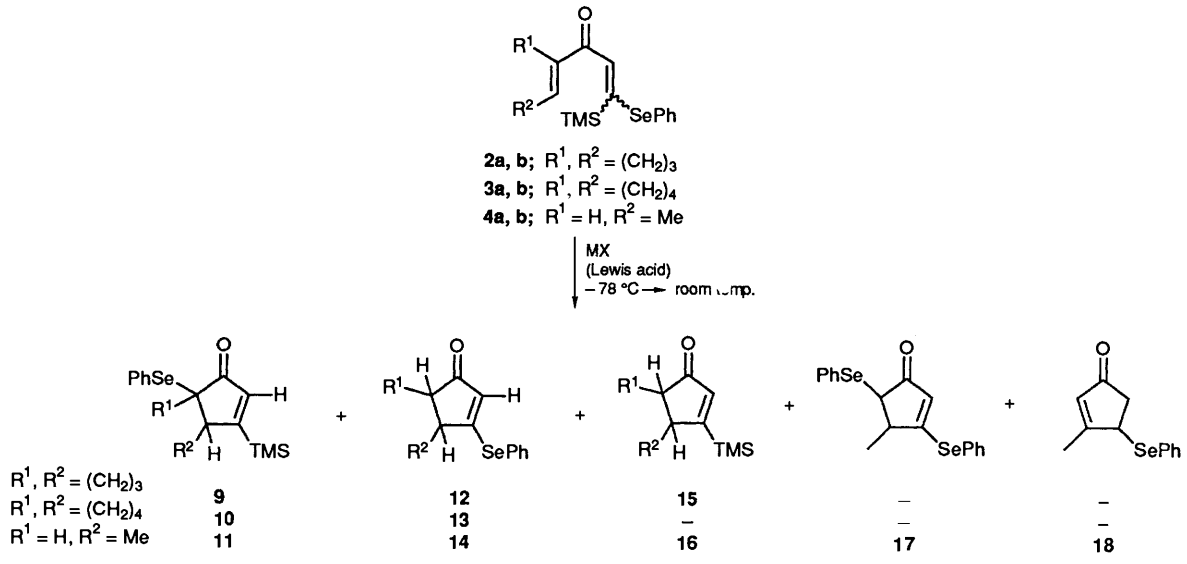

**Scheme 3**

The mechanism of cyclopentenone annulation is shown in Scheme 5. The divinyl ketone affords pentadienyl cation **19** in the presence of Lewis acid. Next, cyclization of **19** to an oxyallyl cation **20** occurs.[7] The complex of $AgBF_4$ and TMSCl, $TMS^{\delta+}$–$Cl^{\delta-}$ ··· $Ag^+$ ··· $BF_4^-$, may coordinate to the carbonyl

* The one-pot cyclopentenone annulations of 1-(phenylseleno)-1-(trimethylsilyl)ethene **8** and α,β-unsaturated acid chlorides **5**–**7** in the presence of Lewis acids were also attempted. In general, the one pot reaction was somewhat capricious, and gave poor yields and low selectivity. For example, when a mixture of **8**, **5** and $TiCl_4$ in $CH_2Cl_2$ at −78 °C, was allowed to warm to room temperature, cyclized products, **9** (42%) and **15** (22%) were obtained. Treatment of **8** and **5** in the presence of $AgBF_4$ at room temperature gave **12** (9%) and the seleno ester **23** (24%) as a by-product.



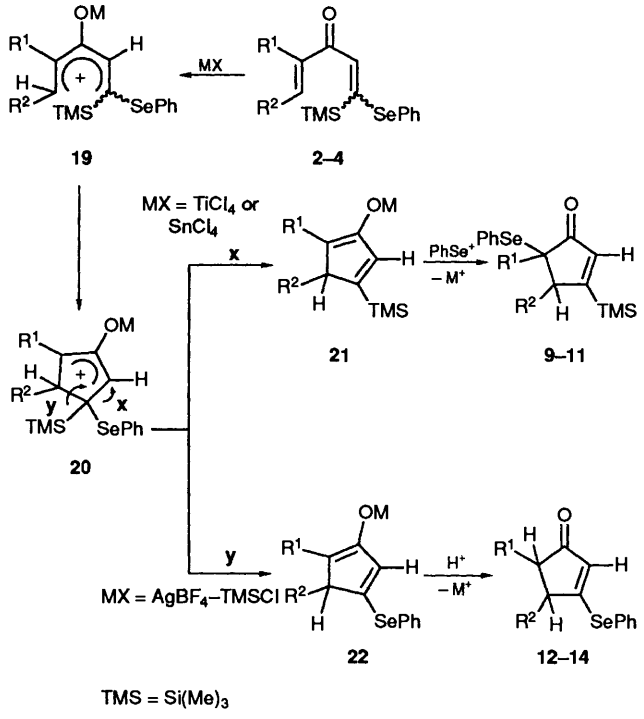

**23**




Scheme 4

oxygen more strongly than $AgBF_4$ or TMSCl alone and facilitate cyclization. By the use of $TiCl_4$ or $SnCl_4$ (path **x**), **20** loses the SePh group to give the diene **21** mainly. The latter is converted into **9–11** by phenylselenenylation with the $PhSe^+$ generated *in situ*. The minor products, **15** and **16** in Scheme 4, were formed by either protonation of **21**, or reduction of **9** and **11**, respectively. With $AgBF_4$–TMSCl, **20** loses the $SiMe_3$ group instead of the SePh group to give the diene **22** (path **y**). The latter is converted into **12–14** by protonation.

