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Alkynyl Phenyl Selenides as Convenient Precursors for the Synthesis of Stereodefined Trisubstituted Alkenes

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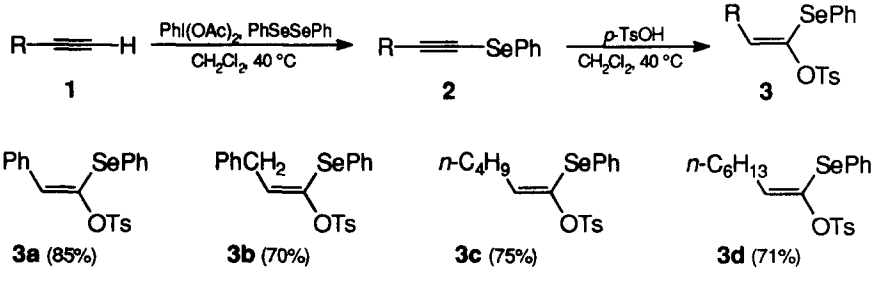
Abstract: The addition of *p*-toluensulfonic acid to alkynyl phenyl selenides is regio- and stereospecific and affords (*Z*)-α-(phenylseleno)vinyl *p*-toluensulfonates in good yield. α-(Phenylseleno)vinyl halides are obtained from the reactions of these compounds with magnesium halides. The reactions of (*Z*)-α-(phenylseleno)vinyl *p*-toluensulfonates with cyanocuprates afford the corresponding trisubstituted alkenes in which the tosyl group has been selectively substituted by an aryl or an alkyl group with retention of configuration. Finally, the cross coupling reaction of these vinyl selenides with methylmagnesium bromide, in the presence of a nickel catalyst, occurs with retention of configuration and affords the selenium free trisubstituted alkenes.

Acetylenic selenides are useful intermediates for the synthesis of several compounds and much attention has been devoted to their preparation and to their synthetic utilizations.[1] We have recently reported a new convenient synthesis of the alkynyl phenyl selenides **2** from the reaction of terminal alkynes **1** (Scheme 1) with iodobenzene diacetate and diphenyl diselenide in methylene chloride,[2] and we now describe a new stereospecific reaction of these compounds which opens the way to new synthetic applications.

Scheme 1

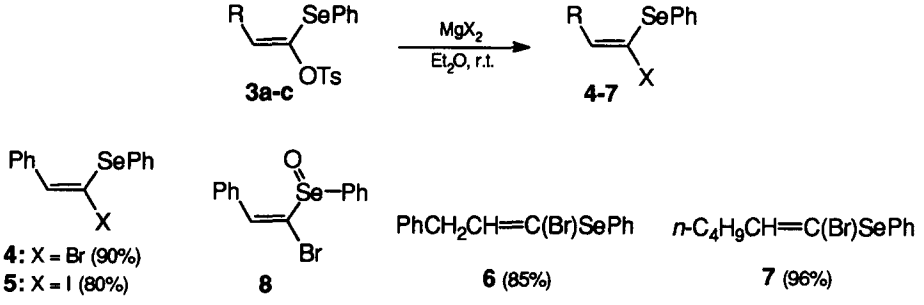


It has recently been reported that the addition of phenylselenenyl *p*-toluensulfonate to alkynes affords β-(phenylseleno)vinyl *p*-toluensulfonates which can be usefully employed for several conversions.[3] It could

be suggested that the same compounds could also be formed by addition of *p*-toluensulfonic acid to the alkynyl phenyl selenides **2**. Indeed this reaction proceeded smoothly at 40 °C in methylene chloride. However, the products obtained, as single stereoisomers, were identified as the (*Z*)-α-(phenylseleno)vinyl *p*-toluensulfonates **3a-d** (Scheme 1). These were slightly contaminated by the corresponding selenol esters, $RCH_2COSePh$, very likely deriving from the hydrolysis of the tosyl group. The orientation of the addition reaction could be deduced from the ^1H NMR spectra of **3b-d** in which the ethylenic proton is found as a triplet at 6.1-5.97 ppm with a vicinal coupling constant of *ca.* 7.7 Hz. The stereochemistry of the addition products, on the contrary, could not unambiguously deduced from the NMR spectra. However, the structure of **3a** was clearly established by an X-Ray diffraction study. The thermal ellipsoid plot of the molecule is shown in Figure 1.[4] These results indicate that the reaction of *p*-toluensulfonic acid with alkynyl phenyl selenides is both a regio- and a stereospecific *cis* addition. This interesting behaviour seems to be peculiar of the alkynyl phenyl selenides since the addition of acids to other alkyne derivatives does not occur with a similar stereoselectivity.[5,6]

The (*Z*)-α-(phenylseleno)vinyl *p*-toluensulfonates **3a-d** are trisubstituted alkenes in which two synthetically versatile groups are linked to the same sp^2-hybridized carbon atom. These intermediates can be considered as vinyl tosylate or vinyl selenides as well as synthetic equivalents of selenol esters. Vinyl selenides, sulfides or enol ethers have all been employed to effect Ni(0) catalyzed cross coupling reactions with Grignard reagents.[7] In these reactions the selenium containing function is much more easily substituted than those containing sulfur or oxygen. On the basis of this different reactivity sequential cross coupling reactions can be easily effected.[7]

