Preparation of Unsymmetrical Diaryl Selenides via S_NAr Reactions in η^6-Chloroarene Transition Metal Complexes

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Unsymmetrical diaryl selenides were prepared by nucleophilic displacement of chloride with areneselenolates in η^6-(arene) $Cr(CO)_3$, $FeCpPF_6$, and $Mn(CO)_3PF_6$ complexes. Areneselenolates were conveniently generated in situ by hydrazine reduction of the corresponding diaryl diselenides and reacted with chloroarene $Cr(CO)_3$ complexes in dimethyl sulfoxide at 70 °C. The reactivity of the cationic $FeCpPF_6$ and $Mn(CO)_3PF_6$ chloroarene complexes was substantially higher, affording substitution products at ambient temperature in ethanol with areneselenolates generated by sodium borohydride reduction. Intermediate (arylseleno)arene chromium and iron complexes were isolated and characterized by ^{77}Se NMR. As compared with the free diaryl selenide, complexation caused a 20−45 ppm downfield shift.

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Introduction

Due to the many useful properties conferred on the aromatic ligand by complexation, transition metal arene complexes have been extensively employed for the functionalization of aromatic molecules. In addition to facilitating deprotonation (ring and benzylic) and nucleophilic addition, the electron-withdrawing properties of the metal also makes nucleophilic displacement of halides possible under very mild reaction conditions. Introduction of hydroxide, alkoxide, phenoxide, carboxylate, amine, thiolate, and various carbanion nucleophiles into neutral (tricarbonychromium) as well as cationic (cyclopentadienyliron) or (tricarbonylmanganese) complexes by nucleophilic displacement has recently been reviewed.[1] To the best of our knowledge, such reactions have not yet been studied for the introduction of selenolates into aromatics. The transition metal-assisted route would seem most useful for the preparation of unsymmetrical diaryl selenides. Conventional aromatic nucleophilic substitution (S_NAr) provides a route to certain members of this class of compounds. However, whereas haloarenes carrying electron-withdrawing groups react readily, copper or unassisted nucleophilic substitution with unactivated haloarenes is usually successful only under harsh conditions.[2,3] Diaryl selenides produced from aromatic Grignard reagents or aryllithiums and diaryl diselenides/arylselenocyanates are often difficult to purify from other organoselenium byproducts formed. Electrophilic organoselenium reagents such as phenylselenenyl sulfate are only reactive enough to furnish diaryl selenides with electron-rich arenes.[4]

Diaryl selenides have many interesting properties. We, and others, have recently reported useful antioxidative properties of this class of compounds.[5] Diaryl selenide fragments are also seen in biologically active organoselenium compounds.[6] Polymeric materials containing the diaryl selenide structural motif, e.g., poly(*p*-phenyleneselenide)[7] or oligothiophenes,[8] have also attracted recent interest. In the following, we describe procedures for the introduction, by nucleophilic substitution, of one or several arylseleno groups into chloroarene or dichloroarene $Cr(CO)_3$, $FeCp^+$, and $Mn(CO)_3^+$ complexes. After proper decomplexation, symmetrical or unsymmetrical diaryl selenides and bis(arylseleno)benzenes were isolated.

Results and Discussion

Displacement of fluoride and chloride in haloarene tricarbonylchromium complexes by nucleophilic alkyl- or arylthiolates occurs efficiently at low temperature under phase-transfer conditions,[9,10] in DMSO[10] or in

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(1) Semmelhack, M. F. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Semmelhack, M. F., Eds.; Pergamon Press: Oxford, 1991; Vol. 4, Chapter 9.1. Pearson, A. J. *Iron Compounds in Organic Synthesis*; Academic Press: London, 1994. Morris, M. J. In *Comprehensive Organometallic Chemistry II*; Labinger, J. A., Winter, M. J., Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, 1995; Vol. 5, Chapter 8.
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(8) Hellberg, J.; Remonen, T.; Johansson, M.; Inganäs, O.; Theander, M.; Engman, L.; Eriksson, P. *Synth. Met.* **1997**, *84*, 251.

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tetrahydrofuran.[11] Under these conditions, the reacting thiolate was conveniently generated from the corresponding thiol by deprotonation. Unlike thiols, selenols can only be handled with difficulty due to their rapid oxidation by atmospheric oxygen. Selenolates are therefore better generated in situ by reduction of the corresponding diselenides. In the present work, we found that areneselenolates suitable for nucleophilic substitution of haloarene tricarbonylchromium complexes could be conveniently generated by hydrazine reduction[12] of diaryl diselenides in DMSO in the presence of potassium carbonate (eq 1). Triethylborate-complexed areneselenolates generated from diaryl diselenides by sodium borohydride reduction[13] in ethanol (eq 2) were suitable for room-temperature nucleophilic substitution of haloarene $FeCp^+$ and $Mn(CO)_3^+$ complexes. Four areneselenolates **1a**−**d** of varying nucleophilicity were prepared from the corresponding diaryl diselenides and used in the nucleophilic displacement reactions. In a typical reaction of chromium compounds **2** (eq 3), the diselenide, the chromium complex, and freshly powdered potassium carbonate were mixed in DMSO and hydrazine hydrate was added. The reaction mixture was then heated under nitrogen at 70 °C for 7 h. The crude product was often a mixture of the diaryl selenide **4** and its corresponding $Cr(CO)_3$ complex **3**. After removal of unreacted selenolate by alkylation with bromoacetic acid, followed by alkaline extraction,[14] decomplexation was effected by treatment of the crude reaction mixture with iodine. As shown in Table 1, diaryl selenides **4**, carrying ester, acetal, and ketal functions were isolated in moderate to good yields (23−73%). Ester complex **2b** was particularly reactive, affording the substitution product at ambient temperature. Product yields increased with increasing reactivity of the complex in the order **2a** < **2c** ≈ **2d** < **2e** < **2b** (cf. ref 15) and with increasing nucleophilicity of the selenolate reagent **1b** < **1a** < **1d**. Chromium complexes **2** were unreactive toward areneselenolates formed from diselenides by sodium borohydride reduction in ethanol according to eq 2. Attempts to react the complexes in DMF with highly nucleophilic sodium benzeneselenolate generated by sodium hydride reduction of diphenyl diselenide[16] did not result in any dramatic improvement in product yields (Table 1; compounds **4a** and **4e**). At 70 °C, both chlorides in 1,3-dichlorobenzene chromium tricarbonyl (**2e**) were substituted by the selenolate reagent **1d**. At 20 °C, monosubstitution was predominantly seen. By reacting complex **2e** (Table 1) with selenolate reagent **1a** at ambient temperature in dioxane in the presence of 18-crown-6, and then with selenolate **1d** generated under similar conditions, it was possible to prepare the unsymmetrical 1,3-bis(arylseleno)benzene **5** in 38% yield.