In summary, β-seleno-β-silyl-substituted divinyl ketones **2–4** in the presence of Lewis acids at room temp. give phenylseleno and/or trimethylsilyl functionalized cyclopentenones. Using $TiCl_4$ or $SnCl_4$ afforded 5-(phenylseleno)-3-(trimethylsilyl)-cyclopent-2-enones **9–11** as major products. In this case, C–Se cleavage predominated over C–Si cleavage during cyclization, which has not been observed for sulphur derivatives[5] probably due to the large C–S bond energy, 269 kJ/mol (C–Se bond energy, 251 kJ/mol). On the other hand, using $AgBF_4$–TMSCl results in C–Si cleavage to give 3-(phenylseleno)cyclopent-2-enones **12–14** (Scheme 4). Thus, the predominant leaving group depends on the nature of Lewis acids, and unprecedented fine tuning of C–Se and C–Si bond cleavages has been observed.




Scheme 5

## Experimental

*General Methods.*—M.p.s are uncorrected. IR spectra were recorded with a JASCO FT-IR 5000 spectrophotometer. NMR spectra were recorded in $CDCl_3$ on a JEOL FX-200 spectrometer. For the $^1H$ and $^{13}C$ spectra, $Me_4Si$ was used as an internal reference. *J* Values are given in Hz. For $^{77}Se$ Spectra, $(CH_3)_2Se$ was used as an external reference. Mass spectra were determined on a JEOL JMS-01SG-2 spectrometer and UV–VIS spectra were measured with a Hitachi 100-50 spectrometer. All reactions were carried out under a nitrogen atmosphere.

*1-Phenylseleno-1-trimethylsilylethene* **8**.—Compound **8** was prepared from vinyl selenide according to the literature[6] or by the following procedure: a flask was charged with magnesium turnings (670 mg, 27.7 mmol) and THF (7.28 $cm^3$); 1,2-dibromoethane (145.6 mg) was added. Then, a solution of 1-(bromovinyl)trimethylsilane (3.3 g, 18.4 mmol) in THF (5.45 $cm^3$) was added dropwise to the stirred mixture at a rate that maintained gentle reflux. After the addition was completed, the reaction mixture was kept at reflux for an additional hour. Then a solution of PhSeBr [made by the addition of $Br_2$ (0.52 $cm^3$, 10.2 mmol) to a solution of diphenyl diselenide (3.18 g, 10.2 mmol) in THF (25.5 $cm^3$)] was added dropwise. After being refluxed for an additional hour, the reaction mixture was cooled, diluted with ether, and hydrolysed by addition of saturated aqueous ammonium chloride. The mixture was extracted with ether. The extracts were washed with water, dried ($MgSO_4$) and concentrated. Column chromatography (silica gel; hexane) of the residue gave the title compound **8**[6] (2.54 g, 54%) ($R_f$ = 0.5), as a colourless oil: $\delta_H$ (200 MHz; $CDCl_3$) 0.17 (9 H, s, $SiMe_3$), 5.68 (1 H, s, 2-H), 6.05 (1 H, s, 2-H), 7.26–7.34 (3 H, m, Ph) and 7.52–7.58 (2 H, m, Ph).

*Acid Chlorides* **5–7**.—Compounds **5** and **6** were prepared by literature methods.[5,7f] Compound **7** was commercially available (Nacalai Tesque).

*Preparation of Divinyl Ketones* **2–4**.—A typical experimental procedure is described for the preparation of 1-(cyclopent-1′-enyl)-3-(phenylseleno)-3-(trimethylsilyl)prop-2-en-1-one **2**. To

a solution of $TiCl_4$ (216 mg, 1.14 mmol) in dry dichloromethane (1.71 $cm^3$), cooled to −78 °C, was added compound **8** (227.2 mg, 0.89 mmol), followed by compound **5** (148.6 mg, 1.14 mmol) *via* a syringe. The mixture was stirred at −78 °C for 3 h. The reaction mixture was diluted with water and extracted with dichloromethane. The organic phases were washed with saturated aqueous $NaHCO_3$ and water, dried ($Na_2SO_4$), and evaporated under reduced pressure. The residue was purified by flash column chromatography over silica gel eluting with hexane–$CHCl_3$ (1:1) to give **2a** (147 mg, 47%) ($R_f$ = 0.3) and **2b** (152 mg, 49%) ($R_f$ = 0.2).

