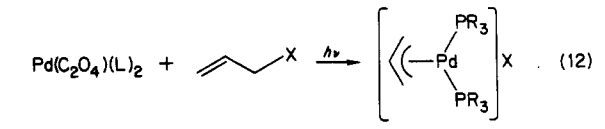
and δ 5.3 (CH_3CN/C_6D_6) when the respective oxalate complexes were irradiated in the presence of a fivefold excess of PhC≡CPh.

One of the more interesting reactions was the clean photochemical conversion of $Pd(C_2O_4)$(diphos) and $Pd(C_2O_4)[P(n\text{-}Bu)_3]$ into η^3-allyl complexes according to eq 12. When L = diphos, the photochemical reaction (X =



X=OAc, Cl, OPh, OH, OEt; L_2=diphos or $[P(n\text{-}Bu)_3]_2$

(12)

Cl, OAc, OPh, OH, OEt in eq 12) proceeded to yield a singlet (δ 51.9) in the ^{31}P NMR spectra. For allyl chloride this initial product underwent secondary photolysis to produce $PdCl_2$(diphos), identified by comparison of its phosphorus chemical shift (δ 65.6) with that of an authentic sample. The allyl complex was isolated in analytically pure form by metathesis with NH_4PF_6. Analogous behavior was observed for the $P(n\text{-}Bu)_3$ derivative (X = Cl, OAc, OPh), and the allyl complex was isolated as the BPh_4^- salt. When similar reactions were attempted with the platinum oxalate system (L = diphos and PEt_3), a complex mixture of products was obtained.

The chemistry of PdL_2 differs from that of PtL_2 in several respects. We have mentioned the instability of the corresponding dihydride, PdH_2L_2, and the lack of well-defined chemistry with alcohol substrates. Qualitative observations suggest that the stability of olefin and alkyne complexes with PdL_2 is less than with PtL_2 analogues. One unusual contrast between the reactions of photogenerated PdL_2 and PtL_2 arises from their reactions with allyl chloride and other substituted allyls. For PdL_2 oxidative addition of the allyl derivative occurs in high yield according to eq 12. When similar reactions were attempted with PtL_2, the ^{31}P NMR spectra revealed a complex mixture of products. The ability of PdL_2 to react stoichiometrically with allyl substrates to form cationic allyl complexes is believed to be a key step in allylic alkylations that are catalyzed by Pd(0) phosphine complexes.[44] The reaction of eq 12 provides an experimental verification that this hypothesis is reasonable.

Acknowledgment. This work was supported by the U.S. Army Research Office and the National Science Foundation (CHE-8312853).