Fluoroarene chromium tricarbonyl complexes are usually more reactive in nucleophilic substitution reactions than the corresponding chloroarene complexes.[1,9] It was therefore surprising to find that fluorobenzene chromium tricarbonyl (**6**) did not afford a substitution product when treated with benzeneselenolate prepared by hydrazine reduction according to eq 3.

To the best of our knowledge, chromium tricarbonyl complexes of diaryl selenides have not been previously described. Some of these compounds (**3a**−**c**) were therefore isolated from the crude reaction mixtures before decomplexation and characterized by ^1H, ^{13}C, and ^{77}Se NMR spectroscopy. Judging from the stability of these complexes, diaryl selenides are good π-ligands for chromium tricarbonyl. In addition, chromium complexes **7a** and **7b** were prepared from chromium hexacarbonyl and selenoanisole and 4-methoxyselenoanisole, respectively, in 84 and 56% isolated yields. As compared with the uncomplexed phenylselenoarenes, complexation caused a 20−45 ppm downfield shift in the ^{77}Se spectrum.

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(12) The reduction of diphenyl diselenide using hydrazine hydrate and sodium hydroxide in DMF has been described by Syper.[12a] Similar results were also obtained using anhydrous hydrazine in DMSO and sodium methoxide as a base.[12b] However, to minimize competing substitution in cloroarene complexes, a weaker base (K_2CO_3) was used in the present work. For example, $(CO)_3CrC_6H_5OMe$ was formed as the major product when $(CO)_3CrC_6H_5Cl$ was treated with benzeneselenolate generated by hydrazine reduction of diphenyl diselenide in MeONa/DMSO. (a) Syper, L.; Mlochowski, J. *Synthesis* **1984**, 439. (b) Stuhr-Hansen, N. Dissertation, Copenhagen, 1999.
(13) Miyashita, M.; Suzuki, T.; Hoshino, M.; Yoshikoshi, A. *Tetrahedron* **1997**, *53*, 12469.
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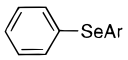
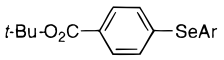
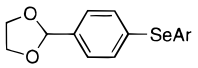
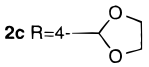
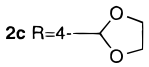
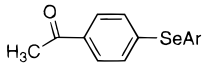
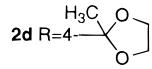
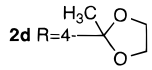
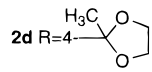
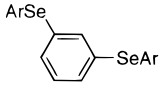
(16) Dowd, P.; Kennedy, P. *Synth. Commun*. **1981**, *11*, 935.

Table 1. Diaryl Selenides 4 Prepared from Chloroarene−Cr(CO)$_3$ Complexes by Nucleophilic Substitution/Decomplexation

Chloroarene complex	Selenolate[a]	T(°C)	Diaryl selenide	Yield (%)[b]
				
2a R=H	**1a**	70	**4a** Ar=C_6H_5	37
2a R=H	**1a**[c]	70	**4a** Ar=C_6H_5	49
2a R=H	**1d**	70	**4b** Ar=C_6H_4-4-NMe_2	72
				
2b R=4-CO_2-*t*-Bu	**1a**	20	**4c** Ar=C_6H_5	63
2b R=4-CO_2-*t*-Bu	**1d**	20	**4d** Ar=C_6H_4-4-NMe_2	61
				
2c R=4- 	**1a**[c]	70	**4e** Ar=C_6H_5	38
2c R=4- 	**1d**	70	**4f** Ar=C_6H_4-4-NMe_2	73
				
2d R=4- 	**1a**	70	**4g** Ar=C_6H_5	55
2d R=4- 	**1b**	70	**4h** Ar=C_6H_4-4-Cl	23
2d R=4- 	**1d**	70	**4i** Ar=C_6H_4-4-NMe_2	71
				
2e R=3-Cl	**1d**	70[d]	**4j** Ar=C_6H_4-4-NMe_2	52

[a] Unless otherwise indicated, selenolate was generated by hydrazine reduction of the corresponding diselenide in DMSO and reacted with the chloroarene complex. [b] Isolated yields. [c] Selenolate was generated by sodium hydride reduction of the corresponding diselenide in THF and reacted in a THF/DMF mixture with the chloroarene complex. [d] Substitution occurred already at 20 °C to give monosubstituted product **3b**.

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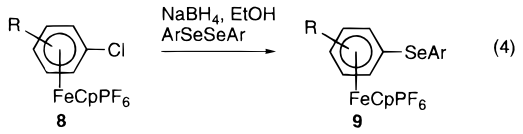
Cationic cyclopentadienyliron and tricarbonylmanganese chloroarene complexes undergo nucleophilic substitution much more readily than the corresponding neutral chromium complexes. However, due to hydrodehalogenation of these complexes in the presence of an excess of a reducing agent, hydrazine was not the reagent of choice for the in situ preparation of the areneselenolates. Sodium borohydride in ethanol rapidly reduces diaryl diselenides to the corresponding triethylborate-complexed sodium areneselenolates (eq 2). To keep the amount of reducing equivalents to a minimum, a THF solution of the diaryl diselenide was added dropwise under nitrogen to an ethanolic solution of sodium borohydride until the yellow color of the diselenide persisted. The (chloroarene)(cyclopentadienyl)-iron hexafluorophosphates (**8**) were then added at ambient temperature and the reaction mixtures stirred overnight. According to ^{1}H NMR analysis of crude reaction mixtures, the conversion to product was almost quantitative with all selenolates **1**. After extraction into methylene chloride and chromatography on deactivated alumina (Table 2), the diaryl selenide cyclopentadienyliron hexafluorophosphates (**9**) (eq 4) were isolated in



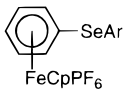
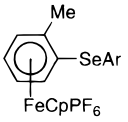
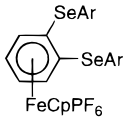
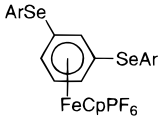
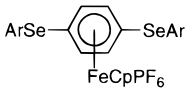
(4)

good yields (60−80%). Attempts to perform selective monosubstitution in the three dichlorobenzene−FeCp complexes **8c**−**e** with areneselenolates met with failure. Even at −78 °C, the reaction resulted in mixtures of unreacted starting material, mono- and disubstituted products. In contrast, the selective monosubstitution of dichlorobenzene−FeCp complexes with less nucleophilic phenolates has been successfully carried out.[17]

Upon photolysis in acetonitrile,[17] diaryl selenides were released from the FeCp complexes **9**. Thus, diphenyl selenide (**4a**), 4-chlorophenyl phenyl selenide (**10**), and 1,4-bis(4-chlorophenylseleno)benzene (**11**) were obtained in practically quantitative yields from complexes **9a**, **9b**, and **9j**, respectively. Complex **9d** similarly afforded 4-(dimethylamino)phenyl phenyl selenide (**4b**) in 40% yield. Methyl 2-chlorobenzoate complex **12** was

(17) Pearson, A. J.; Gelormini, A. M. *J. Org. Chem.* **1994**, *59*, 4561.