**2a**: pale yellow oil; $\nu_{max}$(neat)/$cm^{-1}$ 2956, 1634 (CO), 1578, 1246 and 845; $\lambda_{max}$(MeOH)/nm 289 (log ε 3.16) and 345 (3.96); $\delta_H$(200 MHz; $CDCl_3$) 0.34 (9 H, s, $SiMe_3$), 1.72–1.88 (2 H, m, 4′-H), 2.36–2.48 (4 H, m, 3′,5′-H), 6.14–6.18 (1 H, m, 2′-H), 6.74 (1 H, s, 2-H), 7.44–7.48 (3 H, m, Ph) and 7.56–7.62 (2 H, m, Ph); $\delta_C$(50.1 MHz, $CDCl_3$) −0.391 ($SiMe_3$), 22.70, 30.88, 34.12, 127.6, 129.4, 129.9, 130.4, 137.1, 142.7, 146.6, 165.2 and 184.5 (C-1); $^{77}$Se NMR [$CDCl_3$, relative to $(CH_3)_2Se$] 490.6 ppm; *m/z* 350 ($M^+$, 31%), 335 (100), 255 (83), 95 (100) and 73 (100); (Found: $M^+$, 350.0603. Calc. for $C_{17}H_{22}OSeSi$: *M*, 350.0605).

**2b**: yellow *crystals*; m.p. 85–87 °C (from hexane) (Found: C, 58.0; H, 6.35. $C_{17}H_{22}OSeSi$ requires C, 58.44; H, 6.35%); $\nu_{max}$(KBr)/$cm^{-1}$ 2954, 1619 (CO), 1503, 1246, 945 and 841; $\lambda_{max}$(MeOH)/nm 286 (log ε 3.30) and 349 (4.21); $\delta_H$(200 MHz; $CDCl_3$) −0.046 (9 H, s, $SiMe_3$), 1.88–2.04 (2 H, m, 4′-H), 2.53–2.73 (4 H, m, 3′,5′-H), 6.76–6.81 (1 H, m, 2′-H), 7.30–7.38 (3 H, m, Ph), 7.52 (1 H, s, 2-H) and 7.70–7.75 (2 H, m, Ph); $\delta_C$(50.1 MHz; $CDCl_3$) 1.04 ($SiMe_3$), 22.94, 31.08, 34.21, 128.75, 128.69, 129.0, 130.4, 137.8, 142.4, 146.8, 165.1 and 187.0 (C-1); $^{77}$Se NMR [$CDCl_3$, relative to $(CH_3)_2Se$] 583.1 ppm; *m/z* 350 ($M^+$, 44%), 335 (100), 255 (57), 95 (100) and 73 (88); (Found: $M^+$, 350.0602. Calc. for $C_{17}H_{22}OSeSi$: *M*, 350.0604).

1-(*Cyclohex*-1′-*enyl*)-3-(*phenylseleno*)-3-(*trimethylsilyl*)*prop*-2-*en*-1-*one* **3**. **3a** (30.3%) [$R_f$ = 0.3 (hexane–$CHCl_3$ = 1:1)]; pale yellow oil; $\nu_{max}$(neat)/$cm^{-1}$ 1634 (CO), 1526, 1244 and 1212; $\delta_H$(200 MHz; $CDCl_3$) 0.314 (9 H, s, $SiMe_3$), 1.47–1.61 (4 H, m, 4′,5′-H), 2.08–2.14 (4 H, m, 3′,6′-H), 6.37–6.41 (1 H, m, 2′-H), 6.74 (1 H, s, 2-H), 7.41–7.44 (3 H, m, Ph) and 7.56–7.61 (2 H, m, Ph); $\delta_C$(50.1 MHz, $CDCl_3$) −0.274 ($SiMe_3$), 21.51, 22.00, 23.43, 26.15, 127.7, 129.3, 129.8, 130.2, 137.0, 139.4, 139.9, 163.8 and 188.2 (C-1); *m/z* 364 ($M^+$, 14%), 349 (100), 269 (29), 207 (32) and 73 (38) (Found: $M^+$ 364.0789. Calc. for $C_{18}H_{24}OSeSi$: *M*, 364.0762).

*Compound* **3b** (17.3%) [$R_f$ = 0.2 (hexane–$CHCl_3$ = 1:1)]; yellow crystals; m.p. 64–67 °C (from hexane) (Found: C, 59.5; H, 6.6. $C_{18}H_{24}OSeSi$ requires C, 59.49; H, 6.66%); $\nu_{max}$(KBr)/$cm^{-1}$ 1634 (CO), 1607, 1509 and 1217; $\delta_H$(200 MHz; $CDCl_3$) −0.044 (9 H, s, $SiMe_3$), 1.64–1.69 (4 H, m, 4′,5′-H), 2.27–2.36 (4 H, m, 3′,6′-H), 6.92–6.96 (1 H, m, 2′-H), 7.24–7.37 (3 H, m, Ph), 7.51 (1 H, s, 2-H) and 7.68–7.73 (2 H, m, Ph); $\delta_C$(50.1 MHz, $CDCl_3$) 0.951 ($SiMe_3$), 21.65, 22.09, 34.21, 23.43, 26.24, 128.6, 128.8, 130.6, 137.5, 139.3, 140.1, 163.59 and 190.19 (C-1); *m/z* 364 ($M^+$, 10%), 349 (32) and 109 (100).