Scheme 2



However, when **3a** was treated with PhMgBr, in the presence of $Ni(dppp)Cl_2$, the expected displacement of the phenylseleno group did not take place and the reaction product was the α-(phenylseleno)vinyl bromide **4** (Scheme 2) deriving by the displacement of the tosyl group by bromine. We have then found that these reactions can be better carried out by treating the α-(phenylseleno)vinyl tosylates with magnesium halides. Thus, the reaction of **3a** with magnesium bromide or iodide afforded the α-(phenylseleno)vinyl bromide **4** or iodide **5** in good yield. In these cases the substitution takes place with retention of configuration. The structure of **4** was demonstrated by an X-Ray diffraction study carried out on the selenoxide **8**, easily obtained from **4** by oxidation with *m*-chloroperbenzoic acid. The thermal ellipsoid plot of the molecule is shown in Figure 1.[4] On the contrary, the reaction of **3b** and **3c** with magnesium

bromide afforded compounds **6** and **7** as a 1:1 mixture of the two geometrical isomers. The reactions of the related vinyl triflates with magnesium iodide are also reported to give a mixture of stereoisomers.[8] The reactivity of α-(phenylseleno)vinyl halides has not been investigated so far, but it can be anticipated that they can be employed to effect several conversions. Thus, these reactions with magnesium halides might also find some synthetic applications.

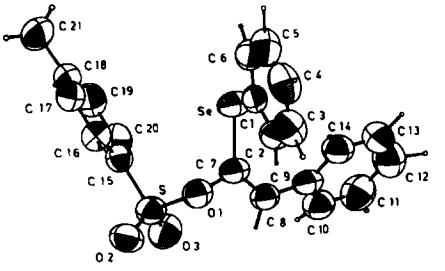


Figure 1. Perspective view of compound **3a**.
Relevant structural parameters (Å, °): Se-C1 1.915(4), Se-C7 1.901(5), C7-C8 1.325(7), C7-O1 1.415(6), S-O1 1.608(4), S-O2 1.416(5), S-O3 1.417(5), S-C15 1.755(5), C1-Se-C7 99.1(2), Se-C7-C8 127.0(4), Se-C7-O1 114.4(3), C7-O1-S 119.5(3).

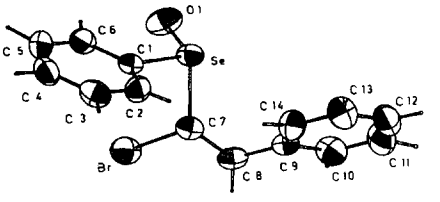
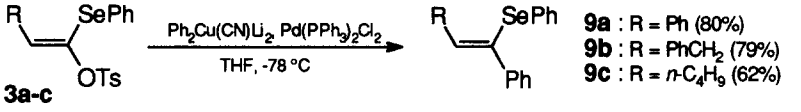


Figure 2. Perspective view of compound **8**.
Relevant structural parameters (Å, °): Se-O 1.646(2), Se-C1 1.938(3), Se-C7 1.949(3), C7-C8 1.321(4), C7-Br 1.885(3), O-Se-C1 103.3(1), O-Se-C7 103.1(1), C1-Se-C7 96.0(1), Se-C7-C8 122.4(3), Se-C7-Br 115.7(2).

The results reported above demonstrate that compounds **3** cannot be employed to effect the cross coupling reaction promoted by Grignard reagents. On the other hand, it is well documented that vinyl triflates react with cuprates and cyanocuprates to give the alkenes deriving from the cross coupling reaction.[9,10] It can be expected that vinyl tosylates can give the same type of reaction. To our knowledge the reaction of vinyl selenides with cuprates has not been investigated. For these reasons, it seemed interesting to effect an investigation on the reactions of the (Z)-α-(phenylseleno)vinyl *p*-toluensulfonates **3** with this important class of organometallic reagents.

Scheme 3

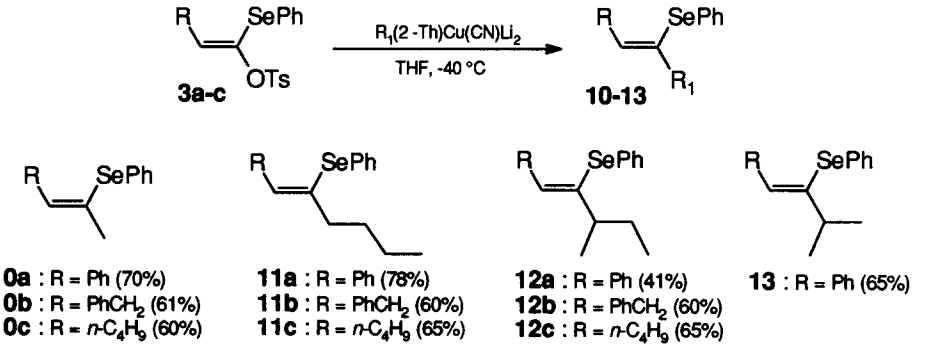


The first experiments were carried out with compounds **3a-c** using $Ph_2Cu(CN)Li_2$. Very satisfactory results were obtained when the reactions were effected in the presence of catalytic amounts of $Pd(PPh_3)_2Cl_2$. Under these conditions, the reaction selectively involved the tosyl group and occurred with retention of configuration (Scheme 3). The trisubstituted alkenes **9a-c** were in fact obtained as single stereoisomers and in good yield. Attempts to introduce alkyl groups using similar cyanocuprates gave unsatisfactory results. However, this problem could be solved using mixed thienyl cyanocuprates.[11,12] Thus, the reactions of **3a-c** with $Me(2\text{-Th})Cu(CN)Li_2$, $n\text{-}C_4H_9(2\text{-Th})Cu(CN)Li_2$ and $s\text{-}C_4H_9(2\text{-Th})Cu(CN)Li_2$ afforded compounds **10a-c**, **11a-c** and **12a-c**, respectively, in reasonable to good yields (Scheme 4). Compound **13** was obtained from the reaction of **3a** with $i\text{-}C_3H_7(2\text{-Th})Cu(CN)Li_2$.