Table 2. Diaryl Selenide–$FeCpPF_6$ Complexes 9 Prepared from Chloroarene–$FeCpPF_6$ Complexes by Nucleophilic Substitution

Chloroarene complex	Selenolate[a]	T(°C)	Diaryl selenide complex **9**	Yield (%)[b]
				
8a R=H	**1a**	20	**9a** Ar=C_6H_5	60
8a R=H	**1b**	20	**9b** Ar=C_6H_4-4-Cl	77
8a R=H	**1c**	20	**9c** Ar=C_6H_4-4-OMe	79
8a R=H	**1d**	20	**9d** Ar=C_6H_4-4-NMe_2	83
				
8b R=2-Me	**1a**	20	**9e** Ar=C_6H_5	64
8b R=2-Me	**1c**	20	**9f** Ar=C_6H_4-4-OMe	84
8b R=2-Me	**1d**	20	**9g** Ar=C_6H_4-4-NMe_2	79
				
8c R=2-Cl	**1b**	20	**9h** Ar=C_6H_4-4-Cl	62
				
8d R=3-Cl	**1b**	20	**9i** Ar=C_6H_4-4-Cl	68
				
8e R=4-Cl	**1b**	20	**9j** Ar=C_6H_4-4-Cl	69

[a] Selenolate was generated by sodium borohydride reduction of the corresponding diselenide in EtOH. [b] Isolated yields.

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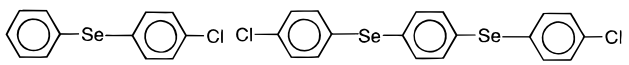
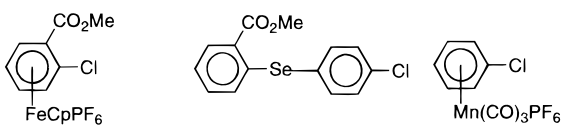
reacted with potassium 4-chlorobenzeneselenolate in methanol to afford an inseparable mixture of the desired substitution product, methoxy-substituted starting material, and some unreacted starting material. After photolysis of the crude product and column chromatography, 4-chlorophenyl 2-methoxycarbonylphenyl selenide (**13**) was isolated in 28% yield.



10 **11**



12 **13** **14**

(Chlorobenzene)tricarbonylmanganese hexafluorophosphate (**14**) was as reactive as iron complexes **8** toward areneselenolates. Sodium benzeneselenolate, generated either by the hydrazine method (eq 1) or by the sodium borohydride method (eq 2) afforded the desired substitution product in high yields at ambient temperature. Decomplexation occurred upon overnight stirring in acetonitrile to afford diphenyl selenide (**4a**) in 80% yield. 4-Chlorophenyl phenyl selenide (**10**) was similarly prepared in 61% isolated yield.

Attempts were also made to extend the synthetic methodology developed to diaryl telluride synthesis. However, under the conditions tried, hydrodechlorination occurred rather than substitution with arenetellurolate ion.

Experimental Section

All melting points are uncorrected. NMR spectra were recorded in $CDCl_3$ (unless specified) at 299.903 MHz (^1H), 75.419 MHz (^{13}C), and 57.213 MHz (^{77}Se). ^{77}Se chemical shifts are given in ppm relative to neat Me_2Se and were measured

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relative to neat Me_2Se_2 (δ 275 ppm[18]), which was inserted into the NMR tube in a sealed capillary. Elemental analyses were performed by Analytical Laboratories, Lindlar, Germany. Diphenyl diselenide and bis(4-chlorophenyl)diselenide are commercially available. *tert*-Butyl 4-chlorobenzoate,[19] 2-(4-chlorophenyl)-1,3-dioxolane,[20] 2-(4-chlorophenyl)-2-methyl-1,3-dioxolane,[21] bis(4-methoxyphenyl)diselenide,[22] bis[4-(dimethylamino)phenyl]diselenide,[23] η^6-(chlorobenzene)tricarbonylchromium,[24] η^6-(1,3-dichlorobenzene)tricarbonylchromium,[10] η^6-(chlorobenzene)-η^5-(cyclopentadienyl)iron hexafluorophosphate,[25] η^6-(1-chloro-2-methylbenzene)-η^5-(cyclopentadienyl)iron hexafluorophosphate,[26] η^6-(1,2-dichlorobenzene)-η^5-(cyclopentadienyl)iron hexafluorophosphate,[25] η^6-(1,3-dichlorobenzene)-η^5-(cyclopentadienyl)iron hexafluorophosphate,[17] η^6-(1,4-dichlorobenzene)-η^5-(cyclopentadienyl)iron hexafluorophosphate,[17] η^6-(methyl 2-chlorobenzoate)-η^5-(cyclopentadienyl)iron hexafluorophosphate,[26] and η^6-(chlorobenzene)tricarbonylmanganese hexafluorophosphate[27] were prepared according to literature procedures. THF, dioxane, and DMF were freshly distilled. DMSO was used as purchased.

The η^6-(arene)tricarbonylchromium complexes were prepared according to a known procedure,[24] by refluxing 5 mmol of the arene and 6 mmol of $Cr(CO)_6$ in a mixture of dibutyl ether (20 mL) and THF (2 mL) for 24−36 h. ^{1}H NMR analyses showed that the conversion never exceeded 30% and that partial dechlorination of the chromium complex had occurred (the extent of which increased significantly on prolonged heating). Increasing the amount of $Cr(CO)_6$ did not lead to improved product yields. After evaporation of the solvents in vacuo, the residue was suspended in ether and filtered. In the case of chlorobenzene and 1,3-dichlorobenzene the filtrate was concentrated to ca. 10 mL volume and hexane (20 mL) was added. Subsequent slow evaporation of the solvents caused precipitation of yellow crystals, which were filtered off and dried. In the case of functionalized chloroarenes, the filtrate was evaporated, coevaporated with toluene, and subjected to column chromatography. This allowed separation of the target complexes from both unreacted arene and the corresponding dechlorinated complex (the latter had a lower R_f -value than the chloroarene complex).