(4E)-1-*Phenylseleno*-1-*trimethylsilylhexa*-1,4-*dien*-3-*one* **4**. **4a** (17%) [$R_f$ = 0.3 (hexane–$CHCl_3$ = 1:1)]; pale yellow oil; $\nu_{max}$(neat)/$cm^{-1}$ 1669 (CO), 1653, 1624 and 1522; $\delta_H$(200 MHz, $CDCl_3$) 0.33 (9 H, s, $SiMe_3$) 1.78 (3 H, dd, $J_{4,6}$ 1.47, $J_{5,6}$ 6.82, 6-H), 5.94 (1 H, qd, $J_{4,6}$ 1.47, $J_{4,5}$ 15.7, 4-H), 6.44 (1 H, s, 2-H), 6.60 (1 H, qd, $J_{5,6}$ 6.82, $J_{4,5}$ 15.7, 5-H), 7.43–7.45 (3 H, m, Ph) and 7.56–7.60 (2 H, m, Ph); $\delta_C$(50.1 MHz; $CDCl_3$) −0.391 ($SiMe_3$), 18.41 (C-6), 127.5, 129.4, 130.0, 131.7, 132.4, 137.0, 142.5, 167.3 and 185.4 (C-3); *m/z* 324 ($M^+$, 22%), 309 (86), 229 (77) and 73 (100) (Found: $M^+$, 324.0449. Calc. for $C_{15}H_{20}OSeSi$: *M*, 324.0448).

*Compound* **4b** (16%) [$R_f$ = 0.2 (hexane–$CHCl_3$ = 1:1)]; yellow crystals; m.p. 42–44 °C (from hexane) (Found: C, 55.8; H, 6.2. $C_{15}H_{20}OSeSi$ requires C, 55.72; H, 6.23%); $\nu_{max}$(neat)/$cm^{-1}$ 1653 (CO), 1609 and 1495; $\delta_H$(200 MHz; $CDCl_3$) −0.053 (9 H, s, $SiMe_3$) 1.93 (3 H, dd, $J_{4,6}$ 1.5, $J_{5,6}$ 7.0, 6-H), 6.32 (1 H, qd, $J_{4,6}$ 1.5, $J_{4,5}$ 15.1, 4-H), 6.98 (1 H, qd, $J_{5,6}$ 7.0, $J_{4,5}$ 15.1, 5-H), 7.19 (1 H, s, 2-H), 7.26–7.38 (3 H, m, Ph) and 7.70–7.75 (2 H, m, Ph); $\delta_C$(50.1 MHz; $CDCl_3$) 1.039 ($SiMe_3$), 18.53 (C-6), 128.7, 129.1, 130.0, 130.4, 132.0, 137.8, 142.8, 167.2 and 187.5 (C-3); *m/z* 324 ($M^+$, 15%), 309 (38) and 229 (38) (Found: $M^+$, 324.0455. Calc. for $C_{15}H_{20}OSeSi$: *M*, 324.0449).

*Reaction of* **2–4** *with* $TiCl_4$.—A typical experimental procedure is described for the reaction of **2a**. To a solution of **2a** (24.9 mg, 0.0713 mmol) in dichloromethane (0.283 $cm^3$) was added $TiCl_4$ (21.5 mg, 0.114 mmol) in dichloromethane (0.283 $cm^3$) dropwise at −78 °C. After 30 min at −78 °C, the mixture was allowed to warm to room temp. and was stirred for 2 h. The reaction mixture was diluted with water and extracted with dichloromethane and the organic phases were washed with saturated aqueous $NaHCO_3$ and water, dried ($Na_2SO_4$) and evaporated under reduced pressure. The residue was purified by TLC [silica gel; hexane–ether (2:1)] to give **9** (16.6 mg, 67%) ($R_f$ = 0.5) and **15** (0.2 mg, 1.4%) ($R_f$ = 0.4).

1-(*Phenylseleno*)-4-(*trimethylsilyl*)*bicyclo*[3.3.0]*oct*-3-*en*-2-*one* **9** was a pale yellow oil (Found: C, 58.45; H, 6.45. $C_{17}H_{22}OSeSi$ requires C, 58.44; H, 6.35%); $\nu_{max}$(neat)/$cm^{-1}$ 2958, 1702 (CO), 1250 and 843; $\delta_H$(200 MHz; $CDCl_3$) 0.066 (9 H, s, $SiMe_3$), 1.17–2.18 (6 H, m, 6,7,8-H), 3.40 (1 H, bd, *J* 9.8, 5-H), 6.13 (1 H, d, *J* 1.47, 3-H), 7.20–7.36 (3 H, m, Ph) and 7.55–7.59 (2 H, m, Ph); $\delta_C$(50.1 MHz; $CDCl_3$) −1.676 ($SiMe_3$), 25.24, 30.00, 36.43, 58.53, 58.71, 127.0, 128.8, 129.0, 137.2, 140.5, 183.9 and 209.8 (C-2); $^{77}$Se NMR [$CDCl_3$, relative to $(CH_3)_2Se$] 487.8 ppm; *m/z* 350 ($M^+$, 66%), 348 (34), 193 (63) and 73 (100) (Found: $M^+$, 350.0622. Calc. for $C_{17}H_{22}OSeSi$: *M*, 350.0605). $^1$H NMR results for **15** were identical with those of **15** which was obtained by a one-pot cyclization of **8** and **5** (*vide post*).

Reaction of **2b** (27 mg) with $TiCl_4$ gave **9** (15.5 mg, 57.4%).

Reaction of **3a** (27 mg) with $TiCl_4$ gave a complex mixture. The mixture was not purified.

Reaction of **3b** (33 mg) with $TiCl_4$ gave a complex mixture. The mixture was not purified.