Registry No. **1**, 81457-59-2; **2**, 23697-36-1; **3**, 94929-00-7; **4**, 94929-01-8; **5**, 94929-02-9; **6**, 94929-03-0; **7**, 94929-04-1; **8**, 94929-05-2; **9**, 94929-06-3; **10**, 76136-93-1; **11**, 53987-15-8; **12**, 39045-37-9; **13**, 76125-09-2; **14**, 13964-96-0; **15**, 81457-60-5; **16**, 80540-37-0; **17**, 13938-93-7; *trans*-**18**, 62945-61-3; *cis*-**18**, 61459-92-5; **18**-d_1, 94929-07-4; **18**-d_2, 94992-28-6; **19**, 18974-13-5; **20**, 94929-08-5; **21**, 84624-81-7; **22**, 94929-09-6; **23**, 94929-11-0; **24**, 81800-05-7; **25**, 48074-87-9; **26**, 72778-83-7; $Pd(C_2O_4)$(diphos), 94929-12-1; $Pd(C_2O_4)[P(n\text{-}Bu)_3]_2$, 94929-13-2; *cis*-$PtCl_2(PEt_3)_2$, 15692-07-6; *cis*-$PtCl_2(PPh_3)_2$, 15604-36-1; $Pt(C_2O_4)(PMe_3)(PPh_3)$, 94929-14-3; *trans*-$PtHCl(PEt_3e_2$, 16842-17-4; Pd(COOMeC≡CCOOMe)(diphos), 52585-44-1; $[(\eta^3\text{-}C_3H_5)Pd(diphos)]PF_6$, 41449-73-4; $\{(\eta^3\text{-}C_3H_5)Pd[P(n\text{-}Bu)_3]_2\}BPh_4$, 94929-15-4; $PtH_2(PEt_3)_3$, 33937-25-6; $PtH_2(C_2F_4)(PEt_3)_2$, 80540-36-9; $Pd(C_2H_4)$(diphos), 94929-16-5; $Pd(C_2F_4)$(diphos, 94929-17-6; $Pd(C_2H_4)[P(n\text{-}Bu)_3]_2$, 94929-18-7; $Pd(C_2F_4)[P(n\text{-}Bu)_3]_2$, 94929-19-8; Pd(PhC≡CPh)(diphos), 94929-20-1; Pd(PhC≡CPh)$[P(n\text{-}Bu)_3]_2$, 94929-21-2; $[(\eta^3\text{-}C_3H_5)$-Pd(diphos)]OAc, 94929-22-3; $[(\eta^3\text{-}C_3H_5)Pd(diphos)]Cl$, 94929-23-4; $[(\eta^3\text{-}C_3H_5)Pd(diphos)]OPh$, 94929-24-5; $[(\eta^3\text{-}C_3H_5)Pd(diphos)]OH$, 94929-25-6; $[(\eta^3\text{-}C_3H_5)Pd(diphos)]OEt$, 94929-26-7; $\{(\eta^3\text{-}C_3H_5)$-$Pd[P(n\text{-}Bu)_3]_2\}OAc$, 94929-27-8; $\{(\eta^3\text{-}C_3H_5)Pd[P(n\text{-}Bu)_3]_2\}Cl$, 94929-28-9; $\{(\eta^3\text{-}C_3H_5)Pd[P(n\text{-}Bu)_3]_2\}OPh$, 94929-29-0; $PdCl_2$-(diphos), 19978-61-1; *cis*-$PtCl_2(SEt_2)_2$, 15442-57-6; *trans*-$PdCl_2$-$[P(n\text{-}Bu)_3]_2$, 17523-47-6; $Pt(PEt_3)_2$, 66916-63-0; *trans*-$PtHI(PEt_3)_2$, 16971-06-5; $PtH_2(PEt)_3$, 94929-30-3; $PtH(O_2CH)(PEt_3)_2$, 81768-78-7; $Ag_2C_2O_4$, 533-51-7; C_2F_4, 116-14-3; C_2H_4, 74-85-1; Et_3SiD, 1631-33-0; CH_3I, 74-88-4; CH_3Cl, 74-87-3; Et_3SiH, 617-86-7; Me_3SiH, 993-07-7; COOMeC≡CCOOMe, 762-42-5; PhCl, 108-90-7; PhC≡CPh, 501-65-5; Pt, 7440-06-4; Pd, 7440-05-3; allyl acetate, 591-87-7; allyl chloride, 107-05-1; allyl phenoxide, 1746-13-0; allyl alcohol, 107-18-6; allyl ethoxide, 557-31-3.

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Synthesis of Aryl Phenyl and Heteroaryl Phenyl Selenides by Nickel(II)-Catalyzed Arylation of Sodium Benzeneselenoate

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The substitution of halogen on various aryl, pyridyl, and thienyl iodides or bromides by sodium benzeneselenolate is catalyzed by various complexes of nickel(II) bromide with chelating phosphine or nitrogen heterocycles. The most efficient catalyst is bis(bipyridyl)nickel(II) bromide. The reaction is regioselective and gives high yields of the corresponding aryl phenyl selenides, pyridyl phenyl selenides, and thienyl phenyl selenides.

A variety of synthetic routes to unsymmetrical diaryl selenides are available. They imply, however, high-energy σ complexes,[1] aryl radicals ($S_{RN}1$ mechanisms),[2] diazonium salts,[3] Grignard reagents[4] alkyllithium reagents,[4b] diarylmercurials,[4a] and, more recently, aryl selenocuprates[5] and (phenylseleno)dimethylsulfonium tetrafluoroborate.[6] The reagents or the intermediates involved are highly reactive, often not compatible with functional groups present in the

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Table I. Influence of Relative Amounts of *p*-Bromotoluene and $(bpy)_2NiBr_2$ on the Amount of Diphenyl Selenide[a]

no. of equiv of p-$CH_3C_6H_4Br$	molar ratio[b] (%) of $(bpy)_2NiBr_2$	molar ratio[c] (%) of $(C_6H_5)_2Se$	yield[a] (%) of p-$CH_3C_6H_4SeC_6H_5$
1	10	12.0	76
1.2	10	8.3	83
1.4	10	9.1	80
2	10	6.3	85
3	10	6.9	81
3	5	4.9	91

[a] Determined by GLC with *n*-pentadecane as internal standard on a 6 ft × 0.125 in. stainless-steel column packed with 10% SE 30 on PAW (80-100 mesh). [b] Molar ratio of catalyst with regard to sodium benzeneselenolate. [c] Molar ratio of diphenyl selenide in the mixture of diphenyl selenide and *p*-tolyl phenyl selenide.