[4-(*tert*-Butoxycarbonyl)chlorobenzene]tricarbonylchromium (2b). Yield: 0.192 g (11%), mp 88 °C. ^{1}H NMR: δ 1.54 (s, 9H), 5.40 (d, J = 6.9 Hz, 2H), 6.14 (d, J = 6.9 Hz, 2H).

[4-(1,3-Dioxolan-2-yl)chlorobenzene]tricarbonylchromium (2c). Yield: 0.497 g (31%), mp 79 °C. ^{1}H NMR: δ 3.95−4.15 (m, 4H), 5.38 (d, J = 6.7 Hz, 2H), 5.48 (s, 1H), 5.67 (d, J = 6.7 Hz, 2H). Anal. Calcd for $C_{12}H_9ClCrO_5$: C, 44.95; H, 2.83. Found: C, 45.15; H, 2.82.

[4-(2-Methyl-1,3-dioxolan-2-yl)chlorobenzene]tricarbonylchromium (2d). Yield: 0.35 g (21%), mp 109 °C. ^{1}H NMR: δ 1.57 (s, 3H), 4.05 (m, 4H), 5.32 (d, J = 6.5 Hz, 2H), 5.77 (d, J = 6.5 Hz, 2H). Anal. Calcd for $C_{13}H_{11}ClCrO_5$: C, 46.66; H, 3.31. Found: C, 46.82; H, 3.17.

(Methylselenobenzene)tricarbonylchromium (7a) was similarly prepared (reaction time 36 h) from methyl phenyl selenide (0.45 g, 2.63 mmol, ^{77}Se NMR: δ 202.0 and purified by crystallization. Yield: 0.685 g (84%), mp 78 °C. ^{1}H NMR: δ 2.37 (s, 3H), 5.19 (t, J = 6.3 Hz, 1H), 5.34 (t, J = 6.2 Hz, 2H), 5.44 (d, J = 6.5 Hz, 2H). ^{13}C NMR: δ 8.5 q, 90.2 d, 92.9 d, 94.7 d, 102.8 s, 232.5 s. ^{77}Se NMR: δ 240.2. Anal. Calcd for $C_{10}H_8CrO_3Se$: C, 39.13; H, 2.63. Found: C, 38.97; H, 2.54.

(1-Methylseleno-4-methoxybenzene)tricarbonylchromium (7b) was similarly prepared (reaction time 21 h) from 1-methoxy-4-methylselenobenzene (0.402 g, 2 mmol, ^{77}Se NMR δ 189.9). The pure material was obtained after column chromatography followed by crystallization from hexane, yield 0.378 g (56%), mp 74−75 °C. ^{1}H NMR: δ 2.34 (s, 3H), 3.69 (s, 3H), 5.06 (d, J = 6.4 Hz, 2H), 5.74 (d, J = 6.4 Hz, 2H). ^{13}C NMR: δ 11.0 q, 55.7 q, 77.8 d, 91.2 s, 99.6 d, 142.3 s, 232.6 s. ^{77}Se NMR: δ 235.8. Anal. Calcd for $C_{11}H_{10}CrO_4Se$: C, 39.21; H, 2.99. Found: C, 39.25; H, 2.86.

Diphenyl Selenide (4a) from (Chlorobenzene)tricarbonylchromium. A mixture of (chlorobenzene)tricarbonylchromium (0.050 g, 0.2 mmol), Ph_2Se_2 (0.062 g, 0.2 mmol), freshly powdered K_2CO_3 (0.070 g), and DMSO (1.5 mL) was degassed several times by using a manifold connected to an oil pump and a nitrogen line. To the stirred mixture, hydrazine hydrate (20 μL) was injected, and the temperature was raised to 70 °C. After 7 h, the reaction mixture was cooled to ambient temperature, additional hydrazine hydrate (15 μL) was injected, and after 10 min, the mixture was cooled to − 78 °C. Bromoacetic acid (0.14 g) in degassed DMSO (1 mL) was then injected, and the temperature was allowed to reach ambient. After 1 h, the reaction mixture was treated with brine (10 mL) containing K_2CO_3 (1 g) and extracted with ether. By this procedure, phenylselenoacetate was extracted into the aqueous phase. The combined ethereal extracts were dried over Na_2SO_4 and filtered through a short pad of silica. The filtrate was evaporated to afford the crude product containing both diphenyl selenide and its corresponding tricarbonylchromium complex. This mixture was dissolved in THF (15 mL), and iodine (0.3 g) was added in small portions until gas evolution ceased. The dark mixture was stirred for 10 min and then treated with an aqueous solution of $Na_2S_2O_3$ containing $NaHCO_3$. The organic components were extracted into ether. Evaporation afforded the title compound, 0.0173 g (37%), identical to an authentic sample. NMR analysis of the crude, iodine-treated reaction mixture (without removal of the excess diselenide by reduction/bromoacetic acid trapping), using methyl 3,5-diiodo-4-methoxybenzoate[28] as an internal standard, indicated a 39% yield of diphenyl selenide.

In another procedure Ph_2Se_2 (0.3 mmol) and NaH (0.024 g, 60% dispersion in mineral oil, 0.6 mmol) were refluxed in THF (3 mL) under nitrogen for 1 h. To the fluffy precipitate thus formed was injected (chlorobenzene)tricarbonylchromium (0.075 g, 0.3 mmol) in DMF (1.5 mL), and the mixture was stirred at 70 °C for 7 h. The cooled reaction mixture was then treated with brine and extracted with ether. The residue obtained after evaporation was dissolved in ethanol (5 mL), and a sodium borohydride solution in EtOH was added dropwise under nitrogen until no more hydrogen was evolved. The mixture was then cooled to −30 °C, bromoacetic acid (0.2 g) in EtOH (2 mL) was injected, and the mixture was allowed to warm to ambient temperature. EtOH was evaporated, and the residue was treated with an $NaHCO_3$ solution and extracted with ether. Decomplexation was then conducted as described above. Column chromatography with pentane afforded the title compound, 0.034 g (49%).