Reaction of **4a** (20 mg) with $TiCl_4$ gave **11** (6.1 mg, 31%), **16** (0.5 mg, 4.8%), **17** (1.9 mg, 7.6%) and **14** (1.8 mg, 11.6%). 4-Methyl-5-(phenylseleno)-3-(trimethylsilyl)cyclopent-2-enone **11** [$R_f$ = 0.5 (hexane–ether = 2:1)]: pale yellow oil; $\nu_{max}$(neat)/$cm^{-1}$ 2962, 1700 (CO), 1251 and 841; $\delta_H$(200 MHz; $CDCl_3$) 0.105 (9 H, s, $SiMe_3$), 1.21 (1 H, d, $J_{4,4\text{-Me}}$ 7.2, 4-Me), 3.04 (1 H, ddq, $J_{2,4}$ 1.7, $J_{4,5}$ 2.0, $J_{4,4\text{-Me}}$ 7.2, 4-H), 3.27 (1 H, d, $J_{4,5}$ 2.0, 5-H), 6.20 (1 H, d, $J_{2,4}$ 1.7, 2-H), 7.25–7.29 (3 H, m, Ph) and 7.56–7.61 (2 H, m, Ph); $\delta_C$(50.1 MHz, $CDCl_3$) −1.588 ($SiMe_3$), 20.08, 48.84, 50.21, 127.1, 128.6, 129.1, 136.0, 140.0, 186.8 and 206.0 (C-1); *m/z* 324 ($M^+$, 92%), 243 (52), 167 (72), 157 (100) and 73 (100) (Found: $M^+$, 324.0411. Calc. for $C_{15}H_{20}OSeSi$: *M*, 324.0448).

**16** ($R_f$ = 0.4 [hexane–ether = 2/1)]: $^1$H NMR results for **16** were identical with those of **16** which was obtained by one-pot cyclization of **8** and **7** (*vide post*).

3,5-Bis(phenylseleno)-4-methylcyclopent-2-enone **17** [$R_f$ = 0.3 hexane–ether = 2:1]: pale yellow oil; $\nu_{max}$(neat)/$cm^{-1}$ 1687 (CO), 1549, 1250 and 738; $\delta_H$(200 MHz; $CDCl_3$) 1.27 (3 H, d, $J_{4.4\text{-Me}}$ 7.2, 4-Me), 3.17 (1 H, ddq, $J_{2.4}$ 1.2, $J_{4.5}$ 2.4, $J_{4,4\text{-Me}}$ 7.2, 4-H), 3.51 (1 H, d, $J_{4.5}$ 2.4, 5-H), 5.59 (1 H, d, $J_{2,4}$ 1.2, 2-H), 7.24–7.48 (8 H, m, Ph) and 7.59–7.64 (2 H, m, Ph); $\delta_C$(50.1 MHz; $CDCl_3$) 20.14, 48.95, 52.08, 125.5, 127.0, 128.3, 128.6, 129.2, 129.8, 130.0, 135.9, 136.1, 184.2 and 200.5 (C-1); *m/z* 408 ($M^+$, 11%), 406 (10), 327 (17), 251 (31) and 157 (100) (Found: $M^+$, 407.9541. Calc. for $C_{18}H_{16}O^{80}Se_2$: *M*, 407.9532 and 405.9564. Calc. for $C_{18}H_{16}O^{78}Se^{80}Se$: *M*, 405.9539).

4-Methyl-3-(phenylseleno)cyclopent-2-enone **14** [$R_f$ = 0.3 (hexane–ether = 2:1)]: pale yellow oil; $\nu_{max}$($CHCl_3$)/$cm^{-1}$

1676 (CO), 1549 and 1263; $\delta_H$(200 MHz; $CDCl_3$) 1.33 (3 H, d, $J_{4,4\text{-Me}}$ 7.3, 4-Me), 2.14 (1 H, dd, $J_{4,5}$ 2.4, $J_{5,5}$ 18.3, 5-H), 2.75 (1 H, dd, $J_{4,5}$ 6.8, $J_{5,5}$ 18.3, 5-H), 3.12–3.27 (1 H, m, 4-H) and 5.64 (1 H, d, $J_{2,4}$ 1.2, 2-H); $\delta_C$(50.1 MHz, $CDCl_3$) 21.14 ($CH_3$, 4-Me), 39.65 (CH, C-4), 45.26 ($CH_2$, C-5), 125.8 (C), 129.4 (CH), 129.7 (CH), 130.0 (CH), 136.1 (CH), 186.1 (C) and 203.9 (C, C-1); *m/z* 252 ($M^+$, 100%), 95 (99) and 67 (95) (Found: $M^+$, 252.0053. Calc. for $C_{12}H_{12}OSe$ *M*, 252.0053).

Reaction of **4b** with $TiCl_4$ gave **11** (55%), **16** (9.7%) and **14** (3.7%).