The stereochemistry of the reaction products was assigned on the basis of the results of differential NOE experiments. Thus irradiation of the ethylenic proton resulted in a positive NOE on the α hydrogen atoms of the alkyl groups linked to the other ethylenic carbon atom.

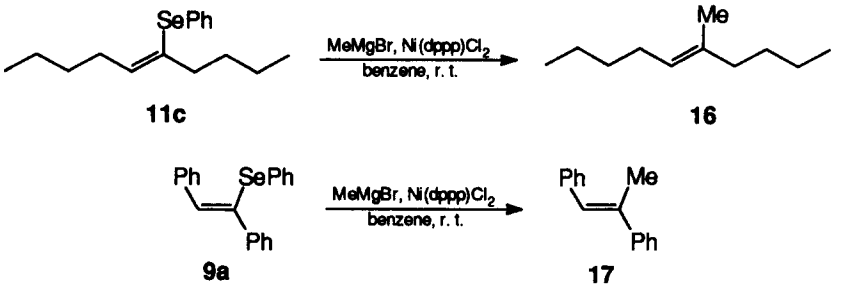
Considerable amounts of the products deriving from the substitution of the tosyl group by an hydrogen atom were also isolated from the reactions carried out with the cyanocuprates containing the *n*-C_4H_9, *s*-C_4H_9 or the *i*-C_3H_7 groups. Thus, together with compounds **11a**, **12a** and **13**, (*Z*)-PhCH=CHSePh **14** was also formed in 10, 30 and 25%, respectively, and, together with **11b** and **12b**, (*Z*)-$PhCH_2CH$=CHSePh **15** was obtained in 10 and 21% yield. The *cis* relationship between the two ethylenic hydrogen atoms was indicated by their coupling constant which was of *ca.* 9-10 Hz. Also in this case therefore, the reaction is stereospecific and occurs with retention of configuration.

Scheme 4



The unprecedented chemoselectivity observed in the reactions of cyanocuprates with (*Z*)-α-(phenylseleno)vinyl *p*-toluensulfonates is noteworthy and the results described above demonstrate that these organoselenium compounds are useful precursors for the synthesis of stereodefined trisubstituted alkenes. Moreover, in the alkenes **9-13** one of the substituents is the phenylseleno group and this can be further manipulated to afford other products. These compounds, for instance, can now be used to effect the Ni(0) catalyzed cross coupling reactions with Grignard reagents.[7] This is illustrated by the two examples reported in Scheme 5 which refer to the reactions carried out with methylmagnesium bromide in the presence of $Ni(dppp)Cl_2$.

Scheme 5



Under these conditions, compounds **11c** and **9a** give the selenium free trisubstituted alkenes **16** and **17** in 66 and 60% yield, respectively. In the latter case a 10% of the other geometrical isomer was also present.

In conclusion, starting from easily available alkynyl phenyl selenides, a convenient synthesis of stereodefined trisubstituted alkenes has been described. This methodology favourably compares with other previously described procedures.[13] The success of these conversions is based on two new and interesting sterospecific processes, *i. e.* the addition of *p*-toluensulfonic acid to alkynyl phenyl selenides and the chemoselective reactions of (*Z*)-α-(phenylseleno)vinyl *p*-toluensulfonates with cyanocuprates. Both the (*Z*)-α-(phenylseleno)vinyl *p*-toluensulfonates **3a-d** and the selenium containing trisubstituted alkenes **9-13** can also be employed for other reactions different from those described in the present paper.

EXPERIMENTAL

GLC analyses and MS spectra were carried out with an HP 5890 gaschromatograph (dimethyl silicone column, 12.5 m) equipped with an HP 5971 Mass Selective Detector. In the spectra described below only the peaks of the most abundant ^{80}Se isotope are reported. ^1H and ^{13}C NMR spectra were recorded at 200 and 50.32 MHz, respectively, on a Bruker AC 200 instrument; $CDCl_3$ was used as solvent and TMS as standard. Elemental analyses were carried out on a Carlo Erba 1106 Elemental Analyzer. Melting points are uncorrected. The alkynyl phenyl selenides **2** were prepared as previously described.[2]

Addition of *p*-Toluensulfonic Acid to Alkynyl Phenyl Selenides. General Procedure. A mixture of the alkynyl phenyl selenide (5 mmol) and *p*-toluensulfonic acid (20 mmol) in methylene chloride (30 mL) was stirred at 40 °C for 3 h and overnight at room temperature. The reaction mixture was filtered through an Al_2O_3 and K_2CO_3 column and the solvent was evaporated. The residue was purified by flash chromatography using a 9:1 mixture of light petroleum and ethyl ether as eluant. Physical and spectral data are reported below.