η^6-(Phenylselenobenzene)tricarbonylchromium, inseparable by column chromatography from unreacted chlorobenzene complex, was detected by NMR in the crude products from the above experiments prior to decomplexation. Characteristic peaks were found in the ^{1}H NMR spectrum at δ 5.19 (t, J = 6.0 Hz, 1H), 5.28 (t, J = 6.0 Hz, 2H), 5.37 (d, J = 6.8 Hz, 2H). ^{77}Se NMR: δ 443.7 ($CDCl_3$), 442.4 (acetone-d_6).

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4-(Dimethylamino)phenyl Phenyl Selenide (4b). Following the hydrazine procedure for the preparation of compound **4a** (without removal of excess diselenide by reduction/$BrCH_2CO_2H$ treatment/extraction), with final column chromatography after decomplexation (1.5% EtOAc in pentane), the title compound was isolated in 72% yield. ^{1}H NMR data were in good agreement with the literature.[29] ^{13}C NMR: δ 40.3 q, 113.1 d, 113.6 s, 125.6 d, 129.0 d, 129.7 d, 134.6 s, 137.1 d, 150.5 s. ^{77}Se NMR: δ 393.1 ($CDCl_3$), 390.1 (acetone-d_6).

η^6-[4-(Dimethylamino)phenylselenobenzene]tricarbonylchromium (3a) was isolated by column chromatography from the reaction prior to decomplexation, mp 170 °C (dec). ^{1}H NMR: δ 3.01 (s, 6H), 5.06 (t, J = 6.0 Hz, 1H), 5.20 (d, J = 6.2 Hz, 2H), 5.29 (t, J = 6.0 Hz, 2H), 6.69 (d, J = 9.0 Hz, 2H), 7.67 (d, J = 9.0 Hz, 2H). ^{77}Se δ 413.2 ($CDCl_3$), 412.1 (acetone-d_6). Anal. Calcd for $C_{17}H_{15}CrNO_3Se$: C, 49.55; H, 3.67. Found: C, 49.58; H, 3.61.

4-(*tert*-Butoxycarbonyl)phenyl Phenyl Selenide (4c). To a stirred mixture of Ph_2Se_2 (0.2 mmol) and K_2CO_3 (0.070 g) in DMSO (1 mL) under nitrogen, was injected hydrazine hydrate (10 μL). After 2 h (*tert*-butyl 4-chlorobenzoate)-tricarbonylchromium (0.035 g, 0.1 mmol) in degassed DMSO (1 mL) was injected, and the mixture was stirred at ambient temperature for 7 h. The mixture was diluted with brine and extracted with ether, and the extracts were dried and evaporated. The residue was decomplexed with iodine in THF as described above. Concentration (with final pumping) and column chromatography (0.5% EtOAc in pentane) afforded 0.021 g (63%) of the title compound, mp 53 °C (hexane). ^{77}Se NMR: δ 426.4. Anal. Calcd for $C_{17}H_{18}O_2Se$: C, 61.26; H, 5.44. Found: C, 61.39; H, 5.30.

4-(*tert*-Butoxycarbonyl)phenyl 4-(dimethylamino)phenyl selenide (4d) was prepared from (*tert*-butyl 4-chlorobenzoate)tricarbonylchromium (0.032 g, 0.092 mmol) and bis[4-(dimethylamino)phenyl] diselenide, using the procedure for compound **4c**. Final column chromatography (2.5% EtOAc in pentane) afforded 0.021 g (61%) of the title compound, mp 143 °C (dec).^{77}Se NMR: δ 404.2. Anal. Calcd for $C_{19}H_{23}NO_2Se$: C, 60.70; H, 6.16. Found: C, 60.55; H, 6.07.

4-(1,3-Dioxolan-2-yl)phenyl Phenyl Selenide (4e). Ph_2Se_2 (0.062 g, 0.2 mmol) and NaH (0.016 g, 60% dispersion in mineral oil, 0.4 mmol) were refluxed in THF (2 mL) under nitrogen for 1 h. To the fluffy precipitate thus formed was injected [1-(1,3-dioxolan-2-yl)-4-chlorobenzene]tricarbonylchromium (0.064 g, 0.2 mmol) in DMF (1 mL), and the mixture was stirred at 70 °C for 7 h. Workup included I_2 treatment as described for compound **4a** (without removal of excess diselenide). Finally, column chromatography (1% EtOAc in pentane) afforded 0.023 g (38%) of the title compound, mp 39 °C (from hexane). ^{77}Se NMR: δ 417.6. Anal. Calcd for $C_{15}H_{14}O_2Se$: C, 59.03; H, 4.62. Found: C, 59.30; H, 4.45.

4-(1,3-Dioxolan-2-yl)phenyl 4-dimethylaminophenyl selenide (4f) was prepared from [1-(1,3-dioxolan-2-yl)-4-chlorobenzene]tricarbonylchromium (0.064 g, 0.2 mmol) and bis-[4-(dimethylamino)phenyl] diselenide following the procedure for compound **4a**. However, instead of $BrCH_2CO_2H$, MeI (100 μL) was added at ambient temperature to quench excess selenolate present. The crude product after decomplexation contained less than 10% of 1-(1,3-dioxolan-2-yl)-4-chlorobenzene. Column chromatography (10% EtOAc in pentane) afforded 0.051 g (73%) of the title compound, mp 109−110 °C. ^{77}Se NMR: δ 394.3. Anal. Calcd for $C_{17}H_{19}NO_2Se$: C, 58.66; H, 5.50. Found: C, 58.78; H, 5.48.

4-Acetylphenyl phenyl selenide (4 g) was prepared from [1-(2-methyl-1,3-dioxolan-2-yl)-4-chlorobenzene]tricarbonylchromium (0.064 g, 0.2 mmol), Ph_2Se_2 (0.062 g, 0.2 mmol), K_2CO_3 (0.070 g), and DMSO (1.5 mL) following the procedure for compound **4f**. After decomplexation, the residue was dissolved in acetone/water (3/1, 4 mL) containing oxalic acid (0.050 g), and the solution was refluxed for 4 h. Acetone was evaporated, the remaining slurry was neutralized with $NaHCO_3$, and the products were extracted with ether. After drying and evaporation, ^{1}H NMR analysis showed a 3/1 mixture of the title compound and 4-chloroacetophenone. Concentration with final pumping at 1 Torr and 40 °C for 3 h and column chromatography (4% EtOAc in pentane) afforded 0.030 g (55%) of the title compound, mp 61 °C (hexane) (lit.[30] mp 47.5−49 °C). ^{77}Se NMR: δ 429.9. Anal. Calcd for $C_{14}H_{12}OSe$: C, 61.10; H, 4.40. Found: C, 61.02; H, 4.21.