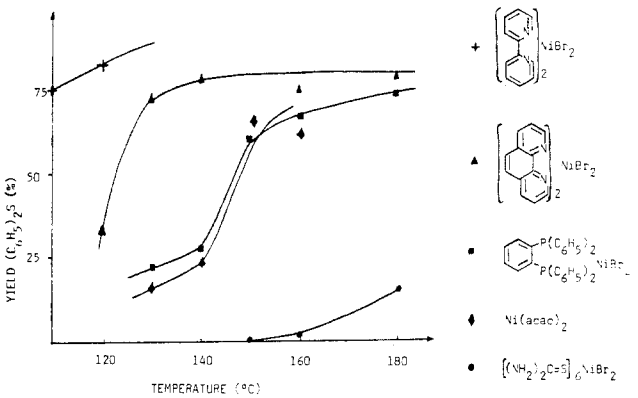


Figure 1. Relative efficiencies of varous nickel complexes as catalysts in the phenylation of sodium phenylthiolate by bromobenzene. Reaction done in diethyleneglycol for 24 h using stoichiometric amounts of C_6H_5Br and C_6H_5SNa with 0.003 equiv of nickel complex. These conditions are not optimum conditions for a maximum yield in $(C_6H_5)_2S$ but conditions of comparison of the catalysts.

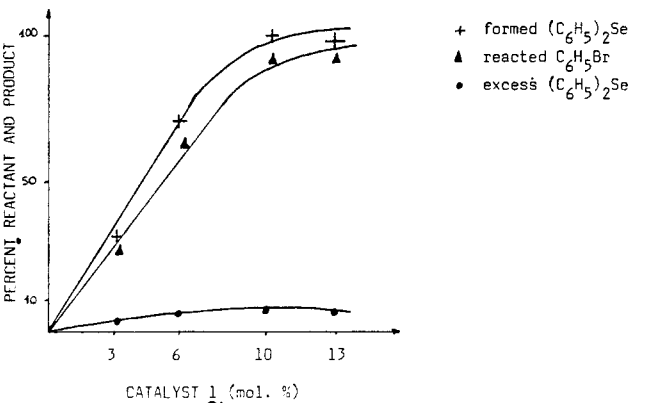


Figure 2. The side reaction as a function of the amount of nickel catalyst used.

molecule. The methods used require sometimes tedious manipulations and are not always regioselective.

Recently we developed a new method for the preparation of diaryl sulfides which involves the reaction of an arenethiolate with an aryl bromide catalyzed by a nickel(II) complex with a chelating phosphorus ligand (e.g., 1,2-bis(diphenylphosphino)benzene).[7] We have improved the method by using new complexes of nickel with chelating nitrogen heterocycles (e.g., 2,2′-bipyridine and *o*-phenanthroline). The best catalytic efficiency was found to be that with bis(bipyridyl)nickel(II) bromide (Figure 1). The latter was easily obtained as an air-stable, green powder by reacting stoichiometric amounts of 2,2′-bipyridine and anhydrous nickel bromide in refluxing ethanol.

The improved synthetic method for the preparation of diaryl sulfides using this complex is shown in eq 1.

$$p\text{-}RC_6H_4SNa + p\text{-}R'C_6H_4Br \xrightarrow[\text{diethylene glycol/120 °C/24 h}]{\text{0.003 M } (bpy)_2NiBr_2} RC_6H_4SC_6H_4R' \quad (1)$$

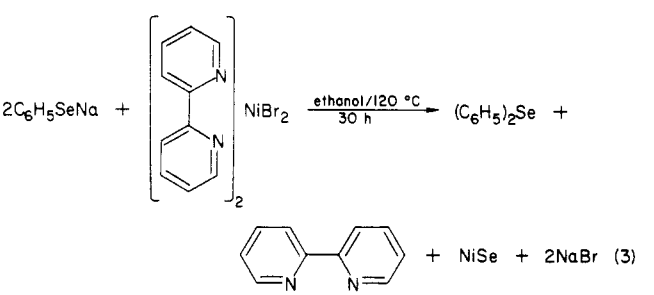
R	R′	yield, %
H	H	81
H	C(O)CH_3	81
H	CF_3	90

The same catalytic efficiency was observed for the arylation of sodium benzeneselenolate, and we report here the synthesis of aryl phenyl selenides by the reaction of sodium benzeneselenolate with an aryl halide catalyzed by complex 1.