(*Z*)-1-(Phenylseleno)-2-phenylethenyl *p*-toluensulfonate (3a) : mp 64-65°C; ^1H NMR δ 7.65 (AA'BB' system, 2 H), 7.4-7.1 (m, 12 H), 6.95 (s, 1 H), 2.4 (s, 3 H); ^{13}C NMR δ 145.2, 133.2, 133.1, 131.1, 129.6, 129.2, 129.1, 128.6, 128.5, 128.2, 127.8, 21.7. Anal. Calcd for $C_{21}H_{18}O_3SSe$: C, 58.74; H 4.23. Found: C, 58.81; H, 4.30.

(*Z*)-1-(Phenylseleno)-3-phenyl-1-propen-1-yl *p*-toluensulfonate (3b) : mp 71-73°C; ^1H NMR δ 7.65 (AA'BB' system, 2 H), 7.4-7.0 (m, 12 H), 6.1 (t, 1 H, J = 7.8 Hz), 3.53 (d, 2 H, J = 7.8 Hz), 2.4 (s, 3 H); ^{13}C NMR δ 145.0, 138.8, 138.2, 134.1, 132.8, 132.5, 129.4, 129.2, 129.0, 128.5, 128.2, 127.5, 126.4, 36.1, 21.6. Anal. Calcd for $C_{22}H_{20}O_3SSe$: C, 59.59; H, 4.55. Found: C, 59.65; H, 4.44.

(*Z*)-1-(Phenylseleno)-1-hexen-1-yl *p*-toluensulfonate (3c): oil; ^1H NMR δ 7.7 (AA'BB' system, 2 H), 7.4-7.1 (m, 7 H), 5.97 (t, 1 H, J = 7.7 Hz), 2.45 (s, 3 H), 2.2 (q, 2 H, J = 7.0 Hz), 1.4-1.1 (m, 4 H), 0.9 (t, 3 H, J = 7.0 Hz); ^{13}C NMR δ 144.9, 137.4, 134.5, 133.1, 131.4, 129.3, 129.0, 128.6, 128.4, 127.1, 30.6, 29.5, 21.8, 21.4, 13.6. Anal. Calcd for $C_{19}H_{22}O_3SSe$: C, 55.74; H, 5.42. Found: C, 55.66; H, 5.49.

(*Z*)-1-(Phenylseleno)-1-octen-1-yl *p*-toluensulfonate (3d): oil; ^1H NMR δ 7.7 (AA'BB' system, 2 H), 7.35-7.15 (m, 7 H), 5.97 (t, 1 H, J = 7.7 Hz), 2.45 (s, 3 H), 2.2 (q, 2 H, J = 7.0 Hz), 1.4-1.2 (m, 8 H), 0.9 (t,

3 H, J = 7.0 Hz); ^{13}C NMR δ 144.8, 137.4, 134.4, 133.1, 131.5, 129.3, 128.9, 128.6, 128.3, 127.1, 31.6, 29.7, 29.0, 28.9, 22.3, 21.4, 13.9. Anal. Calcd for $C_{21}H_{26}O_3SSe$: C, 57.66 ; H, 5,99. Found: C,57.58; H, 6.04.

Reactions of (*Z*)-α-(Phenylseleno)vinyl *p*-Toluensulfonates with Magnesium Halides. General Procedure. A mixture of the (*Z*)-α-(Phenylseleno)vinyl *p*-toluensulfonate (2.5 mmol) and magnesium bromide or iodide[14] (4 mmol) in ether (20 mL) was stirred for 1 h at room temperature. The reaction mixture was poured on water and worked up in the usual way. The reaction product was obtained in a pure form by column chromatography on silica gel using light petroleum as eluant. Physical and spectral data are reported below.

(*E*)-1-Bromo-1-(phenylseleno)-2-phenylethene (4): mp 39-41 °C; ^1H NMR δ 7.58 (s, 1 H), 7.5-7.3 (m, 4 H), 7.3-7.15 (m, 6 H); ^{13}C NMR δ 141.1, 136.2, 133.4, 129.0, 128.6, 128.1, 128.0; MS *m/z* (relative intensity) 340 (58), 338 (75), 259 (38), 178 (100), 157 (42), 102 (69), 77 (50), 51 (52). Anal. Calcd for $C_{14}H_{11}BrSe$: C, 49.73; H, 3.28. Found: C, 49.51; H, 3.15.

(*E*)-1-Iodo-1-(phenylseleno)-2-phenylethene (5): oil: ^1H NMR δ 8.02 (s, 1 H), 7.55-7.25 (m, 10 H); ^{13}C NMR δ 148.5, 138.2, 133.9, 129.2, 128.6, 128.4, 128.2; MS *m/z* (relative intensity) 386 (26), 259 (73), 257 (39), 179 (64), 178 (100), 157 (58), 102 (68), 77 (53), 51 (35). Anal. Calcd for $C_{14}H_{11}ISe$: C, 43.66; H, 2.88. Found: C, 43.27; H, 2.62.

(*E*)-1-Bromo-1-(phenylseleno)-3-phenyl-1-propene (6): oil; ^1H NMR δ 7.6-7.5 (m, 2 H), 7.4-7.15 (m, 8 H), 6.76 (t, 1 H, J = 7.6 Hz), 3.6 (d, 2 H, J = 7.6 Hz); MS *m/z* (relative intensity) 354 (10), 352 (13), 195 (20), 157 (5), 116 (35), 115 (100), 91 (51), 77 (12), 51 (12). Anal. Calcd for $C_{15}H_{13}BrSe$: C, 51.16; H, 3.72. Found: C, 51.08; H, 3.81.