*Reaction of* **2–4** *with* $SnCl_4$.—A typical experimental procedure is described for the reaction of **2a**. To a solution of **2a** (19 mg, 0.0544 mmol) in dichloromethane (0.216 $cm^3$) was added $SnCl_4$ (22.7 mg, 0.0872 mmol) in dichloromethane (0.216 $cm^3$) dropwise at −78 °C. After 1 h at −78 °C, the mixture was allowed to warm to room temp. and stirred for 2 h. The reaction mixture was diluted with water and extracted with dichloromethane and the organic phases were washed with saturated aqueous $NaHCO_3$ and water, dried ($Na_2SO_4$) and evaporated under reduced pressure. The residue was purified by TLC [silica gel; hexane–ether 2:1)] to give **9** (13.7 mg, 72%) ($R_f$ = 0.5), **15** (0.1 mg, 0.9%) ($R_f$ = 0.4) and **12** (0.9 mg, 6%) ($R_f$ = 0.2).

4-(Phenylseleno)bicyclo[3.3.0]oct-3-en-2-one **12**: pale yellow oil; $\nu_{max}$(neat)/$cm^{-1}$ 2956, 1694 (CO), 1549, 1264, 1244, 742 and 690; $\delta_H$(200 MHz; $CDCl_3$) 1.26–1.44 (1 H, m), 1.59–1.96 (5 H, m), 2.83–2.92 (1 H, m, 1-H), 3.47 (1 H, t-like, *J* 7.2, 5-H), 5.70 (1 H, s, 3-H), 7.38–7.44 (3 H, m, Ph) and 7.59–7.64 (2 H, m, Ph); $\delta_C$(50.1 MHz, $CDCl_3$) 24.13, 29.24, 31.14, 50.30, 52.87, 126.0, 129.7, 130.0, 130.4, 136.3, 183.7 and 207.4 (C-2); *m/z* 278 ($M^+$, 74%), 276 (41), 121 (100), 93 (70) and 77 (74) (Found: $M^+$, 278.0207. Calc. for $C_{14}H_{14}O^{80}Se$: *M*, 278.0210; and $M^+$, 276.0214. Calc. for $C_{14}H_{14}O^{78}Se$ *M*, 276.0218).

Reaction of **2b** (27.6 mg) with $SnCl_4$ gave **9** (15.7 mg, 57%).

Reaction of **3a** (34 mg) with $SnCl_4$ gave **10** (12.8 mg, 38%). 6-(Phenylseleno)-9-(trimethylsilyl)bicyclo[4.3.0]non-8-en-7-one **10** [$R_f$ = 0.6 (hexane–ether = 2/1)] pale yellow oil; $\nu_{max}$(neat)/$cm^{-1}$ 3058, 2940, 1700 (CO), 1250 and 841; $\delta_H$(200 MHz; $CDCl_3$) 0.097 (9 H, s, $SiMe_3$), 0.956–1.28 (2 H, m), 1.40–3.08 (6 H, m), 3.04 (1 H, dd, $J_{1,2}$ 6.2, 8.2, 1-H), 7.23–7.41 (3 H, m, Ph) and 7.51–7.55 (2 H, m, Ph); $\delta_C$(50.1 MHz; $CDCl_3$) −1.705 ($SiMe_3$), 20.75, 21.30, 29.24, 29.83, 52.46, 55.20, 127.3, 128.8, 129.3, 138.0, 139.1, 183.1 and 207.2 (C-7); *m/z* 364 ($M^+$, 16%), 207 (27), 157 (100) and 73 (100) (Found: $M^+$, 364.0768. Calc. for $C_{18}H_{24}OSe$: *M*, 364.0761).

Reaction of **3b** (29.1 mg) with $SnCl_4$ gave **10** (14.6 mg, 50%).

Reaction of **4a** (23 mg) with $SnCl_4$ gave **11** (8.1 mg, 35%), **16** (1.1 mg, 9%), **14** (2.4 mg, 13%) and **18** (1.7 mg, 9.5%). 3-Methyl-4-(phenylseleno)cyclopent-2-en-1-one **18** [$R_f$ = 0.1 (hexane–ether = 2:1)]: pale yellow oil; $\nu_{max}$($CHCl_3$)/$cm^{-1}$ 1709 (CO), 1682 and 1613; $\delta_H$(200 MHz; $CDCl_3$) 2.27 (3 H, bs, 3-Me), 2.60 (1 H, d, $J_{5,5}$ 18.8, 5-H), 2.93 (1 H, dd, $J_{4,5}$ 6.8, $J_{5,5}$ 18.8, 5-H), 4.20 (1 H, d, $J_{4,5}$ 6.8, 4-H), 5.90 (1 H, bs, 2-H), 7.23–7.35 (3 H, m, Ph) and 7.43–7.50 (2 H, m, Ph); $\delta_C$(50.1 MHz, $CDCl_3$) 18.35, 44.52, 44.84, 126.6, 129.0, 129.4, 131.9, 136.0, 177.0 and 206.2 (C-1); *m/z* 252 ($M^+$, 86%), 250 (43), 157 (19) and 95 (100) (Found: $M^+$, 252.0031. Calc. for $C_{12}H_{12}OSe$: *M*, 252.0054).

*Reaction of* **2a** *with* $AgBF_4$.—To a solution of $AgBF_4$ (18 mg, 0.0925 mmol) in dry 1,2-dichloroethane (0.3 $cm^3$) and dichloromethane (0.1 $cm^3$), cooled to −50 °C, was added **2a** (20 mg, 0.0572 mmol) in dichloromethane (0.1 $cm^3$). After 30 min at −50 °C, the mixture was allowed to warm to room temp. and then stirred for 22 h. The mixture was extracted with dichloromethane and the organic phases were washed with saturated aqueous $NaHCO_3$ and water, dried ($Na_2SO_4$) and evaporated under reduced pressure. The residue was purified by chromatography on silica gel eluting with hexane–$CHCl_3$ to give **2b** (9 mg, 45%) and **12** (5.5 mg, 35%).