The initial study of the reaction was done on the phenylation of sodium benzeneselenolate with bromobenzene. Whereas the uncatalyzed reaction does not even give a trace amount of diphenyl selenide, the reaction catalyzed by complex 1 gives an excellent yield of diphenyl selenide (eq 2).

$$C_6H_5SeNa + C_6H_5Br \xrightarrow[\text{ethanol/120 °C/24 h}]{(bpy)_2NiBr_2 \text{ cat.}} (C_6H_5)_2Se \quad (2)$$

The amount of diphenyl selenide depends on the ratio of catalyst and, in this reaction, is surprisingly greater than the theoretical amount assuming that all reacted bromobenzene has been transformed into diphenyl selenide (Figure 2). This discrepancy is due to a side reaction of the catalyst with sodium benzeneselenolate. When stoichiometric amounts of catalyst and sodium benzeneselenolate are caused to react under the same conditions as the catalytic arylation reaction, but without bromobenzene, one can isolate diphenyl selenide together with 2,2′-bipyridine and nickel selenide (eq 3).



However, this drawback can be overcome. The amount of diphenyl selenide formed in eq 3 depends on the kinetic competition between the catalytic reaction and the side

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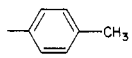
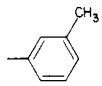
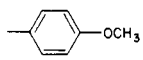
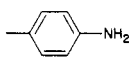
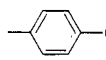
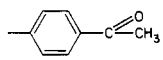
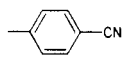
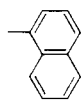
Table II. Aryl Phenyl Selenides, $ArSeC_6H_5$

case	Ar	X	method	yield,[a] %	mp (°C) or dist temp (°C/torr)	mol formula[b] or lit. data (°C)
1		I	A	98	170/0.2	$C_{12}H_{10}Se$
2		I Br	A B	92 88	175/0.15	$C_{13}H_{12}Se$
3		I	A	90	175/0.15	$C_{13}H_{12}Se$
4		I	A	94	175/0.15	$C_{13}H_{12}Se$
5		Br	B	44[c]	44.3	45-46[d]
6		I	A	87	91	92-93[e]
7		Br	B[f]	74	190/0.1	$C_{12}H_9ClSe$
8		Br	C	78	61.2	$C_{14}H_{12}OSe$
9		Br	C	86	49	$C_{13}H_9NSe$
10		Br	B	87	240/0.2	$C_{16}H_{12}Se$
11α		Br	B	78 (40)[g]	200/0.2	$C_{12}H_9BrSe$
11β		Br	B	trace amount (60)[g]	*h*	$C_{18}H_{14}Se_2$
12		Br	B	87	190/0.1	$C_{11}H_9NSe$
13		Br	B	85	190/0.15	$C_{11}H_9NSe$
14		Br	B	88	165/0.1	$C_{10}H_8SSe$
15		Br	B	88	170/0.1	$C_{10}H_8SSe$

[a] Yields of pure isolated compounds. [b] Microanalyses were in satisfactory agreement with calculated values. Analytical samples were obtained by Kugelrohr distillation or recrystallization. [c] The low yield in *p*-anisyl phenyl selenide is due to a side reaction giving $C_6H_5SeCH_3$. [d] See ref 4b. [e] See ref 6. [f] *p*-Bromochlorobenzene is a particular case. Although chlorine is considered as an electron-attracting group, method B was necessary to get a good yield in the corresponding selenide. [g] In order to isolate 11β, method B was modified with the following conditions: 2 equiv of benzeneselenolate, 20% of catalyst, 120 °C, 6 h in ethanol. [h] This compound was not distilled but freed of solvent by heating at 200 °C under 0.2 torr for 30 min.

reaction, and two parameters, the relative amounts of aryl halide and nickel catalyst to benzeneselenolate, can be modified to minimize it. This was done in one of the most unfavorable cases (i.e., the arylation with *p*-bromotoluene), and the best balance for a minimum ratio of diphenyl selenide was found to be a 3 molar equiv of aryl halide with a 5% molar ratio of catalyst (Table I). Under these conditions, the diphenyl selenide contaminant (less than 5% relative ratio to the desired selenide) is easily removed from the aryl phenyl selenide either by distillation or by chromatography.