(*E*)-1-Bromo-1-(phenylseleno)-1-hexene (7): oil;[1] ^1H NMR δ 7.55-7.45 (m, 2 H), 7.35-7.25 (m, 3 H), 6.6 (t, 1 H, J = 7.6 Hz), 2.35-2.2 (m, 2 H), 1.5-1.3 (m, 4 H), 0.92 (t, 3 H, J = 7.3 Hz); ^{13}C NMR δ 145.5, 132.2, 129.2, 127.6, 33.4, 30.8, 22.2, 13.8; MS *m/z* (relative intensity) 320 (32), 318 (41), 316 (19), 195 (20), 157 (33), 116 (55), 115 (63), 91 (22), 81 (100), 77 (27).

(*E*)-1-Bromo-1-(phenylseleninyl)-2-phenylethene (8): mp 136-138 °C; ^1H NMR δ 7.79 (s, 1 H), 7.7-7.62 (m, 2 H), 7.56-7.36 (m, 8 H); ^{13}C NMR δ 142.9, 134.3, 132.5, 131.6, 129.5, 129.0, 128.6, 126.3. Anal. Calcd for $C_{14}H_{11}BrOSe$: C, 47.48; H, 3.14. Found: C, 47.19; H, 3.14.

Reactions of (*Z*)-α-(Phenylseleno)vinyl *p*-Toluensulfonates with $Ph_2Cu(CN)Li_2$. General Procedure. To a solution of the cyanocuprate, prepared,[15] under argon, from PhLi (6.5 mmol) and CuCN (3.5 mmol) in THF (20 mL) at -78 °C, $Pd(PPh_3)_2Cl_2$ (0.1 mmol) and the (*Z*)-α-(Phenylseleno)vinyl *p*-toluensulfonate (1.0 mmol) were added. The mixture was stirred at -78 °C for few minutes and then it was allowed to slowly warm to 0 °C. Stirring was continued for 3-5 h. The progress of the reaction was monitored by TLC. The reaction mixture was poured into aqueous ammonium chloride and worked up in the usual way. The reaction product was obtained in a pure form by column chromatography on silica gel using light petroleum as eluant. Physical and spectral data are reported below.

(*Z*)-1-Phenyl-1-(phenylseleno)-2-phenylethene (9a): oil; ^1H NMR δ 7.6-6.9 (m); ^{13}C NMR δ 142.0,

137.6, 135.0, 132.4, 129.2, 128.6, 128.0, 127.9, 127.5, 126.6; MS *m/z* (relative intensity) 336 (18), 179 (100), 178 (93), 177 (10), 176 (12), 77 (9). Anal. Calcd for $C_{20}H_{16}Se$: C, 71.64; H, 4.81. Found: C, 71.70; H, 4.73.

(Z)-1-Phenyl-1-(phenylseleno)-3-phenyl-1-propene (9b): oil; ^1H NMR δ 7.6-7.4 (m, 2 H), 7.4-7.0 (m, 13 H), 6.45 (t, 1 H, J = 7.1 Hz), 3.85 (d, 2 H, J = 7.1 Hz); ^{13}C NMR δ 141.6, 139.9, 137.5, 133.9, 131.2, 128.9, 128.6, 128.3, 128.0, 127.5, 126.3, 126.3, 126.2, 39.4; MS *m/z* (relative intensity) 350 (13), 193 (42), 178 (25), 157 (3), 115 (99), 91 (100), 65 (21). Anal. Calcd for $C_{21}H_{18}Se$: C, 72.20; H, 5.19. Found: C, 72.31; H, 5.28.

(Z)-1-Phenyl-1-(phenylseleno)-1-hexene (9c): oil; ^1H NMR δ 7.6-7.0 (m, 10 H), 6.31 (t, 1 H, J = 7.2 Hz), 2.5 (q, 2 H, J = 7.1 Hz), 1.7-1.2 (m, 4 H), 0.95 (t, 3 H, J = 7.1 Hz); ^{13}C NMR δ 141.8, 139.7, 131.4, 130.8, 128.7, 128.0, 127.8, 127.0, 126.0, 32.7, 31.3, 22.3, 13.8; MS *m/z* (relative intensity) 316 (17), 158 (5), 157 (4), 129 (13), 117 (83), 115 (42), 91 (100), 55 (19). Anal. Calcd for $C_{18}H_{20}Se$: C, 68.57; H, 6.39. Found: C, 68.49; H, 6.31.

Reactions of (Z)-α-(Phenylseleno)vinyl *p*-Toluensulfonates with $R_1(2\text{-Th})Cu(CN)Li_2$. General Procedure. The mixed cyanocuprates were prepared[11] by adding MeMgBr, *n*-BuLi, *s*-BuLi or *i*-PrMgCl (3.5 mmol) at -40 °C to the solution of 2-thienyllithium (3.5 mmol) and CuCN (3.5 mmol) in THF (20 mL). A solution of the (Z)-α-(Phenylseleno)vinyl *p*-toluensulfonate (1.0 mmol) in THF (10 mL) was slowly added. The mixture was stirred at -40°C for 3-5 h. The progress of the reaction was monitored by TLC. The reaction mixture was poured into aqueous ammonium chloride and worked up in the usual way. The reaction product was obtained in a pure form by column chromatography on silica gel using light petroleum as eluant. Physical and spectral data are reported below.