*Reaction of* **2–4** *with* $AgBF_4$–TMSCl.—A typical experimental procedure was described for the reaction of **3a**. To a solution of $AgBF_4$ (25.7 mg, 0.132 mmol) in dry 1,2-dichloroethane (0.94 $cm^3$) and dichloromethane (0.21 $cm^3$), cooled to −50 °C, was added **3a** (30 mg, 0.0825 mmol) in dichloromethane (0.42 $cm^3$), followed by chlorotrimethylsilane (10.4 mg, 0.096 mmol). After 30 min at −50 °C, the mixture was allowed to warm to room temp. and stirred overnight. The mixture was extracted with dichloromethane and the organic phases were washed with saturated aqueous $NaHCO_3$ and water, dried ($Na_2SO_4$) and evaporated under reduced pressure. The residue was purified by chromatography on silica gel eluting with hexane–ether (2:1) to give **3b** (3.8 mg, 13%) ($R_f$ = 0.8) and **13** (13.4 mg, 56%) ($R_f$ = 0.2).

9-(*Phenylseleno*)*bicyclo*[4.3.0]*non*-8-*en*-7-*one* **13** was a colourless oil (Found: C, 61.95; H, 5.75. $C_{15}H_{16}OSe$ requires C, 61.86; H, 5.54%); $\nu_{max}$(neat)/$cm^{-1}$ 2934, 2858, 1694 (CO), 1547, 1439, 1256, 1163, 742 and 692; $\delta_H$(200 MHz; $CDCl_3$) 1.24–1.76 (6 H, m), 1.88–2.12 (2 H, m), 2.58 (1 H, ddd, *J* 6.5, 6.8 and 11.6, 6-H), 3.12 (1 H, dd, *J* 6.8 and 7.0, 1-H), 5.68 (1 H, d, *J* 0.8, 8-H), 7.34–7.48 (3 H, m, Ph) and 7.56–7.66 (2 H, m, Ph); $\delta_C$(50.1 MHz; $CDCl_3$) 21.33 ($CH_2$), 21.33 ($CH_2$), 22.73 ($CH_2$), 30.03 ($CH_2$), 44.57 (CH), 47.96 (CH), 125.7 (C), 127.6 (CH), 129.6 (CH), 130.0 (CH), 136.1 (CH), 183.9 (C) and 206.2 (C, C-7); *m/z* 292 ($M^+$, 100%), 290 (50), 157 (58), 135 (68), 107 (58), 91 (57) and 79 (93) (Found: $M^+$, 292.0319. Calc. for $C_{15}H_{16}OSe$: *M*, 292.0367).

Reaction of **2b** (20.8 mg) with $AgBF_4$–TMSCl gave **12** (8.5 mg, 52%).

Reaction of **3b** (30.7 mg) with $AgBF_4$–TMSCl gave **13** (6.2 mg, 25%) and recovered **3b** (14.5 mg, 47%).

Reaction of **4a** (25 mg) with $AgBF_4$–TMSCl gave **14** (6.7 mg, 35%) and **4b** (6.6 mg, 26%).

Reaction of **4b** (23 mg) with $AgBF_4$–TMSCl gave **14** (4.6 mg, 26%) and recovered **3b** (8.5 mg, 37%).

*Reaction of* **3b** *with* $AgOSO_2CF_3$.—To a solution of **3b** (4.0 mg, 0.011 mmol) in dry dichloromethane (0.1 $cm^3$) was added $AgOSO_2CF_3$ (9.0 mg, 0.035 mmol). The mixture was stirred for 32 h at room temp. The mixture was extracted with dichloromethane and the organic phases were washed with saturated aqueous $NaHCO_3$ and water, dried ($Na_2SO_4$) and evaporated under reduced pressure. The residue was purified by TLC [silica gel; hexane–ether 2:1)] to give **13** (1.5 mg, 47%).

*One Pot Cyclization of* **8** *and* **5** *in the Presence of* $TiCl_4$.*—To a solution of $TiCl_4$ (237 mg, 1.25 mmol) in dry dichloromethane (0.5 $cm^3$), cooled to −78 °C, was added **8** (204 mg, 0.799 mmol) in dichloromethane (1.0 $cm^3$) slowly, followed by **5** (120 mg, 0.919 mmol) *via* a syringe. After 3 h at −78 °C, the mixture was stirred at room temp. for 20 h and then diluted with water and extracted with dichloromethane. The organic phases were washed with saturated aqueous $NaHCO_3$ and water, dried ($Na_2SO_4$) and evaporated under reduced pressure. The residue was purified by chromatography over silica gel eluting with $CHCl_3$ to give **9** (117 mg, 42%) ($R_f$ = 0.4) and **15** (34 mg, 22%) ($R_f$ = 0.2).