Aryl bromides with electron-attracting groups are more reactive, and the amount of diphenyl selenide is almost negligible as detected by gas chromatography. An even more favorable case is that of aryl iodides which in all instances (i.e., with or without electron-donating substituents) are much more reactive. No diphenyl selenide was present in these cases.

Therefore, depending on the reactivity of the aryl halide, three methods can be applied to the synthesis of various aryl phenyl selenides starting with aryl iodides (method A) and aryl bromides substituted with either electron-donating (method B) or electron-attracting groups (method C) (Scheme I and Table II).

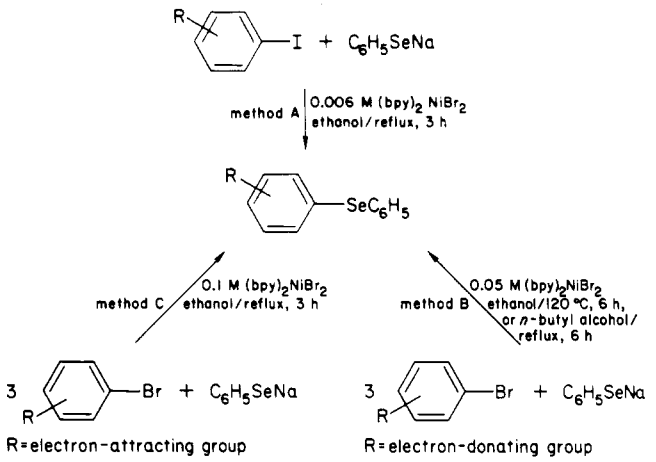
All these three methods give good yields of aryl phenyl selenides with aryl halides bearing either electron-donating or electron-attracting groups (Table II, cases 1–11). They have been successfully applied to the substitution of heteroaryl bromides (Table II, cases 12–15). In case 6, the nickel catalysis is a good alternative to either a two-step method starting from *p*-bromonitrobenzene[1] or a recently proposed direct selenation procedure for electron-rich aromatic systems which gives a modest yield of *p*-aminophenyl phenyl selenide.[6] Finally the reaction is regiose-