(Z)-1-Phenyl-2-(phenylseleno)-1-propene (10a): oil; ^1H NMR δ 7.65-7.5 (m, 2 H), 7.45-7.25 (m, 8 H), 6.85 (q, 1 H, J = 1.4 Hz), 2.1 (d, 3 H, J = 1.4 Hz); ^{13}C NMR δ 137.8, 135.1, 132.6, 130.7, 130.4, 128.9, 128.7, 128.0, 127.5, 126.9, 27.2; MS *m/z* (relative intensity) 274 (30), 193 (8), 167 (12), 157 (3), 115 (100), 91 (33), 77 (13), 51 (13). Anal. Calcd for $C_{15}H_{14}Se$: C, 65.94; H, 5.16. Found: C, 65.87; H, 5.09.

(Z)-2-(Phenylseleno)-4-phenyl-2-butene (10b): oil; ^1H NMR δ 7.65-7.5 (m, 2 H), 7.45-7.2 (m, 8 H), 6.05 (tq, 1 H, J = 1.3 and 7.2 Hz), 3.75 (d, 2 H, J = 7.2 Hz), 2.15 (q, 3 H, J = 1.3 Hz); ^{13}C NMR δ 140.3, 133.3, 130.0, 129.0, 128.6, 128.4, 127.0, 126.0, 38.3, 26.5; MS *m/z* (relative intensity) 288 (14), 157 (4), 131 (100), 115 (27), 91 (71), 77 (13). Anal. Calcd for $C_{16}H_{16}Se$: C, 66.90; H, 5.61. Found: C, 67.01; H, 5.54.

(Z)-2-(Phenylseleno)-2-heptene (10c): oil; ^1H NMR δ 7.5-7.4 (m, 2 H), 7.3-7.1 (m, 3 H), 5.8 (tq, 1 H, J = 1.3 and 7.1 Hz), 2.4-2.2 (m, 2 H), 2.0 (q, 3 H, J = 1.2 Hz), 1.5-1.2 (m, 4 H), 0.9 (t, 3 H, J = 7.0 Hz); ^{13}C NMR δ 134.8, 133.1, 129.0, 128.9, 127.3, 126.8, 31.6, 26.5, 22.3, 14.0; MS *m/z* (relative intensity) 254 (25), 211 (10), 209 (9), 183 (9), 158 (24), 157 (13), 130 (47), 97 (28), 78 (20), 77 (19), 55 (100). Anal. Calcd for $C_{13}H_{18}Se$: C, 61.66; H, 7.16. Found: C, 61.72; H, 7.24.

(Z)-1-Phenyl-2-(phenylseleno)-1-hexene (11a): oil;[16] ^1H NMR δ 7.75-7.35 (m, 10 H), 7.05 (s, 1 H), 2.5 (t, 2 H, J = 7.5 Hz), 1.75-1.6 (m, 2 H), 1.5-1.3 (m, 2 H), 1.0 (t, 3 H, J = 7.2 Hz); ^{13}C NMR δ 137.7, 136.0, 134.2, 131.3, 129.0, 128.0, 127.4, 127.0, 39.3, 31.6, 21.9, 13.8; MS *m/z* (relative intensity) 316 (39), 274 (10), 179 (12), 157 (11), 117 (100), 115 (83), 91 (80), 77 (18), 55 (17).

(Z)-1-Phenyl-3-(phenylseleno)-2-heptene (11b): oil; ^{1}H NMR δ 7.52-7.4 (m, 2 H), 7.4-7.15 (m, 8 H), 6.05 (t, 1 H, J = 7.1 Hz), 3.7 (d, 2 H, J = 7.1 Hz), 2.25 (t, 2 H, J = 7.2 Hz), 1.6-1.4 (m, 2 H), 1.35-1.15 (m, 2 H), 0.85 (t, 3 H, J = 7.1 Hz); ^{13}C NMR δ 140.4, 134.3, 133.7, 132.4, 130.3, 129.0, 128.5, 126.7, 126.0, 39.1, 38.3, 31.1, 22.0, 13.9; MS *m/z* (relative intensity) 330 (15), 288 (4), 167 (9), 158 (9), 129 (34), 117 (98), 91 (100). Anal. Calcd for $C_{19}H_{22}Se$: C, 69.29; H, 6.73. Found: C, 69.34; H, 6.70.

(Z)-5-(Phenylseleno)-5-decene (11c): oil;[17] ^{1}H NMR δ 7.45-7.35 (m, 2 H), 7.25-7.15 (m, 3 H), 5.85 (t, 1 H, J = 7.0 Hz), 2.4-2.15 (m, 4 H), 1.5-1.1 (m, 8 H), 0.95 (t, 3 H, J = 7.1 Hz), 0.85 (t, 3 H, J = 7.1 Hz); ^{13}C NMR δ 135.6, 132.8, 132.2, 130.7, 128.9, 126.4, 39.1, 31.6, 31.2, 22.3, 21.9, 14.0, 13.9; MS *m/z* (relative intensity) 296 (24), 198 (30), 183 (11), 158 (44), 97 (39), 95 (27), 91 (20), 83 (51), 55 (100).