4-Acetylphenyl 4-chlorophenyl selenide (4h) was prepared from bis(4-chlorophenyl)diselenide, following the procedure for the preparation of compound **4g**. The crude product after decomplexation and ketal hydrolysis was a 2/3 mixture of the title compound and 4-chloroacetophenone. Concentration (with final pumping), followed by column chromatography (5% EtOAc in pentane), gave 0.010 g (23%) of the title compound, mp 61 °C. ^{77}Se NMR: δ 425.2. Anal. Calcd for $C_{14}H_{11}ClOSe$: C, 54.34; H, 3.58. Found: C, 54.36; H, 3.46.

4-Acetylphenyl 4-(dimethylamino)phenyl selenide (4i) was prepared from bis[4-(dimethylamino)phenyl] diselenide, following the procedure for the preparation of compound **4g**. The crude reaction mixture after decomplexation and ketal hydrolysis was purified by column chromatography (10% EtOAc in pentane) to afford 0.044 g (71%) of the title compound, mp 131 °C. ^{77}Se NMR: δ 408.2. Anal. Calcd for $C_{16}H_{17}NOSe$: C, 60.42; H, 5.39. Found: C, 60.38; H, 5.32.

1,3-Bis[4-(dimethylamino)phenylseleno]benzene (4j) was prepared from chromium complex **2e** and bis[4-(dimethylamino)phenyl] diselenide, following the procedure for the preparation of compound **4a**. Column chromatography (5% EtOAc in pentane) afforded 0.049 g (52%) of the title compound, mp 139 °C (hexane). ^{77}Se NMR: δ 397.9. Anal. Calcd for $C_{22}H_{24}N_2Se_2$: C, 55.75; H, 5.10. Found: C, 55.55; H, 5.01.

η^6-[3-[4-(Dimethylamino)phenylseleno]chlorobenzene]-tricarbonylchromium (3b). To a stirred, degassed mixture of (1,3-dichlorobenzene)tricarbonylchromium (0.057 g, 0.2 mmol), bis[4-(dimethylamino)phenyl] diselenide (0.060 g, 0.15 mmol), and freshly powdered K_2CO_3 (0.052 g) in DMSO (2 mL) under nitrogen was injected hydrazine hydrate (10 μL), and the mixture was stirred at ambient temperature for 7 h. After dilution with brine and extraction with ether, the combined extracts were dried and evaporated. Column chromatography (3% EtOAc in pentane) afforded 0.032 g (43%) of the title compound, mp 142 °C (dec). ^{77}Se NMR: δ 414.7. Anal. Calcd for $C_{17}H_{14}ClCrNO_3Se$: C, 45.73; H, 3.16. Found: C, 46.00; H, 2.96. Decomplexation in the usual manner with I_2 afforded 4-(dimethylamino)phenyl 3-chlorophenyl selenide. ^{77}Se NMR: δ 404.3.

η^6-[1,3-Bis[4-(dimethylamino)phenylseleno]benzene]-tricarbonylchromium (3c). To a stirred, degassed mixture of (1,3-dichlorobenzene)tricarbonylchromium (0.028 g, 0.1 mmol), bis[4-(dimethylamino)phenyl] diselenide (0.040 g, 0.1 mmol), freshly powdered KOH (0.056 g), 18-crown-6 (0.005 g), and dioxane (1.5 mL) was injected hydrazine hydrate (15 μL) under nitrogen, and the mixture was stirred at ambient temperature for 36 h. Dilution with brine, extraction with ether, drying, evaporation, and column chromatography (3−6% EtOAc in pentane) afforded 0.011 g (23%) of the uncomplexed arene **4j** and 0.028 g (46%) of the title complex, mp 153 °C. ^{77}Se NMR: δ 414.3. Anal. Calcd for $C_{25}H_{24}CrN_2O_3Se_2$: C, 49.19; H, 3.96. Found: C, 49.35; H, 3.86.

3-(Phenylseleno)phenyl 4-(Dimethylamino)phenyl Selenide (5). To a stirred degassed mixture of (1,3-dichlorobenzene)tricarbonylchromium (0.056 g, 0.2 mmol), Ph_2Se_2 (0.046 g, 0.15 mmol), freshly powdered KOH (0.112 g), 18-crown-6 (0.010 g), and dioxane (2 mL) was injected hydrazine hydrate (15 μL) under nitrogen, and the mixture was stirred for 24 h.

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An additional amount of hydrazine hydrate (15 μL) was then injected followed by a solution of bis[4-(dimethylamino)-phenyl] diselenide (0.060 g, 0.15 mmol) in dioxane (1 mL). The reaction mixture was stirred for 24 h. The residue obtained after dilution with brine, extraction with ether, drying, and evaporation was dissolved in degassed EtOH (5 mL) and titrated with ethanolic $NaBH_4$ until the gas evolution had ceased. The mixture was then cooled to − 40 °C, $BrCH_2CO_2H$ (0.25 g) in EtOH (3 mL) was injected, and the mixture was allowed to reach ambient temperature. Ethanol was removed in vacuo, and the resulting slurry was treated with $NaHCO_3$ (aqueous), extracted with ether, and evaporated. Decomplexation with I_2 in THF was performed in the usual manner. Finally, column chromatography (2.5% EtOAc in pentane) afforded 0.033 g (38%) of the title compound, mp 60 °C (hexane). Anal. Calcd for $C_{20}H_{19}NSe_2$: C, 55.70; H, 4.40. Found: C, 56.01; H, 4.22.

η^6-(Phenylseleno)benzene-η^5-(cyclopentadienyl)iron Hexafluorophosphate (9a). To a degassed solution of sodium borohydride (0.031 g, 0.8 mmol) in EtOH (10 mL) was added dropwise Ph_2Se_2 in THF until the yellow color of the diselenide persisted. A suspension of (chlorobenzene)(cyclopentadienyl)-iron hexafluorophosphate (0.114 g, 0.3 mmol) in acetone (1 mL) was then injected, and the mixture was stirred at ambient temperature overnight. The residue was evaporated to dryness, treated with 0.1 M HCl containing NH_4PF_6, and neutralized with solid $NaHCO_3$. Extraction with CH_2Cl_2, drying, and evaporation afforded a crude product, containing the title compound, Ph_2Se, and Ph_2Se_2. Short column chromatography on deactivated alumina (eluting with ether) afforded iron-free components and then (eluting with acetone) the title iron complex. Crystallization of the product from acetone/ether afforded 0.090 g (60%) of the title compound. ^{1}H NMR (acetone-d_6): δ 5.20 (s, 5H), 6.37−6.49 (m, 5H), 7.55−7.64 (m, 3H), 7.85 (dm, J = 8.2 Hz, 2H). ^{13}C NMR (acetone-d_6): δ 79.2 d,87.3 d, 88.9 d, 89.0 d, 102.9 s, 126.4 s, 131.3 d, 131.4 d, 137.5 d. ^{77}Se NMR (acetone-d_6): δ 438.8.