4-(*Trimethylsilyl*)*bicyclo*[3.3.0]*oct*-3-*en*-2-*one* **15** was a pale yellow oil; b.p. 80–90 °C/15 mmHg (Found: C, 67.3; H, 9.2. $C_{11}H_{18}OSi$ requires C, 67.98; H, 9.33%); $\nu_{max}$(neat)/$cm^{-1}$ 2958, 1705 (CO), 1253 and 841; $\delta_H$(200 MHz; $CDCl_3$) 0.225 (9 H, s, $SiMe_3$), 1.21–1.33 (2 H, m), 1.53–1.853 (4 H, m), 2.67 (1 H, ddd, *J* 9.1, 5.9 and 3.0, 1-H), 3.40–3.49 (1 H, m, 5-H) and

* See footnote page 1556.

6.29 (1 H, d, $J$ 1.47, 3-H); $\delta_C$(50.1 MHz; $CDCl_3$) −1.384 ($SiMe_3$), 24.54, 29.83, 30.00, 50.35, 50.76, 141.8, 186.7 and 214.2 (C-2); $m/z$ 195 ($M^+$, 100%), 179 (74), 166 (69), 151 (47), 120 (57), 83 (59) and 73 (72) (Found: $M^+$, 194.1135. Calc. for $C_{11}H_{18}OSi$: $M$, 194.1127).

*One Pot Cyclization of* **8** *and* **5** *in the Presence of* $AgBF_4$.*—To a solution of $AgBF_4$ (250 mg, 1.28 mmol) in dry 1,2-dichloroethane (0.9 $cm^3$) and dichloromethane (0.6 $cm^3$), cooled to −50 °C, was added 1-phenylseleno-1-trimethylsilylethene **8** (204 mg, 0.799 mmol) slowly, followed by cyclopent-1-enoyl chloride **5** (120 mg, 0.919 mmol) *via* a syringe. After 30 min at −50 °C, the mixture was allowed to warm to room temp. and stirred for 2 h. The mixture was extracted with dichloromethane and the organic phases were washed with saturated aqueous $NaHCO_3$ and water, dried ($Na_2SO_4$) and evaporated under reduced pressure. The residue was purified by chromatography on silica gel eluting with $CHCl_3$ to give **23** (48 mg, 24%) ($R_f$ = 0.7) and **12** (19 mg, 9%) ($R_f$ = 0.3). *Se*-Phenyl cyclopent-1-ene-1-carboselenoate **23** was an orange oil; $\nu_{max}$(neat)/$cm^{-1}$ 2956, 1688 (CO), 1613, 1578, 1476, 1439, 1154, 762, 738 and 688; $\delta_H$(200 MHz; $CDCl_3$) 1.92–2.08 (2 H, m), 2.48–2.60 (2 H, m), 2.62–2.74 (2 H, m), 6.92–6.97 (1 H, m, 2-H), 7.35–7.42 (3 H, m, Ph) and 7.49–7.56 (2 H, m, Ph); $\delta_C$(50.1 MHz; $CDCl_3$) 23.00, 31.24, 33.57, 126.2, 128.8, 129.2, 136.1, 144.0, 145.7 and 189.0 (CO); $m/z$ 252 ($M^+$, 4%), 250 (2), 157 (5), 95 (100) and 67 (30) (Found: $M^+$, 252.0017. Calc. for $C_{12}H_{12}OSe$: $M$, 252.0053).

*One Pot Cyclization of* **8** *and* **7** *in the Presence of* $TiCl_4$.*—To a solution of $TiCl_4$ (216 mg, 1.14 mmol) in dry dichloromethane (1.706 $cm^3$), cooled to −78 °C, was added **8** (227 mg, 0.89 mmol), followed by crotonoyl chloride **7** (119 mg, 0.706 mmol) *via* a syringe. After 40 min at −78 °C, the mixture was stirred at room temperature overnight. The reaction mixture was diluted with water and extracted with dichloromethane and the organic phases were washed with saturated aqueous $NaHCO_3$ and water, dried ($Na_2SO_4$) and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexane–ether (4:1) to give **16** (32 mg, 17%) ($R_f$ = 0.4).

4-Methyl-3-(trimethylsilyl)cyclopent-2-en-1-one **16**: colourless oil; b.p. 70 °C/23 mmHg; $\nu_{max}$(neat)/$cm^{-1}$ 2962, 1716 (CO), 1250 and 839; $\delta_H$(200 MHz; $CDCl_3$) 0.232 (9 H, s, $SiMe_3$), 1.22 (3 H, d, $J_{4,4\text{-Me}}$ 7.3, 4-Me), 1.94 (1 H, dd, $J_{5,5}$ 18.8, $J_{4,5}$ 2.19, 5-H), 2.60 (1 H, dd, $J_{5,5}$ 18.8, $J_{4,5}$ 6.35, 5-H), 3.09–3.16 (1 H, m, 4-H) and 6.29 (1 H, d, $J_{2,4}$ 1.71, 2-H); $\delta_C$(50.1 MHz; $CDCl_3$) −1.46 ($SiMe_3$), 20.94, 39.65, 44.15, 141.2 (C-2), 188.6 (C-3) and 210.6 (C-1); $m/z$ 168 ($M^+$, 40%), 153 (34), 125 (25), 83 (75) and 73 (100) (Found: $M^+$, 168.0979. Calc. for $C_9H_{16}OSi$: $M$, 168.0970).

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* See footnote page 1556.