(Z)-1-Phenyl-2-(phenylseleno)-3-methyl-1-pentene (12a): oil; ^{1}H NMR δ 7.7-7.05 (m, 10 H), 6.90 (s, 1 H), 2.3 (sext, 1 H, J = 6.8 Hz), 1.8-1.55 (m, 1 H), 1.55-1.35 (m, 1 H), 1.14 (d, 3 H, J = 6.8 Hz), 0.85 (t, 3 H, J = 7.4 Hz); ^{13}C NMR δ 137.2, 132.7, 131.6, 130.0, 129.0, 128.3, 127.5, 127.0, 44.2, 29.2, 20.2, 11.6; MS *m/z* (relative intensity) 316 (42), 159 (28), 157 (12), 143 (21), 129 (46), 117 (100), 91 (37), 77 (20). Anal. Calcd for $C_{18}H_{20}Se$: C, 68.57; H, 6.39. Found: C, 68.50; H, 6.48.

(Z)-1-Phenyl-3-(phenylseleno)-4-methyl-2-hexene (12b): oil, ^{1}H NMR δ 7.45-7.35 (m, 2 H), 7.3-7.05 (m, 8 H), 6.05 (t, 1 H, J = 7.0 Hz), 3.78-3.52 (m, 2 H), 2.28 (sext, 1 H, J = 7.0 Hz), 1.7-1.5 (m, 1 H), 1.5-1.3 (m, 1 H), 1.1 (d, 3 H, J = 7.0 Hz), 0.8 (t, 3 H, J = 7.3 Hz); ^{13}C NMR δ 140.2, 134.3, 131.6, 131.0, 129.0, 128.5, 128.4, 126.1, 126.0, 45.0, 38.4, 28.8, 20.0, 11.8; MS *m/z* (relative intensity) 330 (27), 167 (19), 157 (18), 143 (29), 131 (58), 117 (96), 115 (31), 105 (16), 91 (100). Anal. Calcd for $C_{19}H_{22}Se$: C, 69.29; H, 6.73.Found: C, 69.21; H, 6.81.

(Z)-4-(Phenylseleno)-3-methyl-4-nonene (12c): oil; ^{1}H NMR δ 7.45-7.30 (m, 2 H), 7.25-7.1 (m, 3 H), 5.9 (t, 1 H, J = 6.8 Hz), 2.4-2.15 (m, 3 H), 1.65-1.2 (m, 6 H), 1.05 (d, 3 H, J = 7.0 Hz), 0.85 (t, 3 H, J = 7.0 Hz), 0.8 (t, 3 H, J = 7.0 Hz); ^{13}C NMR δ 138.0, 136.3, 130.7, 128.8, 125.8, 45.0, 31.7, 31.5, 28.7, 22.3, 20.1, 14.0, 11.7; MS *m/z* (relative intensity) 296 (26), 158 (16), 157 (11), 109 (8), 95 (24), 83 (62), 69 (35), 55 (100). Anal. Calcd for $C_{16}H_{24}Se$: C, 65.07; H, 8.19. Found: C, 65.00; H, 8.27.

(Z)-1-Phenyl-2-(phenylseleno)-3-methyl-1-butene (13): oil; ^{1}H NMR δ 7.65-7.05 (m, 10 H), 6.95 (br s, 1 H), 2.5 (sept, 1 H, J = 7.3 Hz), 1.15 (d, 6 H, J = 7.3 Hz); ^{13}C NMR δ 137.1, 132.6, 131.5, 130.0, 129.0, 128.3, 127.5, 127.1, 37.3, 22.7; MS *m/z* (relative intensity) 302 (39), 179 (9), 157 (7), 145 (100), 128 (34), 117 (40), 105 (21), 91 (51), 77 (22). Anal. Calcd for $C_{17}H_{18}Se$: C, 67.77; H, 6.02. Found: C, 67.85; H, 5.93.

(Z)-1-Phenyl-2-(phenylseleno)ethene (14): oil;[18] ^{1}H NMR δ 7.6-7.45 (m, 2 H), 7.4-7.1 (m, 8 H), 6.93 (d, 1 H, J = 10.4 Hz), 6.75 (d, 1 H, J = 10.4 Hz); ^{13}C NMR δ 137.2, 132.6, 131.6, 130.0, 129.2, 128.3, 127.5, 127.2, 123.9 ; MS *m/z* (relative intensity) 260 (68), 180 (85), 179 (90), 178 (52), 169 (39), 165 (32), 103 (30), 102 (36), 77 (100), 51 (51).

(Z)-1-(Phenylseleno)-3-phenyl-1-propene (15): oil; ^{1}H NMR δ 7.55-7.45 (m, 2 H), 7.35-7.05 (m, 8 H), 6.6 (d, 1 H, J = 9.3 Hz), 6.22 (dt, 1 H, J = 7.1 and 9.3 Hz), 3.54 (d, 2 H, J = 7.1 Hz); MS *m/z* (relative intensity) 274 (15), 117 (100), 115 (67), 91 (28). Anal. Calcd for $C_{15}H_{14}Se$: C, 65.94; H, 5.16. Found: C, 66.02; H, 5.11.

Reactions of the Vinyl Phenyl Selenides 11c and 9a with MeMgBr and Ni(dppp)Cl_2. To a stirred suspension of the nickel catalyst (0.1 mmol) in dry benzene (10 mL) an ethereal solution of MeMgBr (0.2 mmol) was added under argon. After 15 min at room temperature, first MeMgBr (1.5 mmol) and then a solution of **11c** or **9a** (1.0 mmol) in dry benzene (5 mL) were added. The mixture was stirred at room temperature for 24 h. After the usual work up the residue was chromatographed through a silica gel column using light petroleum as eluant. Physical and spectral data of the products obtained are reported below. The data of the (*E*)-α-methylstilbene were identical to those of a commercially available sample.