η^6-(4-Chlorophenylseleno)benzene-η^5-(cyclopentadienyl)iron hexafluorophosphate (9b) was obtained from (chlorobenzene)(cyclopentadienyl)iron hexafluorophosphate (0.114 g, 0.3 mmol) and bis(4-chlorophenyl) diselenide following the procedure for the preparation of compound **9a**. Yield: 0.123 g (77%). ^{77}Se NMR (acetone-d_6): δ 433.8.

η^6-(4-Methoxyphenylseleno)benzene-η^5-(cyclopentadienyl)iron hexafluorophosphate (9c) was obtained from (chlorobenzene)(cyclopentadienyl)iron hexafluorophosphate (0.077 g, 0.20 mmol) and bis(4-methoxyphenyl) diselenide following the procedure for the preparation of compound **9a**. Yield: 0.085 g (79%). Anal. Calcd for $C_{18}H_{17}F_6FeOPSe$: C, 40.86; H, 3.24. Found: C, 41.21; H, 3.26.

η^6-[4-(Dimethylamino)phenylseleno]benzene-η^5-(cyclopentadienyl)iron hexafluorophosphate (9d) was obtained from (chlorobenzene)(cyclopentadienyl)iron hexafluorophosphate (0.095 g, 0.25 mmol) and bis[4-(dimethylamino)-phenyl] diselenide following the procedure for the preparation of compound **9a**. Yield: 0.112 g (83%). ^{77}Se NMR (acetone-d_6): δ 412.7. Anal. Calcd for $C_{19}H_{20}F_6FeNPSe$: C, 42.09; H, 3.72. Found: C, 42.30; H, 3.54.

η^6-(Phenylseleno)-2-methylbenzene-η^5-(cyclopentadienyl)iron hexafluorophosphate (9e) was obtained from (1-chloro-2-methylbenzene)(cyclopentadienyl)iron hexafluorophosphate (0.098 g, 0.25 mmol) and diphenyl diselenide following the procedure for the preparation of compound **9a**. Yield: 0.082 g (64%).

η^6-(4-Methoxyphenylseleno)-2-methylbenzene-η^5-(cyclopentadienyl)iron hexafluorophosphate (9f) was obtained from (1-chloro-2-methylbenzene)(cyclopentadienyl)iron hexafluorophosphate (0.0981 g, 0.25 mmol) and bis(4-methoxyphenyl) diselenide following the procedure for the preparation of compound **9a**. Yield: 0.114 g (84%). Anal. Calcd for $C_{19}H_{19}F_6FeOPSe$: C, 42.02; H, 3.53. Found: C, 42.19; H, 3.29.

η^6-[4-(Dimethylamino)phenylseleno]-2-methylbenzene-η^5-(cyclopentadienyl)iron hexafluorophosphate (9 g) was obtained from (1-chloro-2-methylbenzene)(cyclopentadienyl)-iron hexafluorophosphate (0.098 g, 0.25 mmol) and bis[4-(dimethylamino)phenyl] diselenide following the procedure for the preparation of compound **9a**. Yield: 0.110 g (79%). Anal. Calcd for $C_{20}H_{22}F_6FeNPSe$: C, 43.19; H, 3.99. Found: C, 43.27; H, 3.88.

η^6-1,2-Bis(4-chlorophenylseleno)benzene-η^5-(cyclopentadienyl)iron hexafluorophosphate (9h) was obtained from (1,2-dichlorobenzene)(cyclopentadienyl)iron hexafluorophosphate (0.082 g, 0.2 mmol) and bis(4-chlorophenyl) diselenide following the procedure for the preparation of compound **9a**. Yield: 0.090 g (62%). HRMS−FAB$^+$: calcd for $C_{23}H_{17}Cl_2FeSe_2$; 578.838667; found 578.8389.

η^6-1,3-Bis(4-chlorophenylseleno)benzene-η^5-(cyclopentadienyl)iron hexafluorophosphate (9i) was obtained from (1,3-dichlorobenzene)(cyclopentadienyl)iron hexafluorophosphate (0.082 g, 0.2 mmol) and bis(4-chlorophenyl) diselenide following the procedure for the preparation of compound **9a**. Yield: 0.099 g (68%). Anal. Calcd for $C_{23}H_{17}Cl_2F_6FePSe_2$: C, 38.21; H, 2.37. Found: C, 38.22; H, 2.22.

η^6-1,4-Bis(4-chlorophenylseleno)benzene-η^5-(cyclopentadienyl)iron hexafluorophosphate (9j) was obtained from (1,4-dichlorobenzene)(cyclopentadienyl)iron hexafluorophosphate (0.082 g, 0.2 mmol) and bis(4-chlorophenyl) diselenide following the procedure for the preparation of compound **9a**. Yield: 0.100 g (69%).^{77}Se NMR (acetone-d_6): δ 429.4.

Decomplexation of arene FeCp complexes was performed according to the literature.[17] The complex was dissolved in acetonitrile (5 mg/mL) and was irradiated (300 W sunlamp, Osram Ultra-Vitalux) in a round-bottom Pyrex flask with stirring for 3−4 h at 0 °C. The progress of the reaction was monitored by TLC (eluent: MeOH−2M NH_4Cl−$MeNO_2$, 7/2/1). The resulting brown slurry was diluted with a 5-fold volume of ether and filtered through Celite**.** Removal of the solvents in vacuo, followed by column chromatography, afforded the corresponding diaryl selenides. Diphenyl selenide (**4a**) and 4-chlorophenyl phenyl selenide (**10**) were obtained in almost quantitative yields, whereas 4-dimethylaminophenyl phenyl selenide (**4b**) was isolated in 40% yield. All three compounds were identical to those prepared from the corresponding chromium and/or manganese complexes.