Table III. Spectroscopic Data of Aryl Phenyl Selenides

compd	IR[a] ν cm^{-1}	NMR[b,c] δ	MS,[d] m/e (relative intensity)	elemental anal.[e]
2	1000 (w), 1018 (m), 1025 (m), 1066 (m)	7.63-7.13 (m, 5 H, C_6H_5) AB system: 7.55 (2 H ortho), 7.125 (2 H meta), J_{AB} = 8.1 Hz 2.33 (s, 3 H, CH_3)	248 (M, 45), 233 (M - CH_3, 16), 168 (M - Se, 100), 153 ($C_{12}H_9$, 11), 91 (C_7H_7, 29), 77 (C_6H_5, 18)	calcd: C, 63.16; H, 4.89 found: C, 63.23; H, 5.03
3		7.70-6.9 (m, 5 H, C_6H_5), 2.28 (s, 3 H, CH_3)		
4		7.80-6.90 (m, 5 H, C_6H_5), 2.40 (s, 3 H, CH_3)		
5	1004 (w), 1021 (s), 1028 (m), 1062 (w)	7.42-7.13 (m, 5 H, C_6H_5) AB system: 7.55 (2 H ortho), 6.88 (2 H meta), J_{AB} = 8.4 Hz 3.79 (s, 3 H, CH_3O)	264 (M, 45), 184 (M - Se), 100), 169 ($C_{12}H_9O$, 41), 77 (C_6H_5, 17)	
6	3340-3430 (NH_2), 999 (w)	7.54-7.02 (m, 5 H, C_6H_5) AB system: 7.42 (2 H ortho), 6.61 (2 H meta), J_{AB} = 8.6 Hz	249 (M, 36), 169 (M - Se, 100), 77 (C_6H_5, 6)	
7	1001 (w), 1012 (s)	8.03-6.57 (m)	268 (M, 51), 190 (M ^{37}Cl - Se, 37.5), 153 ($C_{12}H_9$, 16), 152 ($C_{12}H_8$, 25), 77 (C_6H_5, 34)	calcd: C, 53.86; H, 3.39 found: C, 53.62; H, 3.24
8	1675 (C=O), 1000 (m), 1008 (m), 1021 (w), 1059 (w)	7.77-7.27 (m, 5 H, C_6H_5) AB system: 7.85 (2 H meta), 7.45 (2 H ortho), J_{AB} = 8.6 Hz 2.40 (s, 3 H, CH_3)	276 (M, 100), 261 (M - CH_3, 74), 232 ($C_{12}H_8Se$, 29), 181 ($C_{13}H_{12}O$, 24), 152 ($C_{12}H_8$, 24), 77 (C_6H_5, 21)	calcd: C, 61.10; H, 4.39 found: C, 61.02; H, 4.46
9	2225 (C≡N), 999 (w), 1015 (m), 1021 (w), 1059 (m)	7.80-7.27 (m)	259 (M, 60), 179 (M - Se, 100), 77 (C_6H_5, 31)	calcd: C, 60.48; H, 3.51; N, 5.43 found: C, 60.43; H, 3.60; N, 5.41
10	1000 (w), 1022 (s), 1070 (m)	8.52-8.14 (m, 1 H), 8.03-7.02 (m, 11 H)	284 (M, 44), 204 (M - Se, 100), 77 (C_6H_5, 8)	calcd: C, 67.85; H, 4.27 found: C, 67.74; H, 4.32
11α	1001 (m), 1013 (s), 1022 (m), 1058 (w)	7.83-6.7 (m)	312 (M ^{79}Br, 90), 232 (M ^{79}Br - Se, 100), 153 ($C_{12}H_9$, 42), 77 (C_6H_5, 70)	calcd: C, 46.18; H, 2.91 found: C, 46.00; H, 2.98
11β	1001 (m), 1018 (s), 1022 (m), 1058 (m)	7.73-6.92 (m)	390 (M, 79), 232 (M - C_6H_5Se, 100), 152 ($C_{12}H_8$, 86), 77 (C_6H_5, 53)	calcd: C, 55.69; H, 3.63 found: C, 55.64; H, 3.63
12	1001 (w), 1023 (m), 1058 (w)	8.54-8.32 (m, 1 H, ortho)	234 (M, 100), 78 (C_5H_4N, 68)	calcd: C, 56.42; H, 3.87; N, 5.98 found: C, 55.62;[f] H, 3.82; N, 5.70
13	1001 (w), 1012 (s), 1022 (s), 1069 (m)	8.78-8.64 (m, 1 H ortho), 8.51 (dd, 1 H ortho, J = 4.7 Hz, J = 1.5 Hz), 7.88-7.04 (m, 7 H)	235 (M, 76), 155 (M - Se, 100), 78 (C_5H_4N, 32), 77 (C_6H_5, 26)	calcd: C, 56.42; H, 3.87; N, 5.98 found: C, 56.50; H, 4.07; N, 5.79
14	1001 (w), 1023 (s), 1068 (w)	7.63-6.92 (m)	240 (M, 50), 160 (M - Se, 100), 77 (C_6H_5, 29)	calcd: C, 50.21; H, 3.37; N, 13.40 found: C, 50.41; H, 3.37; N, 13.36
15	1001 (w), 1023 (m), 1068 (w)	7.57-7.00 (m)	240 (M, 37), 160 (M - Se, 100), 77 (C_6H_5, 29)	calcd: C, 50.21; H, 3.37; N, 13.40 found: C, 50.31; H, 3.48; N, 13.03

[a] In addition to characteristic frequencies for monosubstituted and p-disubstituted phenyl rings, one can observe four bands stable in frequency in the range 1000–1070 cm^{-1} which may be assigned to the Ar-Se and/or C_6H_5Se groups: 1001 ± 3 (w or m), 1013 ± 5 (m or s), 1023 ± 5 (m or s), 1064 ± 6 (w or m). These bands are also present for phenyl vinyl selenides (to be published later). [b] Satellite bands due to ^{77}Se-H couplings have not been taken into account for the analysis of NMR spectra. [c] When ortho and meta positions are indicated, they refer to the phenylseleno substituent. In compound **13**, the H indicated as ortho is the one in position 2 on the pyridyl ring. [d] The isotopic distribution in selenium containing fragments was as follows: ^{74}Se, 1.8; ^{76}Se, 18.1; ^{77}Se, 15.2; ^{78}Se, 47.2; ^{82}Se, 18.5; based on the most abundant ^{80}Se peak which was taken into account for the description of all MS spectra. [e] Microanalytical measurements were performed by Centre National de la Recherche Scientifique, Service Central d' Analyse, 69390 Vernaison, France. [f] Although all other data including H and N microanalyses and IR and NMR spectra were in agreement with the proposed structure, carbon microanalyses were found different from the theoretical value.