(*E*)-5-Methyl-5-decene (16): oil;[19] ^{1}H NMR δ 5.1 (t, 1 H, J = 6.5 Hz), 1.9 (t, 4 H, J = 6.7 Hz), 1.58 (s, 3 H), 1.45-1.15 (m, 8 H), 0.9 (t, 6 H, J = 6.9 Hz); ^{13}C NMR δ 128.5, 124.5, 39.4, 32.1, 30.2, 27.6, 22.3, 15.8, 14.0; MS *m/z* (relative intensity) 154 (14), 97 (25), 84 (11), 70 (21), 69 (75), 57 (26), 55 (100), 43 (13), 41 (40).

(*E*) and (*Z*)-α-Methylstilbene (17): oil; ^{1}H NMR *(E) isomer* δ 7.5-7.0 (m, 10 H), 6.72 (m, 1 H), 2.17 (d, 3 H, J = 1,2 Hz), *(Z) isomer* δ 7.5-7.0 (m, 10 H), 6.35 (m, 1 H), 2.1 (d, 3 H, J = 1.5 Hz); ^{13}C NMR δ 144.0, 138.4, 129.1, 128.9, 128.4, 128.3, 128.2, 127.8, 127.7, 127.1, 126.9, 126.6, 126.4, 126.0, 27.0, 17.5; MS *m/z* (relative intensity) *(E) isomer* 194 (81), 179 (100), 178 (56), 165 (10), 115 (29), 89 (15), 77 (9), *(Z) isomer* 194 (77), 179 (100), 178 (57), 165 (11), 115 (32), 89 (18), 77 (11).

X-Ray Crystallography. All diffraction experiments were made at room temperature using either an Enraf-Nonius CAD-4 (compound **8**) or a Siemens AED (compound **3a**) diffractometer. MoKα radiation was used for **8** and CuKα for **3a**. Automatic peak search, centering and indexing procedures gave a monoclinic cell in each case, with systematic absences consistent with the space group $P2_1/n$. Crystal data are as follows:

8: $C_{14}H_{11}BrOSe$, M=354.10; a=6.206(1), b=11.457(2), c=18.192(3)Å, β=93.91(1)°, V=1290.5(4) Å^3, Z=4, D_c=1.823 g cm^{-3}, μ(MoKα)=59.9 cm^{-1}.

3a: $C_{21}H_{18}O_3SSe$, M=429.39; a=10.617(4), b=9.775(4), c=19.655(7)Å, β=105.39(3)°, V=1967(1)Å^3, Z=4, D_c=1.450 g cm^{-3}, μ(CuKα)=37.2 cm^{-1}.

4544(**8**) and 4063(**3a**) reflections were collected by a Θ-2Θ scan technique up to 2Θ=50°(**8**) and 140°(**3a**). On all reflections profile analysis was performed. No correction for decay was required for **8**. The data of both compounds were corrected for Lorentz and polarization factors. Further corrections for crystal decay as well as for absorption effects were applied for **3a**, which showed also sign of some twinning.

Both structures were solved by a combination of direct methods and difference Fourier techniques and refined on F^2 using full-matrix least-squares. All non-hydrogen atoms were assigned anisotropic thermal parameters. The hydrogen atoms were located from difference Fourier maps and refined isotropically except those of the methyl group in **3a**, which were introduced at their calculated positions and refined as riding atoms. At convergence: (**8**) R=0.0189 for 1503 observed reflections and 199 variables; (**3a**) R=0.0817 for 3136 observed reflections and 297 variables. All calculations were performed on Gould Powernode-6040 and Encore-91 computers using the SHELXL92 program package (G.M. Sheldrick, Program for Structure Refinement, University of Göttingen, 1992). Other crystallographic programs have been cited elsewhere.[20]

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4. In compound **8** the selenium atom is three-coordinated and shows an approximate pyramidal geometry being 0.83 Å out of the plane defined by the three donor atoms. Bond angles around selenium are all less than the tetrahedral value, thus suggesting that the lone pair has some *s* character. Bond distances at selenium are near those normally expected for Se=O and Se-C bonds and are close to those reported for related compounds in which Se=O, Se-C(aryl) and Se-C(alkyl) bonds are present.[21,22] It can be added, however, that unlike the above compounds, in both **8** and **3a** the Se-C bonds do not reflect the expected differences in the hybridization of the carbon atoms. In compound **3a** the coordination around selenium is twofold and the Se-C distances are significantly shorter than those in **8**. The planes of the two phenyl rings make an angle of 51.0(1)° in **8**, while are nearly perpendicular in **3a**, 84.9(2)°. The geometry of the ethylenic double bond is well evident by the following torsional angles: **8**, Se-C7-C8-C9 5.2(5)°, Br-C7-C8-C9 178.2(2)°; **3a**, Se-C7-C8-C9 4.2(9)°, O1-C7-C8-C9 -174.5(5)°. In both compounds the molecules are held together by van der Waals forces, with normal contact distances. Lists of refined coordinates and e.s.d.'s were deposited at the Cambridge Crystallographic Data Centre.
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