Diphenyl Selenide (4a) from η^6-(Chlorobenzene)tricarbonylmanganese Hexafluorophosphate (14). To a suspension of Ph_2Se_2 (0.2 mmol) in EtOH (5 mL) was injected under nitrogen an ethanolic sodium borohydride solution until the yellow color of the diselenide had disappeared. η^6-(Chlorobenzene)tricarbonylmanganese hexafluorophosphate (0.035 g, 0.1 mmol) in a minimum of DMF (0.4 mL) was injected, and the mixture was stirred at ambient temperature overnight. The solvents were removed *in vacuo*, and the residue was treated with 0.1 M HCl, neutralized with $NaHCO_3$, extracted with CH_2Cl_2, dried, and evaporated. The residue was dissolved in MeCN (5 mL) and stirred at ambient temperature overnight. The solvent was evaporated, and the residue was treated with 0.1 M HCl, washed with brine, extracted with ether, and dried. NMR analysis, using methyl 3,5-diiodo-4-methoxybenzoate as an internal standard, indicated a 79% yield of diphenyl selenide.

In an alternative procedure, hydrazine hydrate (15 μL) was injected into a degassed suspension of Ph_2Se_2 (0.2 mmol) and K_2CO_3 (0.08 g) in DMSO (1 mL) under nitrogen, and the mixture was stirred for 1 h. η^6-(chlorobenzene)tricarbonylmanganese hexafluorophosphate (0.1 mmol) in DMSO (1 mL) was then injected, and the mixture was stirred at ambient temperature overnight. After workup and decomplexation as described above, NMR analysis with internal standard indicated a 76% yield of diphenyl selenide.

4-Chlorophenyl Phenyl Selenide (10) from η^6-(Chlorobenzene)tricarbonylmanganese Hexafluorophosphate

(14). To a degassed solution of sodium borohydride (0.015 g, 0.4 mmol) in EtOH (10 mL) was added dropwise bis(4-chlorophenyl) diselenide in THF under nitrogen until the yellow color of the diselenide persisted. η^6-(Chlorobenzene)-tricarbonylmanganese hexafluorophosphate (0.070 g, 0.2 mmol) in acetone (1 mL) was then injected, and the mixture was stirred at ambient temperature overnight. Solvents were removed in vacuo, and the residue was treated with brine (15 mL) containing NH_4PF_6 (0.3 g) followed by extraction with CH_2Cl_2. The extracts were dried with Na_2SO_4 and concentrated in vacuo. The residue was dissolved in MeCN (15 mL), and the stirred solution was exposed to daylight in the open air for 1 day. Filtration and removal of MeCN afforded a mixture of the title selenide and bis(4-chlorophenyl) diselenide. The latter was removed by reduction, alkylation with bromoacetic acid, and extraction as described for the preparation of compound **4a**. Column chromatography (pentane) afforded 0.033 g (61%) of the title compound as a colorless oil. ^{1}H NMR: δ 7.23 (d, J = 8.6 Hz, 2H), 7.26−7.31 (m, 3H), 7.38 (d, J = 8.6 Hz, 2H), 7.46 (m, 2H). ^{13}C NMR: δ 127.6 d, 129.4 d (two CH), 129.5 s, 130.6 s, 133.1 d, 133.4 s, 134.1 d. ^{77}Se NMR: δ 416.2. The corresponding Se,Se-dichloride, prepared by sulfuryl chloride treatment, melted at 143−146 °C (lit.[31] mp 144−145 °C).

1,4-Bis(4-chlorophenylseleno)benzene (11) was obtained by irradiation of η^6-1,4-bis(4-chlorophenylseleno)benzene-η^5-(cyclopentadienyl)iron hexafluorophosphate in MeCN with a sunlamp for 3 h. Filtration through silica, evaporation, and column chromatography afforded the title compound in an almost quantitative yield, mp 141−143 °C. ^{1}H NMR: δ 7.27 (dm, J = 8.5 Hz, 4H), 7.32 (s, 4H), 7.41 (dm, J = 8.5 Hz, 4H). ^{13}C NMR: δ 128.6 s, 129.6 d, 130.6 s, 133.3 d, 134.0 s, 134.7 d. ^{77}Se NMR: δ 414.8. Anal. Calcd for $C_{18}H_{12}Cl_2Se_2$: C, 47.30; H, 2.65. Found: C, 47.18; H, 2.53.

2-Methoxycarbonylphenyl 4-Chlorophenyl Selenide (13). Into a stirred solution of KBH_4 (0.016 g, 0.3 mmol) in degassed MeOH (5 mL) was slowly added bis(4-chlorophenyl) diselenide in THF under nitrogen until the yellow color persisted. This mixture was then cannulated into a stirred solution of methyl 2-chlorobenzoate-η^5-(cyclopentadienyl)iron hexafluorophosphate (**12**) (0.131 g, 0.3 mmol) in MeCN under nitrogen, and stirring was continued overnight. Solvents were removed, and the residue was treated with 0.1 M HCl (5 mL) containing NH_4PF_6 (0.4 g) and neutralized with solid $NaHCO_3$. The slurry was extracted with CH_2Cl_2, and the organic extracts were dried and evaporated. The residue was subjected to column chromatography on deactivated alumina. By eluting first with ether and then with acetone, an inseparable mixture (78/11/11) of η^6-[1-methoxycarbonyl-2-(4-chlorophenylseleno)-benzene]-η^5-(cyclopentadienyl)iron hexafluorophosphate, δ 4.15 (s, 3H), 5.22 (s, 5H), 6.12 (d, 1H), 6.54−6.62 (m, 2H), 7.12 (d, 1H), 7.62 (d, 2H), 7.90 (d, 2H), starting material, and an *o*-methoxy substitution product (^{1}H NMR (acetone-d_6) δ 3.93 (s, 3H), 4.00 (s, 3H), 5.27 (s, 5H)) was isolated**.** This mixture was subjected to decomplexation by irradiation in MeCN with a sun lamp (see above). Final column chromatography (1% AcOEt in pentane) afforded 0.027 g (28%) of the title compound, mp 104 °C. ^{1}H NMR: δ 3.97 (s, 3H), 6.87 (d, J = 7.4 Hz, 1H), 7.15−7.26 (m, 2H), 7.39 (d, J = 8.6 Hz, 2H), 7.63 (d, J = 8.6 Hz, 2H), 8.06 (d, J = 7.4 Hz, 1H). ^{13}C NMR: δ 52.39 q, 124.9 d, 127.0 s, 127.1 s, 128.8 d, 130.0 d, 131.4 d, 132.8 d, 135.7 s, 138.8 d, 140.0 s, 167.2 s. ^{77}Se NMR: δ 460.7. Anal. Calcd for $C_{14}H_{11}ClO_2Se$: C, 51.64; H, 3.40. Found: C, 51.78; H, 3.40.

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Supporting Information Available: A listing of ^{1}H and/or ^{13}C data for compounds **3b**, **3c**, **4c**−**j**, **9b**−**j**. This material is available free of charge via the Internet at http://pubs.acs.org.

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