Scheme I



lective and gives the pure regioisomeric products[11] in cases 2–4 and 12–15.

In conclusion, the nickel catalysis in the arylation of benzeneselenolate allows a simple preparation under mild conditions and in good yield of a variety of aryl phenyl selenides. The synthesis of aryl vinyl selenides using this rapid method (i.e., the vinylation of benzeneselenolate) is now under investigation.

Experimental Section

All reactions, except the preparation of $(bpy)_2NiBr_2$, were carried out under an inert atmosphere of N_2 which was not, however, necessary for the workup of reaction mixtures. Melting points are uncorrected and were measured on an automatic Mettler FP 51 melting point apparatus (heating rate 2 °C/min). Infrared spectra were recorded on a Perkin-Elmer Model 221 spectrophotometer by using samples as solutions in CCl_4 or KBr disks. ^1H NMR spectra were measured in solution in $CDCl_3$ with a Varian EM-360 L spectrometer with Me_4Si as internal standard. Mass spectra were recorded at 75 eV using a JEOL JMS D-100 spectrometer.

Aryl bromides and iodides and diphenyl diselenide were supplied by Aldrich or Fluka and used as received. The preparation of bis(*o*-phenanthroline)nickel(II) bromide was identical with that of bis(bipyridine)nickel(II) bromide (vide infra). $Ni(acac)_2$ was the commercial compound. $[((NH_2)_2C{=}S)]_6NiBr_2$ was prepared according to Holt et al.[8]

Bis(bipyridine)nickel(II) Bromide (1). Bipyridine (1.11 g, 7.11 mmol) in ethanol (10 mL) was added to anhydrous $NiBr_2$ (0.78 g, 3.57 mmol) in ethanol (70 mL) at 40 °C. The reaction mixture was stirred under reflux for 15 h and filtered. Green crystals formed on concentrating and cooling which were washed (ethanol) and dried (70 °C, P_2O_5, 0.5 torr, 24 h), giving 1 (1.5 g, 2.8 mmol) in 79% yield. Anal. Calcd for $C_{20}H_{16}Br_2N_4Ni$:C, 45.25; H, 3.04; N, 10.55; Ni, 11.05. Found: C, 45.10; H, 3.09; N, 10.39; Ni, 11.05.

(11) The regioisomeric purity of the three regioisomers has been determined by coinjection in GLC and ^1H NMR spectroscopy.

Improved Synthesis of Diaryl Sulfides. A mixture of sodium thiophenolate (4.6 mmol), $(bpy)_2NiBr_2$ (0.012 mmol) and aryl bromide (3.84 mmol) in diethylene glycol (6 ml) was heated at 120 °C for 24 h. The reaction mixture was diluted with ether (80 mL), washed with water (35 mL, three times), dried (Na_2SO_4), and concentrated in vacuo. The crude product was chromatographed (silica gel, hexane) and either distilled (Kugelrohr) or recrystallized. R = R′ = H: IR and MS (75 eV) spectra identical with those of an authentic sample. R = H and R′ = $C(O)CH_3$: recrystallized in ethanol; mp 64 °C (lit.[9] mp 67 °C). Anal. Calcd $C_{14}H_{12}OS$: C, 73.65; H, 5.30. Found: C, 73.30; H, 5.54. R = H and R′ = CH_3: crystals obtained by slow crystallization of the pure liquid; mp 36 °C. Anal. Calcd for $C_{13}H_9F_3S$: C, 61.41; H, 3.57. Found: C, 61.66; H, 3.71.

Aryl Phenyl Selenides. General Procedures. Method A. Aryl iodide (4.6 mmol) and $(bpy)_2NiBr_2$ (14.7 mg, 0.028 mmol) were added to a solution of sodium benzeneselenolate[10] (4.6 mmol) in ethanol (6 mL). The reaction mixture was stirred under reflux for 3 h and diluted with ether (80 mL). The organic phase was washed with water (30 mL, three times), dried (Na_2SO_4), and concentrated in vacuo. The crude product was chromatographed on silica gel (eluant hexane for cases 1 and 2 and hexane/ethyl acetate for case 6) and either distilled (Kugelrohr) or recrystallized (case 6, hexane).

Method B. Aryl bromide (13.8 mmol) and $(bpy)_2NiBr_2$ (122 mg, 0.023 mmol) were added to sodium benzeneselenolate (4.6 mmol) in ethanol (6 mL) in a Schlenk tube. The tube was sealed and the reaction mixture stirred at 120 °C for 6 h. Alternately, *n*-butyl alcohol instead of ethanol was used as solvent and the reaction was run for the same time under reflux. the following was identical with that in method A (eluant hexane for cases 3, 4, 5, 7, 10, 11, 14, and 15 and hexane/ethyl acetate for cases 12 and 13; solvent of recrystallization, ethanol for case 5).

Method C. Aryl bromide (2.3 mmol) and $(bpy)_2NiBr_2$ (122 mg, 0.23 mmol) were added to a solution of sodium benzene selenolate (2.3 mmol) in ethanol (7 mL). The reaction mixture was stirred under reflux for 3 h. The following was identical with that in method A (eluant hexane/ethyl acetate for cases 8 and 9; solvent of recrystallization, ethanol/hexane for cases 8 and 9).

Registry No. 1, 15555-11-0; $C_6H_5SeC_6H_5$, 1132-39-4; *p*-$CH_3C_6H_4SeC_6H_5$, 83859-32-9; *m*-$CH_3C_6H_4SeC_6H_5$, 94800-49-4; *o*-$CH_3C_6H_4SeC_6H_5$, 94800-50-7; *p*-$CH_3OC_6H_4SeC_6H_5$, 80448-01-7; *p*-$H_2NC_6H_4SeC_6H_5$, 16089-79-5; *p*-$ClC_6H_4SeC_6H_5$, 94800-51-8; *p*-$AcC_6H_4SeC_6H_5$, 85972-34-5; *p*-$NcC_6H_4SeC_6H_5$, 94800-52-9; *o*-$BrC_6H_4SeC_6H_5$, 94800-53-0; *o*-$C_6H_5SeC_6H_4SeC_6H_5$, 90454-87-8; *o*-$C_6H_5SeC_6H_4Br$, 94800-53-0; $(phe)_2NiBr_2$, 42992-98-3; $[o\text{-}(C_6H_5)_2P]_2C_6H_4NiBr_2$, 94782-43-1; $Ni(acac)_2$, 3264-82-2; $[(NH_2)_2C{=}S]_6NiBr_2$, 14976-06-8; *p*-$AcC_6H_4SC_6H_5$, 10169-55-8; *p*-$F_3CC_6H_4SC_6H_5$, 53451-90-4; C_6H_5I, 591-50-4; *p*-$CH_3C_6H_4I$, 624-31-7; *p*-$CH_3C_6H_4Br$, 106-38-7; *m*-$CH_3C_6H_4I$, 625-95-6; *o*-$CH_3C_6H_4I$, 615-37-2; *p*-$CH_3OC_6H_4Br$, 104-92-7; *p*-$H_2NC_6H_4I$, 540-37-4; *p*-ClC_6H_4Br, 106-39-8; *p*-AcC_6H_4Br, 99-90-1; *p*-BrC_6H_4CN, 623-00-7; *o*-BrC_6H_4Br, 583-53-9; C_6H_5Br, 108-86-1; *p*-$F_3CC_6H_4Br$, 402-43-7; *p*-$BrC_6H_4SC_6H_5$, 65662-88-6; sodium thiophenolate, 930-69-8; sodium benzeneselenolate, 23974-72-3; 1-bromonaphthalene, 90-11-9; 2-bromopyridine, 109-04-6; 3-bromopyridine, 626-55-1; 2-bromothiophene, 1003-09-4; 3-bromothiophene, 872-31-1; (1-naphthyl)phenylselenium, 65490-21-3; (2-pyridyl)phenylselenium, 87803-47-2; (3-pyridyl)phenylselenium, 94800-54-1; (2-thiophenyl)phenylselenium, 94800-55-2; (3-thiophenyl)phenylselenium, 94800-56-3.